Programme Area: Carbon Capture and Storage

Project: Mineralisation

Title: Carbon Capture and Storage by Mineralisation Stage Gate 1 Report

Abstract:

Geologic sequestration is not appropriate for smaller lone emitters located remotely from geological storage sites. CCS by mineralization has been demonstrated on laboratory and pilot scales, with capture efficiencies of up to 90% using naturally occurring minerals high in magnesium, such as serpentine. The UK reserve of readily accessible serpentine is 2-10Gt and typically located within 2km of the coast, enabling cost-effective mass transport links. Emissions from the (75) UK industrial emitters (<1.0Mt CO2) totals 24Mt CO2, half of which are coastal. The cost of CCSM ranges from 85-254£/tonne CO2, with potential opportunity to decrease cost by £30/tonne or more by direct flue gas capture, process optimisation, and system integration at each site. To achieve this goal further experimentation is required to validate suitability of UK rock resources, direct CO2 capture from flue gas on UK minerals, optimization of CCSM process fundamentals and system integration at each site. CCSM has the potential to become an economically viable alternative to capture and store CO2 from small and medium emitters. The ETI is grateful for the contributions made by all participants of the Mineralisation project; Perkins Engines Company Limited, Shell Global Solutions International B.V., Natural Environment Research Council as represented by the British Geological Survey, and the University of Nottingham.

Context:

CCS by mineralisation has been identified as a promising additional method of sequestering CO2 emissions. Minerals and CO2 can react together to permanently store CO2 as a solid carbonate product, which can then be safely stored, used as an aggregate or turned into useful end products such as bricks or filler for concrete. This £1m project, launched in May 2010 carried out a detailed study of the availability and distribution of suitable minerals across the UK along with studying the technologies that could be used to economically capture and store CO2 emissions. The project consortium involved Caterpillar, BGS and the University of Nottingham. The objective was to investigate the potential for CCS Mineralisation to mitigate at least 2% of current UK CO2 emissions and 2% of worldwide emissions over a 100- year period. The project has found that there is an abundance of suitable minerals available in the UK and worldwide to meet these mitigation targets. However, challenges remain to make the capture process economically attractive and to reduce its energy use. Significant niche opportunities exist where waste materials are used as feedstock and/or the process produces value-added products, but markets would not be at the level required to meet the mitigation targets.

Carbon Capture and Storage by Mineralisation Stage Gate 1 Report

CCSM Programme

Stage Gate Report

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ENERGY TECHNOLOGIES INSTITUTE

CCSM PROGRAMME
STAGE GATE 1 REPORT

Carbon Capture and Storage by Mineralisation Stage Gate 1 Report

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Contents

FIGURES

TABLES

Executive Summary

The current prime path solution for large-scale energy-intensive processes emitting >1Mt CO_2 per year is geologic sequestration. Geologic sequestration is a less economically viable option for smaller lone emitters, who are located remotely from geological storage sites, due to the high CO_2 handling and transportation costs. There are currently no commercialized processes that specifically address this technology gap. Carbon capture and sequestration by mineralization has been demonstrated in various forms on laboratory and pilot scales, with CO_2 capture efficiencies of up to 90% using naturally occurring minerals high in magnesium, such as serpentine. The UK reserve of readily accessible serpentine is 2-10Gt, 2-10 times the amount required to sequester 2% of UK CO_2 emissions for 100 years. These reserves are typically located within 2km of the coast, enabling cost-effective mass transport via ship to small and medium power stations and industrial emitters that are located in close proximity to the coast. The emissions from the (75) UK industrial emitters (<1.0Mt CO_2) totals 24Mt CO_2, and roughly, half of those are coastally located. Implementing CCSM at those coastal sites will meet the project target of capturing 11Mt CO_2/year. The cost of CCSM ranges from 85-254£/tonne CO_2 avoided operating costs, with potential opportunity to decrease cost by £30/tonne or more by direct flue gas capture, process optimisation, and system integration at each site. To achieve this goal further experimentation is required to validate suitability of UK rock resources, direct CO_2 capture from flue gas on UK minerals, optimization of CCSM process fundamentals and system integration at each site. CCSM has the potential to become an economically viable alternative to capture and store CO_2 from small and medium emitters.

1 Introduction

Carbon Capture and Storage by Mineralisation (CCSM) is the process by which carbon dioxide is reacted with divalent metal cations to form a stable carbonate compound, thus locking away the CO_2 in perpetuity. Mineral carbonation is an accelerated form of the rock weathering process, one of our planet's natural major CO_2 capture effects (Seifritz, 1990). Ex-situ carbon dioxide mineralisation is defined as the reaction of Cations (Mg^{2+}, Ca^{2+}) from the feedstock with CO_2 to form a carbonate product stream. CCSM is envisaged as being complementary to underground storage rather than a direct competitor. It is anticipated that the process can be scaled for use with intermediate and small emitters, and used in places where underground storage is not possible or is uneconomic. CCSM has an advantage over underground storage in that the method can operate directly on flue gases (or CO_2 containing process gases in general), without a pre-separation of CO_2. The separation of CO_2 typically accounts for 70% of the costs of the CCS chain.

Magnesium is the metal most commonly used for this process and occurs in nature in various forms of magnesium silicate mineral. These minerals occur as ultramafic rocks such as peridotite composed largely of olivine [Mg_2SiO_4] or serpentinite composed of serpentine [$Mg_3Si_2O_5(OH)_4$]. Serpentine is the hydrous alteration product of olivine and is the most commonly occurring ultramafic rock type in the UK. Most deposits, while predominantly composed of one mineral type, also contain inclusions of other minerals. This factor is important in the pretreatment step as the minerals have a range of properties and hence may respond differently to particular activation processes.

1.1 ASSESSMENT ROCK RESOURCES FOR CCSM

The overall assessment of UK mineral resource availability shows the capacity to capture 6-10 times the project goal of 11 Mt CO_2 per year (2% of current UK CO_2 emissions) for 100 years. A high level review of Global mineral resources also shows the capacity to capture 2% of worldwide CO_2 emissions for more than 250 years at 2006 emissions levels. The maps of the different types of ultramafic rock resources show that many are in places where potential for underground geological storage is limited or impractical. These include substantial resources in northern Europe (Finland and Sweden), Japan, India, South Africa, Australia, and parts of North America. There is potential for implementation in many more countries.

1.2 WASTE MATERIALS

The current state of the art indicates that only about 2-15% of the annual CO_2 target can be achieved using waste as a feed material. This investigation also indicates that most likely recycled concrete aggregate (RCA) and pulverised fuel ash (PFA) would be available in a life span of 100 years. However, the consideration of waste is in many ways more complex than natural minerals. A material previously considered as waste may find a use due to developments in technology. A second factor that can radically change things is legislation that imposes penalties on disposal of waste and creates markets for low value by-products. In addition, the high variability of their volumes and chemical composition represent a major obstacle to the deployment of these materials in CCSM. In particular, the presence of contaminants might affect the efficiency of CO_2 sequestration and the possibility to produce some valuable products. For these reasons mineral waste does not represent a preferential option at this stage of the programme.

1.3 CCSM PROCESS

Mineralisation processes comprise three basic steps:

- Pretreatment of the mineral through grinding and chemical or thermal activation
- Carbonation where the mineral or leached cations are reacted with carbon dioxide to produce mainly carbonate and silica
- Post processing to separate and upgrade the carbonate and silica to a suitable quality and state for sale to an appropriate market

1.3.1 Pretreatment

The purpose of the pretreatment (or activation) step is to transform relatively inert raw silicate minerals into highly reactive materials for CCSM processes, promoting and accelerating carbonation reaction rates and efficiencies through surface activation. High-energy mechanical activation increases specific surface area and "amorphisation" of the solids due to the distortion of the mineral crystal structure. Chemical activation accelerates the rate and extent of mineral dissolution, producing aqueous solutions enriched with highly reactive chemical species (such as $[Mg^{2+}]aq$) required for CCSM processes. Serpentines are not significantly activated by simple particle size reduction due to the nature of its crystal structure; therefore, heat treatment methods are applied to drive dehydroxylation and consequently accelerate dissolution. Another approach involving the mineral pre-treatment step only combines mechanical and "wet" chemical treatments. This increases the mineral surface area with 10% less energy as well as accelerates the dissolution rates of silicates in presence of various acids, alkalis, complexing agents, or electrolytes (ionic strength modifiers).

1.3.2 Carbonation

The main barriers to the commercial deployment of carbonation are high-energy intensity, low reaction conversion, slow reaction kinetics, and the competition with other technologies such as renewable energy.

The controlling mechanisms for the carbonation reaction can be summarized with three main phenomena: diffusion of CO_2 in the aqueous medium, diffusion of CO_2 in the fluid film around the solid particles, and product layer (SiO_2) diffusion inhibition of CO_2. Within these three controlling mechanisms, four key parameters have been identified which ultimately control the carbonation reaction. Particle size governs the surface area of the solid available for the carbonation reaction as well as reduces the thickness of the product layer (SiO_2) that inhibits diffusion of CO_2 further into the particles. Physical grinding and sonication are the two most common techniques used to reduce particle size and remove the inert product layer, respectively. Temperature is another key parameter that mainly influences the dissolution of CO_2 in the aqueous phase with the lower temperatures having the higher dissolution rates. Pressure also influences the carbonation reaction by increasing the dissolution of CO_2 in the aqueous phase that inherently increases the diffusion of CO_2 through the fluid film and product layer. The last key parameter is the liquid to solid mass ratio. A liquid to solid mass ratio lower than 2 cannot be stirred sufficiently which may result in poor CO_2 mass transfer.

However, a reduction in the liquid to solid ratio can lead to a substantial improvement in heat transfer rates that will accelerate the reaction.

1.3.3 CCSM System Technologies

The descriptions of the various process routes reported in the technical and patent literature revealed that while a number of processes are novel, little or no experimental work was completed or made public. Despite the dearth of technical information, some of processes look promising. Leading researchers at ARC performed experimental work that is considered the state-of-art technology, demonstrating 85% CO_2 capture efficiency using either Olivine or Serpentine, but the cost of storage is still considered high. This is partly because the ARC's process requires a separated CO_2 stream, driving additional cost.

The Caterpillar and Shell processes have demonstrated up to 75% CO_2 capture efficiency directly from flue gas streams using non-optimized, laboratory-scale process equipment. The Caterpillar process uses spray dry absorber technology, a production process that is currently used for scrubbing SOx from flue gas.

A new pH-swing CO_2 mineralisation process using recyclable ammonium salts was proposed by the University of Nottingham to overcome the low efficiency of mineral dissolution and unrecyclable use of additives, two of the barriers for the development of CO_2 mineral carbonation. NH_3 is used to capture CO_2 from power plant's flue gas using 60% less energy than a typical capture process. NH_4HSO_4 is used to extract Mg from serpentine in the mineral dissolution step. The overall process is able to dissolve up to 100% of Mg, sequester about 80-90% of CO_2 from flue gas and produce three separated materials: silica, iron oxides and magnesite with high purity. In addition, ammonia can be virtually completely regenerated with NH_3 emissions below 10ppm and the ammonium salts make up resulted below 5%. For the work in Åbo Akademi, a recovery of 71% ammonium sulphate has been attained (not yet optimised).

1.3.4 Post-Processing

The current global market for the raw commodities, which could be produced by rock and/or industrial waste/by-product mineralisation, is valued at about £2.9B. However, global success of CCSM could flood markets and erode margins and also a higher value will require more sophisticated processing including drying leading to large cost penalties.

Post-processing of multistage CCSM processes to low-end products seems competitive with landfilling while post-processing towards high-end products might present a high cost between 60-70£/tonne CO_2 (±£20/tonne CO_2). The exact CCSM technology chosen will play a very important role on the available post-processing routes and accessible markets due to the purity of the resultant materials. Land reclamation may allow for transport and grinding synergies representing at this stage of the programme the only viable opportunity. However, the available literature does not clarify if the quality of the CCSM products would be enough to access the high-value market where micro-silica and PCC have selling prices above 200-300£/tonne, which might render the process economical. Therefore, further investigation is required to establish the technical and economic feasibility of this pathway.

1.4 UK INDUSTRIAL POINT SOURCES OF CO_2

Power plants account for approximately 70% (187 Mt) of the total reported industrial CO_2 emissions in 2006. The 50 largest sources comprise 36 power plants, 9 refineries, 4 integrated steel plants and 2 aluminium smelters, with total emissions of 212Mt of CO_2 per year, which is almost 79% of emissions from reporting sites. The largest sites contain relatively low percentages of CO_2 in their waste streams and would need to be fitted for CO_2 capture. The current prime path solution for such large emitters is geologic sequestration. For smaller emitters, which are greater in number, geologic sequestration is not economically viable.

Analysis of the CO_2 emissions data used shows that emitters can be categorised into 2 main groups:

- Power (or CHP) producers
- Industrial processes

Power producers in turn were grouped by capacity into the following 4 bands:

- 110MW and smaller
- 110 – 300MW
- 300 – 1,000MW
- 1,000 MW and greater

Industrial processes were grouped by reported annual CO_2 emissions in the following 4 bands:

- 0.25Mt CO_2 and less
- 0.25 – 1.0Mt CO_2
- 1.0 – 2.0Mt CO_2
- 2.0Mt CO_2 and more

CCSM deployment linked to smaller emitters as the only currently recognizable alternative to capture and store CO_2. The 75 industrial emitters <1Mt CO_2/year produced a total of 24Mt CO_2 in the year reported, and half of those are coastally located. Addressing those emitters satisfies the 11Mt CO_2 set as a target for this project. This means that a coastal resource in a remote location such as Shetland could be utilised for CCSM in a wide range of locations.

1.5 POSSIBLE SCENARIOS FOR CCSM IMPLEMENTATION

1.5.1 North-east Scotland

There is a large resource at the coastal location of Belhelvie, just north of Aberdeen and at Portsoy. The 1Gt Belhelvie resource and the smaller resource at Portsoy have the capacity to capture 700Mt of CO_2. This could be utilised at the gas/oil-burning power station immediately south of Peterhead, emitting 3.6Mt CO_2 per year, with a capture capacity of 150 years. In this instance, transport by road, rail or sea might be possible. Sea transport would also make the group of coastal emitters located around the Firth of Forth an outlet for Belhelvie-Portsoy rock. There is the capacity to capture all the major emissions for eastern Scotland about 40 years or part of the emissions for a much longer period.

1.5.2 South-west Scotland

There is a large resource of 2.5Gt at Ballantrae in southwest Scotland. The Ballantrae resource would most likely be exploited using sea transport. There are relatively local sources such as the power stations on the coast of Northern Ireland and the small industrial sources near Glasgow. Further, afield, there are numerous coastal emitters in northwest England, particularly those located within the Mersey-Dee Basin. The resource has the capacity to capture all the major coastal emissions for 60 years or part for a much longer period.

1.5.3 South-west England

There is a very large (5Gt) resource centred on the Lizard peninsula in SW England. The coastal location of the Lizard resource, and its remoteness with respect to emitters, makes sea transport essential. There are numerous emitters with coastal locations relatively nearby, such as the power stations and steel works in South Wales, and the oil refineries in Pembrokeshire and Southampton. The Lizard resource could capture the CO_2 from all these sources for over 100 years. Further afield, there are numerous coastal emitters located within the Thames Basin, amounting to a further 20Mt pa, that could use Lizard rock.

The conclusion of this analysis is that the logical target markets for CCSM deployment in the UK are power producers up to 300MW capacity and industrial processes with emissions up to 1Mt CO_2 per year. In both cases, the target deployment site should ideally be within 1km of the coast or, if inland, co-located with a suitable waste or process by-product stream.

1.6 CURRENT ESTIMATED COSTS OF CCSM AND POTENTIAL COST REDUCTION

The estimated cost of geological sequestration (GS) was considered as a baseline to establish the penalty cost of CCSM. About £45-55/tonne CO_2 avoided were assigned to GS considering the values reported in the IPCC report (£1-6/tonne CO_2) and the energy cost of the amine capture stage of £45/tonne CO_2 (Kothandaraman, 2010). CCSM using Ca-silicate rocks or waste materials shows an average cost of £94/tonne CO_2 while the CCSM cost increases to £155/tonne CO_2 in average if Mg-rocks are used as feedstock. The recent industrial assessments made by Shell and Caterpillar indicates a most likely cost ranging from £200 to 300/tonne CO_2 for direct carbonation using flue gases instead pure carbon dioxide. The ARC process, considered the mineralisation state-of-the-art, shows costs between £85/tonne CO_2 to £260/tonne CO_2. Other processes such as the UoN, Kodama show promising estimated energy cost between £65-70/tonne CO_2, but capital and operational costs were not analysed. Åbo Akademi processes has an estimated cost of £70-100 CO_2.

Two extreme scenarios were considered:

- In the first case, we considered the ARC process economics assuming the average cost of the technology (£135/tonne CO_2)(IPCC, 2005), a CO_2 capture stage, no value generated by the powders produced with transport and landfilling of all the products.
- In the second case we assume that the new pre-treatment and conversion processes would be able to decrease the cost the pretreatment and conversion costs of 50% and sell part of the powders produced 100% of silica sand and iron ore pellets for steel production.

Serpentine was chosen to assess the carbonation technology being the main resource in the UK among the usable minerals. In addition, mineral wastes such as steel slag and cement waste were reported to compare their costs with that of serpentine.

The general assessment indicates that the mineralisation costs of ARC process using serpentine is around £250/tonne CO_2 when costs of material extraction and transport, transport of products, and landfill costs are added while the mineralisation of mineral wastes can be done at £150/tonne CO_2 and at £120/tonne CO_2 using steel slag and waste cement, respectively. The overall costs of mineralisation using serpentine would decrease to about £140/tonne CO_2, if the technology employed would be able to decrease the pre-treatment and conversion costs of 50% and sell part of the products (100% of silica and iron products). The development of such new technologies would significantly decrease the costs of mineral waste carbonation to £40/tonne CO_2 and £50/tonne CO_2 for waste cement and steel slag, respectively.

1.7 GAPS AND DEVELOPMENT NEEDS

The initial technology assessment centred on the core mineral carbonation technologies and produced an initial ranking. A grouping has been done that will serve to aggregate insights, gaps, and development needs.

1.7.1 Proposed experimental pathway

Pre-treatment:

- In-depth energy analysis for heat activation of serpentine
- Mechano-chemical activation process of serpentine

Carbonation:

- Capex/opex study of the chemical processes requiring large volumes of NH_3
- Life Cycle Analysis / carbon foot print evaluation of selected carbonation processes
- Evaluation of various large-scale carbonation chemical reactors (SDA, autoclave, Fluidized beds, underground pipeline) and the respective energy consumption for CO_2 carbonation from $\leq$300MW power plant.
- Develop an energy penalty tool / model for building block process elements

Post-processing

- Establish the technical and economic feasibility of producing micro silica as an end product
- Quantify energy cost of drying of aqueous-based by-products
- Long-term action plan
- Develop roadmap to take CCSM from the current TRL 3/4 to TRL 9

Part 1 – Identification of Resources and Emitters

2 Resource definition

The classification and range of compositions of ultramafic rocks are described. It is identified that experimental studies of mineral carbonation have only used the simple olivine-rich or serpentine-rich end-members and the vast majority of ultramafic rock compositions must currently be regarded as untested. This is shown graphically where the composition of these tested samples is shown in relation to the full range of rock compositions.

2.1 BACKGROUND

The Carbon Capture and Storage by Mineralisation (CCSM) process will require a large stock of material that can, after appropriate processing, provide a source of cations for combination with CO_2 to form stable carbonate. There are few elements present at or near the earth's surface, in large amounts suitable for forming carbonates that are not used for other industrial purposes; in practice these elements are limited to Mg and Ca. By far the commonest Ca-rich rock is limestone, where the Ca is already present as carbonate, and other Ca-rich rocks are rare. Sources from rocks will have to be those that are Mg-rich, known as ultramafic rocks. The detailed reasons for concentrating on ultramafic rocks are given in section 2.2.3.

Waste and by-products from human activities also have the potential to act as a source material. These encompass a wide range of materials that contain various amounts of suitable elements, particularly Ca.

The following sections describe possible source materials, and identify those that can seriously be considered feedstock resources, taking into account the current level of technology and testing of feed materials.

2.2 ULTRAMAFIC ROCKS

2.2.1 Classification of ultramafic rocks

Ultramafic rocks are composed of more than 90% mafic (i.e. dark-coloured) minerals in various proportions with trace amounts of other minerals. The main mafic minerals are the Mg-silicates olivine (specifically forsterite, chemical formula Mg_2SiO_4), orthopyroxene (specifically enstatite, chemical formula $MgSiO_3$) and clinopyroxene (specifically diopside, chemical formula $(MgCa)SiO_3$). In most rocks, a proportion of the Mg in the crystal structure of these minerals is substituted by Fe^{2+}. In the rocks considered in this study, that substitution is only around 10 % and for the sake of simplicity only the names of the mineral or the Mg end-member will be used.

Ultramafic rocks are formed by the crystallisation of an anhydrous, Mg-rich silicate melt at temperatures around 1200°C. This usually occurs in the middle or lower parts of the earth's crust or in the earth's mantle at considerable depths, perhaps 15km, and at pressures of 500MPa or greater. The internationally accepted classification for ultramafic rocks, with the rock names used for the various proportions of minerals, is shown in Figure 1. The apices of the triangle show rocks composed of 100% of a particular mineral, and the inner parts of the triangle show various proportionate mixtures of the minerals. The Mg contents of the different minerals are indicated in red, and this indicates that rocks rich in olivine are the best targets in terms of their Mg content. Rocks consisting dominantly of olivine are known as peridotites, whereas those in which pyroxene is dominant are termed pyroxenites.

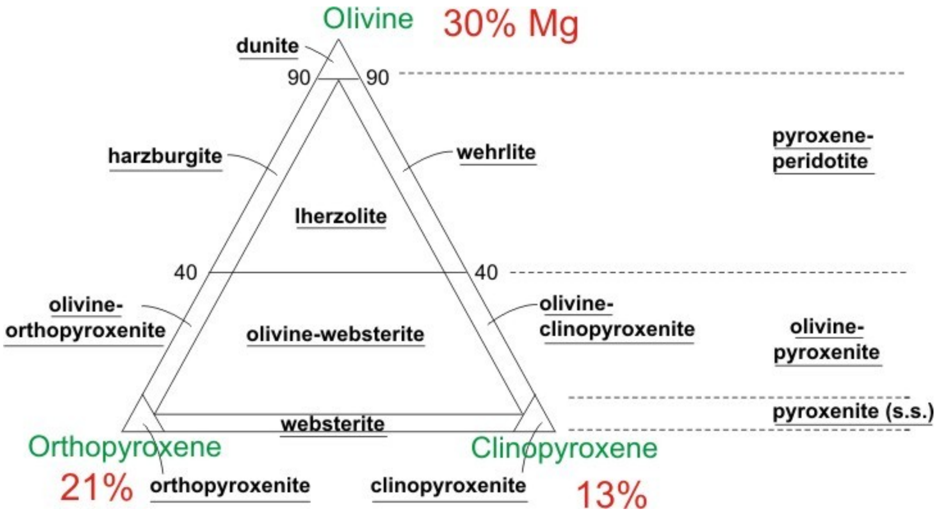


Figure 1 The classification of fresh, anhydrous ultramafic rocks. The Mg content of the rocks at each apex is shown in red (weight% element) [© British Geologic Survey].

After formation of the ultramafic rocks, tectonic processes and erosion over millions of years bring them to the near surface environment where they are now located and potentially available as a source material. The rocks that were in equilibrium in an anhydrous, high temperature environment become highly unstable during this transport to the surface and final residence and undergo a range of mineralogical changes. These changes are principally due to hydrous fluids causing hydration, but other components in the fluids can cause changes in bulk chemical composition, and in particular, the presence of CO_2 causes carbonation. The interaction with hydrous fluids rarely happens as a single-stage alteration process and rocks may contain mineral assemblages reflecting partial equilibration at several temperatures, pressures, and fluid compositions.

There is no accepted classification of altered ultramafic rocks or indeed wide consistency in the names used. Here the following scheme is proposed as a working model for use during this project. This is essentially a variation of Figure 1, but with the anhydrous minerals replaced by their commonest hydrous equivalents: serpentine, amphiboles, or talc.

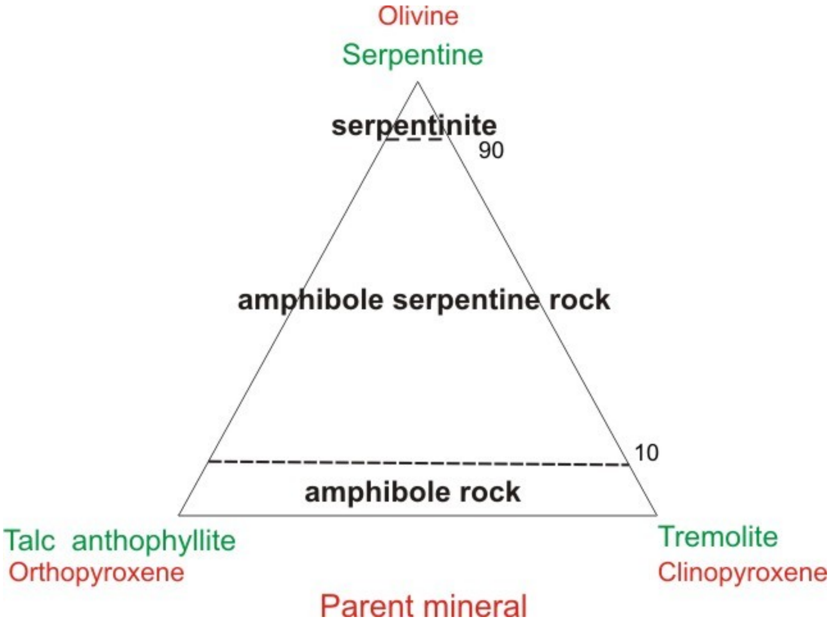


Figure 2 Classification of hydrated ultramafic rocks. The actual minerals present are shown in green and the parent anhydrous minerals in red. [Copyright BGS, NERC]

In nature, rocks at the surface are rarely free from any hydration, but in some geological settings, rocks with little alteration are found. In other settings, rocks that are totally hydrated are common. However, many occurrences fall between these extremes. This continuum of compositions is shown graphically in Figure 3 to demonstrate the wide range of possible mineralogical make-up of naturally occurring ultramafic rocks.

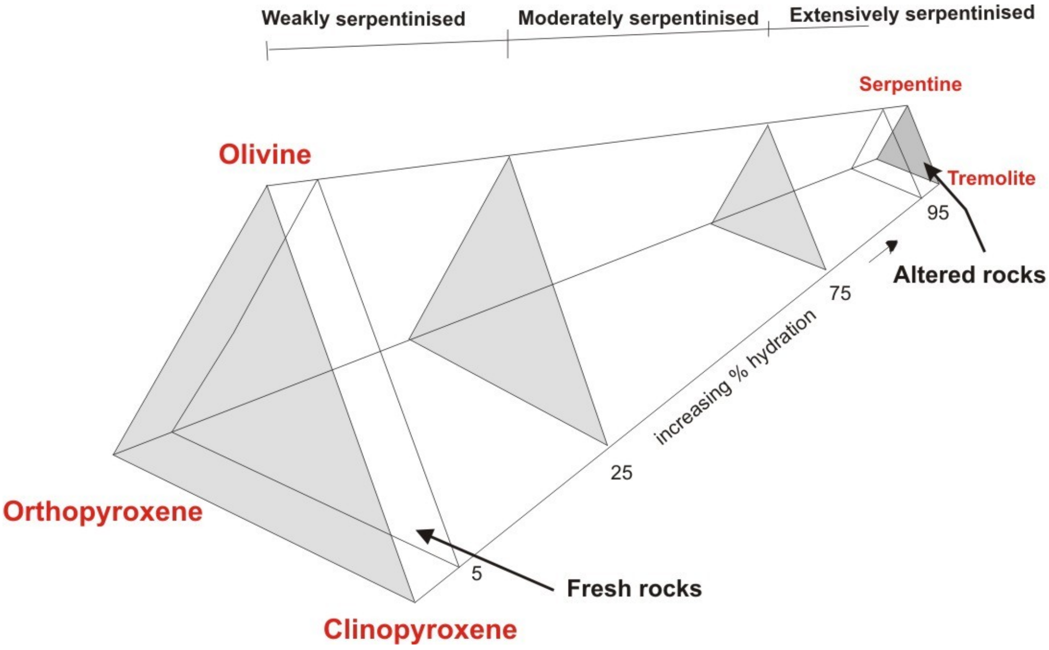


Figure 3 The range of mineralogical compositions of naturally occurring ultramafic rocks. [Copyright BGS, NERC]

The compositional space of ultramafic rocks forms a prism, but trying to plot and compare compositions is difficult in a 3D space. However it is inferred from previous studies of mineral carbonation (O'Connor et al., 2004) that (i) orthopyroxene and clinopyroxene behave similarly, but significantly inferior to olivine in terms of CO_2 capture and that (ii) amphiboles also behave similarly, but are inferior to serpentine. The compositional prism can then be simplified to a vertical section through the apex to give a simple plot (Figure 4).

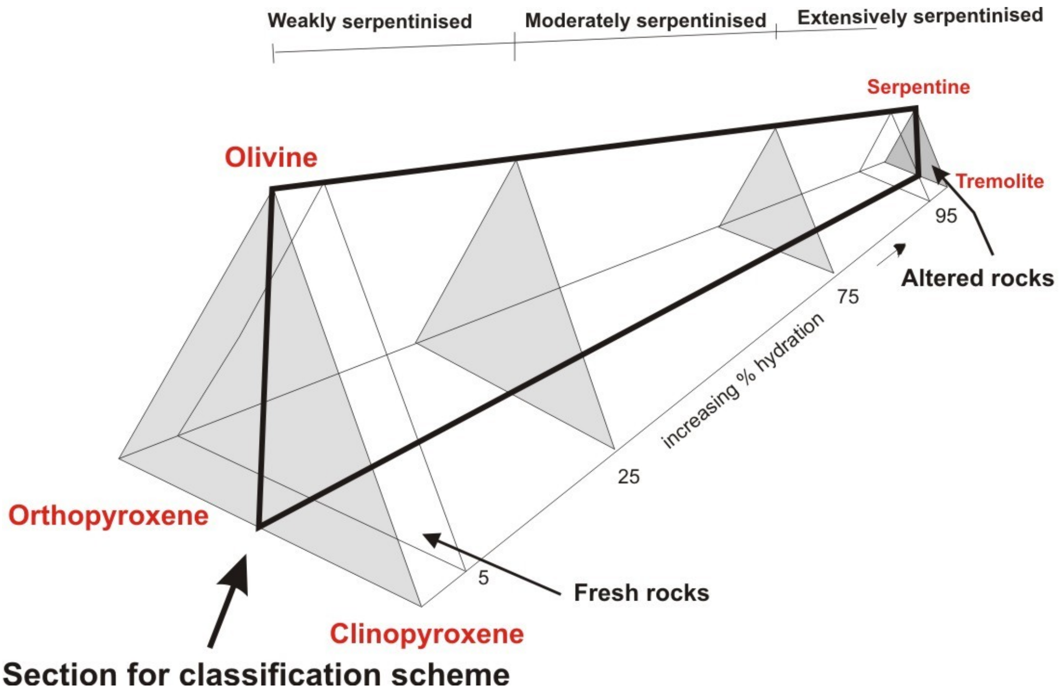


Figure 4 vertical sections through composition prism. [Copyright BGS, NERC]

The vertical section can then be divided in to composition classification fields (Figure 5) and used to compare rocks of various types. The fields have been chosen to categorise very fresh rocks (1, 6, 11), very altered rocks (5, 10, 15), olivine-serpentine-rich rocks (1 – 5), pyroxene-amphibole-rich rocks (11 – 15) and rocks with a range of both alteration and mineral types (6 – 10).

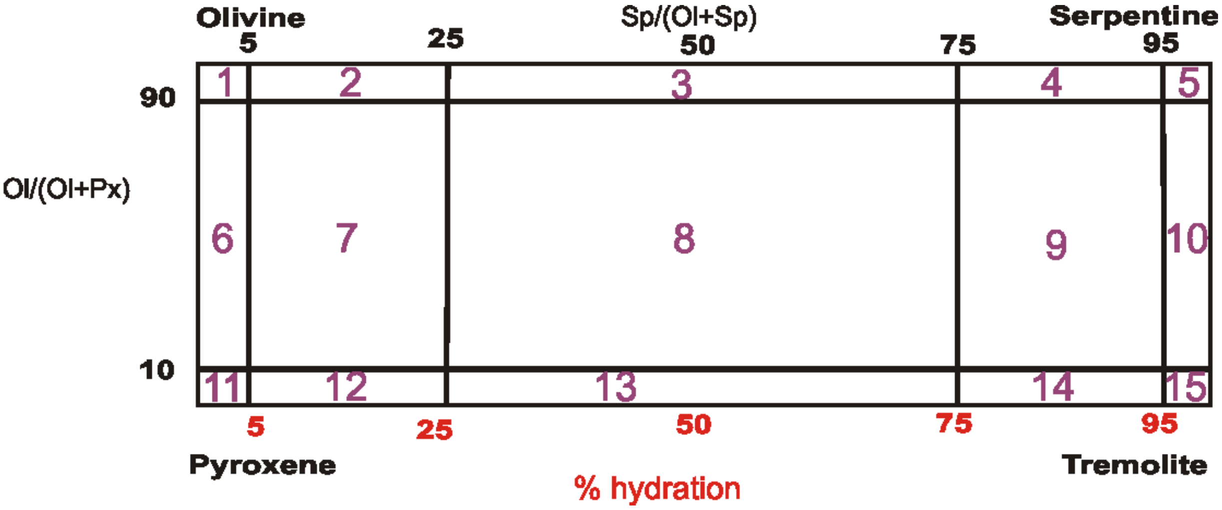


Figure 5 A classification diagram for ultramafic rocks based on the proportions of constituent minerals. [Copyright BGS, NERC]

The plot of compositions is based on the modal proportions of constituent minerals as shown in black and this is closely allied to the degree of hydration as shown in red. These composition fields are used in the database of UK rock resources and the descriptions of resource areas in Appendix 2.

2.2.2 The nature of ultramafic rocks

The nature of ultramafic rocks is complex, and to assist the reader a detailed account is included in Appendix 1. This describes and demonstrates the variability and inhomogeneous nature of ultramafic rocks that will have an effect on their use as a source material. In addition, an account of the serpentine mineral group is included as these are likely to be a very important source material. In particular the differences between the main polymorphs, lizardite, antigorite and chrysotile, is explained.

2.2.3 Laboratory testing of ultramafic rocks

A range of rock types and minerals has been tested in the laboratory for their suitability for use in mineral carbonation (see report of Work Package 2 Verduyn et al 2010). A source of information often quoted is the results of the studies by the Albany Research Centre in the USA (O'Connor et al., 2004). They used two parameters to categorise the source materials:

R CO_2 Theoretical mass ratio of ore necessary to carbonate a unit mass of CO_2 (the theoretical capture capacity; a small number is good)

Rx % Reaction efficiency, percent stoichiometric conversion of Ca, Fe^{2+}, and Mg cations in silicate feed to carbonate (a large number is good), but this is dependent on the experimental procedures used

Here an extra column, **R CO_2*100/Rx** has been added, to combine these two parameters to estimate the number of tonnes of mineral required to capture 1 tonne of CO_2 according to the data presented.

The data from O'Connor et al. (2004) are given in Table 1 and from this a few general points can be seen. First, the main constituents of ultramafic rocks, forsteritic olivine, serpentine and to a lesser extent, pyroxene have much higher suitability values than a mafic rock such as basalt. This is presumably due to the high content of poorly reacting feldspar in mafic rocks. Therefore, ultramafic rocks specifically are regarded as the main target for source materials.

			Concentration, wt %					
Rock/mineral	**Mineral**	**Formula**	**Ca**	**Fe2+**	**Mg**	**R CO2**	**Rx, %**	**RCO2*100/Rx**
Feldspar	Anorthite (An)	$CaAl_2Si_2O_8$	10.3	3.1	4.8	4.4	9	48.9
Serpentine	Antigorite (Ant)	$Mg_3Si_2O_5(OH)_4$	<0.1	2.4	24.6	2.1	92	2.3
Pyroxene	Augite (Aug)	$CaMgSi_2O_6$ + (Fe,Al	15.6	9.6	6.9	2.7	33	8.2
Basalt	An, Aug, Mt, Ol		6.7	6.7	4.3	4.9	15	32.7
Olivine (Ol)	Fayalite (Fa)	Fe_2SiO_4	0.6	44.3	0.3	2.8	66	4.2
Olivine (Ol)	Forsterite (Fo)	Mg_2SiO_4	0.1	6.1	27.9	1.8	81	2.2
Serpentine	Lizardite (Liz)	$Mg_3Si_2O_5(OH)_4$	0.3	1.5	20.7	2.5	40	6.3
Oxide	Magnetite (Mt)	Fe_3O_4	0.6	21.9	0.3	5.5	8	68.8
Ultramafic	Talc	$Mg_3Si_4O_{10}(OH)_2$	2.2	9.2	15.7	2.8	15	18.7
Ultramafic	Wollastonite (Wo)	$CaSiO_3$	31.6	0.5	0.3	2.8	82	3.4

Table 1 Mineral chemistry, carbonation potential, and reactivity [from O'Connor et al., 2004]

Second, a very pertinent fact from the O'Connor 2004 report is that lizardite serpentinite is much less reactive and hence less suitable than antigorite serpentinite. This is a rather surprising result as the two polytypes of serpentine are very similar, and indeed other results reported by Gerdermann et al (2003), from the same research group, show that in some experiments lizardite is only about 10% less efficient than antigorite and in other experiments 10% better. Two possible causes of this difference are mentioned by O'Connor et al. (2004). Firstly they note that the antigorite sample appeared to contain brucite, which is much more reactive and will produce a much higher efficiency. Secondly, the antigorite showed an increase in BET surface area of 200% after heat treatment, which should improve reactivity, while in contrast, the lizardite showed a 300% decrease in surface area and the surface area of the treated material was then even lower than the untreated antigorite. They do not discuss the findings in detail, but speculate that it might be due to the different crystal structure.

It will be very important to establish if this difference in reactivity is a feature of their particular samples and experimental procedure or a more general rule. If lizardite serpentinites are of much lower suitability this has a big impact on the resources available, as lizardite serpentinites are considered the most abundant type. Data from other unpublished sources suggest that lizardite may be equally or even more reactive than antigorite. For the purpose of this review, it is assumed that antigorite and lizardite have roughly the same reaction efficiency. The processes options for activation are discussed in the chapter on Pretreatment (Chapter 11). Consistent testing of the abundance of serpentine polytypes in samples and of the reactivity of the different serpentine polytypes should be an important feature of the Phase 2 laboratory studies to enable a more reliable assessment of serpentinite resources.

Other laboratory studies of carbonation have used olivine grains from San Carlos and fresh dunite from Twin Sisters and Green Mountain, North Carolina, described in Appendix 1 and Part 2 of this report, covering CCSM technologies, (Verduyn et al. 2011). Serpentinite samples have also been tested by various workers, particularly antigorite serpentinite from Cedar Hill, Pennsylvania, southwest Oregon and serpentinite mine waste from Hitura in Finland. The Hitura serpentinite is described as consisting of chrysotile, lizardite and antigorite, in that order of abundance but no figures are given (Teir et al., 2007). Several laboratory studies on serpentinite only describe the material as serpentinite and do not identify the polytypes present. Several of these rocks, such as the dunites and Cedar Valley serpentinite have been distributed to various laboratories as a 'standard' test material. This is very good for comparing the efficiency of the various procedures. However, this does mean that only a very restricted range of compositions has actually been tested.

2.3 SUMMARY

The preceding sections have described the classification and range of compositions of ultramafic rocks. However, experimental studies of mineral carbonation have only used the simple olivine-rich or serpentine-rich end-members and the vast majority of ultramafic rock compositions must currently be regarded as untested. This is shown graphically in Figure 6 where the composition of these tested samples is shown in relation to the full range of rock compositions.

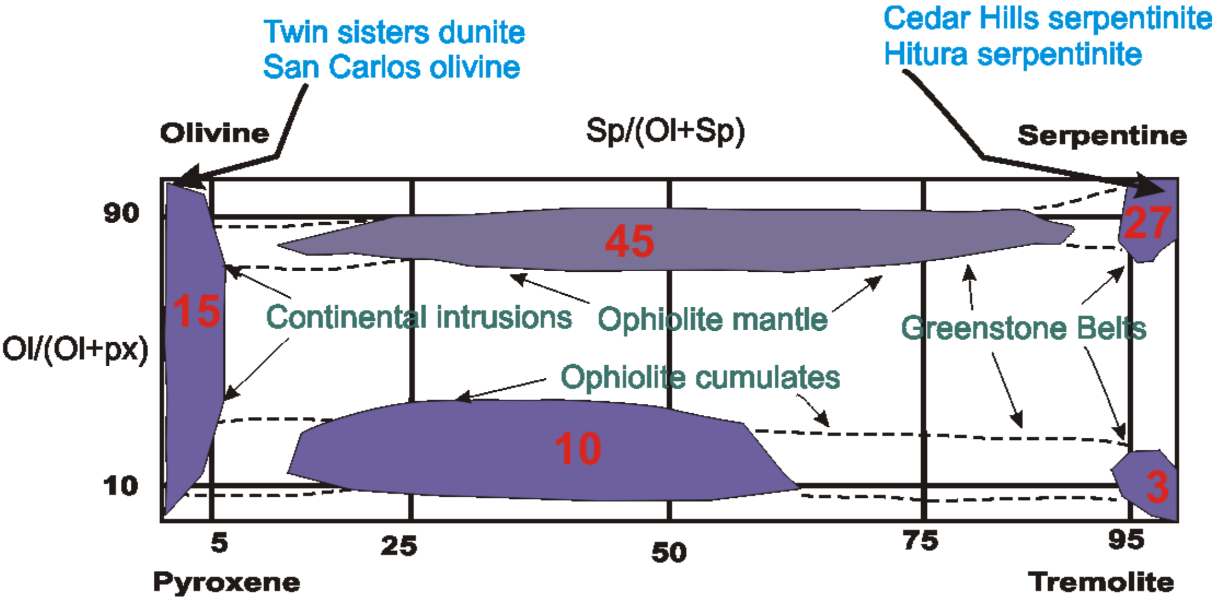


Figure 6 The range of compositions of ultramafic rocks showing the main types tested by experiments. [Copyright BGS, NERC]

The nature and complex variability of most natural ultramafic rocks has been described in detail in Appendix 1 and emphasises the fact that many ultramafic rocks consist of intimate mixtures of olivine, pyroxene and serpentinite as shown in Figure 7.

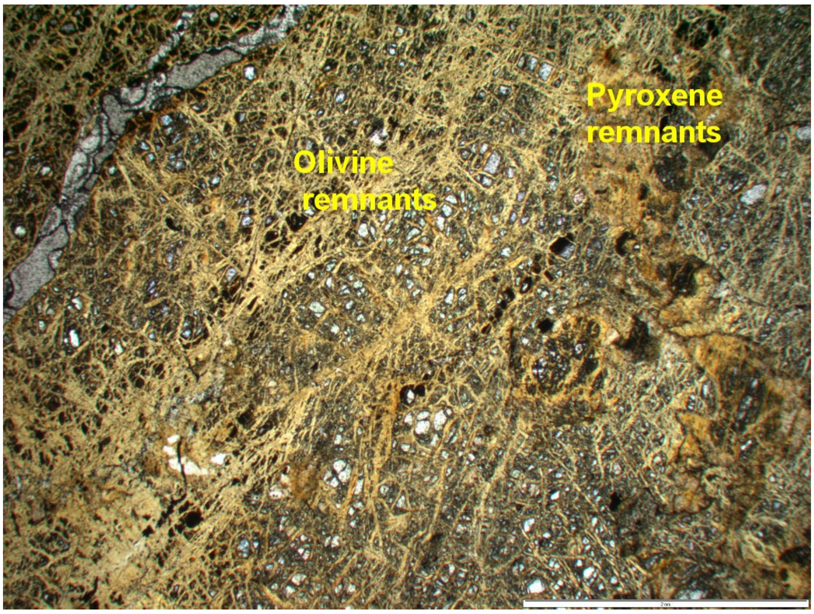


Figure 7 Typical partially altered peridotite from UAE, scale bar 2 mm. (ppl), consisting of serpentine with numerous tiny remnants of olivine and pyroxene. [Copyright BGS, NERC]

A further factor that needs to be taken into account is that olivine rocks and serpentine rocks are subjected to different types of pre-treatment and processing. As discussed in more detail in Part 2 (Chapter 11) Olivine rocks are treated by very fine grinding and serpentine by heating (Verdyn et al. 2011). The processes are mutually exclusive. If the vast bulk of ultramafic rocks are to be considered as a potential resource, a process that can deal with mixed olivine-serpentine rocks needs to be developed. The descriptions and photos in Appendix 1 show that it will be extremely difficult to separate the olivine and serpentine in these rocks at an economically viable cost.

At the current stage of technology development, only dunites should be considered as a source for an olivine-based process and serpentinites as a suitable resource for a serpentine-based process. Figure 8 shows clearly, what a small proportion of possible ultramafic rocks this is.

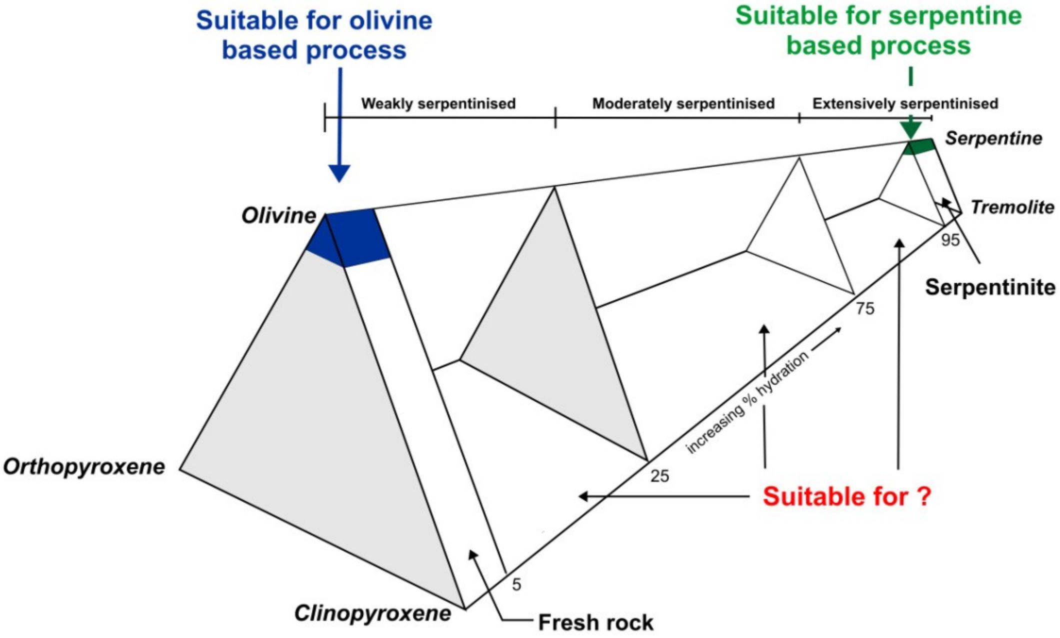


Figure 8 The composition space of ultramafic rocks showing those that can be considered as suitable resources for mineral carbonation. [Copyright BGS, NERC]

3 Assessment of UK rock resources for CCSM

The BGS digital geology maps have been used to identify all the bodies of ultramafic rock in the UK. There are 276 such bodies, but many are very small and when the data were filtered to remove those areas covering less than $0.5km^2$, the number of suitable bodies was shown to be 27. This indicates a resource of around 20Gt, roughly 10 times the project target of 2.2Gt. A more detailed examination of the data led to the rating of these possible resources based on rock type and location. The top six areas, rated as A, give a possible resource of 13.5Gt – roughly six times the project target. The information from this survey suggests that there is sufficient rock source material in the UK for CCSM to be a viable proposition.

3.1 INTRODUCTION

The overall aim of the assessment of UK resources is to demonstrate the potential to capture at least 2% of current UK CO_2 emissions (11Mt CO_2 per year) for 100 years i.e. a total capacity of 1.1Gt CO_2. It requires roughly 2 tonnes of rock to capture each tonne of CO_2, hence 2.2Gt of rock resource is required at a rate of roughly 22Mt of rock per year.

3.2 METHODOLOGY

The assessment of UK resources is based on the BGS solid geology maps of the UK. Most people are familiar with topographic maps of roads, hills etc. that are used in everyday life, but are generally less aware of geological maps and their use. Geological maps will therefore be described in detail in the following section.

The geological maps produced by BGS are in various forms, and this study uses the digital 1:50,000 scale DigMap50 dataset (examined using ArcView software). To calculate the volume of resource, we assume that the rock body shown on the map can be quarried to a depth of 35m. This is a conservative estimate, erring on the side of caution, as we are not making any study of the details of possible sites at this stage. Larger quarries in the UK work to depths of 100m or more and this might be possible for some of the resources described in the following sections. Estimates of resources in other countries have used depths of up to 500m (Lackner et al. 2008). This might be justified for very large rock bodies such as those in Oman, the UAE, and parts of the USA. However, it is not likely applicable to locations in the UK.

To calculate a tonnage of resource from its volume, we need to know the specific gravity (SG) of the rock. The resource definition (Section 2) showed that possible resource rocks ranged from fresh dunite with a SG of around 3.3 to serpentinite with a SG of 2.55. The exact nature of the rock makes a significant difference to the tonnage calculated. A few of the references we use actually quote SG values and, when available, these values are used. In some cases, the descriptions of the mineralogy, particularly in areas where our team members have worked, enable us to make an estimate of the SG. In other areas where there is little information, we use a default, mid-range value of 2.85.

Using the assumptions outlined above, a quarry with an area of $1km^2$, a depth of 35m, and a rock SG of 2.85 has a resource of 100 million tonnes (Mt). This would capture 50Mt CO_2, as roughly 2 tonnes of rock is required to capture each tonne of CO_2 (section 2.2.3). A large quarry in the UK extracts around 5Mt per year, thus an area of $1km^2$ would have resources for a life of 20yrs. To achieve the target of 22Mt per year, four to five quarries of this size would be required. It is quite likely that in some places, a lower rate of extraction from a smaller quarry could be considered appropriate, and hence for the purpose of this survey we have taken as the lower limit a rock body with a surface area of 0.5km^2 (a resource of 50Mt). Rock bodies with an area less than 0.5km^2 have been excluded from this assessment. The total requirement to meet the resource target is 22km^2 of extractable resource.

3.2.1 Geological maps

Most people are familiar with topographic maps such as those produced by the Ordnance Survey in the UK. These maps are based on surface features that are easily and accurately measured by surveyors on the ground and, more recently, from high-resolution satellite images. Most geological maps are fundamentally different, despite the fact that they may be superficially similar. The type of map required for a study such as this is a **solid or bedrock geology map**. Such a map portrays the rocks occurring at or near the surface down to a depth of tens of metres or more. In an arid, mountainous area such as the UAE, there is little or no vegetation or soil, and in most places, the bedrock is at the surface.

Figure 9 Typical scenery in the mountains of the UAE. [Copyright BGS, NERC]

In this type of setting, the changes in rock type can be clearly seen on air photographs and satellite images due to changes in colour and topographical features (Figure 10).

Figure 10 Google earth satellite image of part of the UAE showing the contrast between brown ultramafic rocks and grey schists.

Conditions in the UAE enable very accurate solid geology maps to be made. In the UK, however, conditions are very different and, with the exception of a few upland areas, solid bedrock is rarely seen at the surface (Figure 11).

Figure 11 Scenery in northeast Scotland where several ultramafic rock bodies are found. [Copyright BGS, NERC]

The bedrock is typically covered by thicknesses of superficial deposits or drift (such as boulder clay, river gravels, peat and soil), which are usually up to a few metres thick. The widespread presence of superficial deposits and soils mean that bedrock is only exposed in a few places – often amounting to less than 1% of the surface area. This means that the solid geology map has to be constructed from small amounts of widely spaced information. A solid geology map of a lowland area of the UK is therefore inherently less accurate than one of the UAE as there is far less information available to construct the map.

The information available to create the geological map is sparse and widely spaced, meaning that most of the final map is based on the geologist's interpretation of the available data and on interpolation. The accuracy of the final map is thus controlled by a combination of the amount of data available and the knowledge and experience of the geologist making the interpretation. The final 2D map is based on a 3D interpretation of all available information.

The following figures demonstrate how the same outcrop pattern can be interpreted in different ways and thus can lead to over- or under-estimates of the amount of a resource. Figure 12 shows how a large subsurface body has two small areas exposed through the surrounding sedimentary rock. The map shows the areas **a** and **b** as ultramafic rocks, and the most conservative estimate of the resource is to use only these areas. There may be sufficient information for the geologist to assume that the rock body is continuous beneath the surface, and then the area c can be used as a reasonable estimate. If, however, the same geology is covered by a thin layer of superficial deposits and soil, only area **a** is visible, and there would be a very considerable underestimate of the resource.

Figure 13 shows two bodies of intrusive ultramafic rock that produce exactly the same outcrop pattern. If the rocks comprising both intrusions are very similar, the geologist might assume they were continuous. In this instance, however, it is the wrong assumption, leading to an overestimate of the resource. When the area is covered with superficial deposits and only one small area of rock is exposed this gives a small underestimate of the resource.

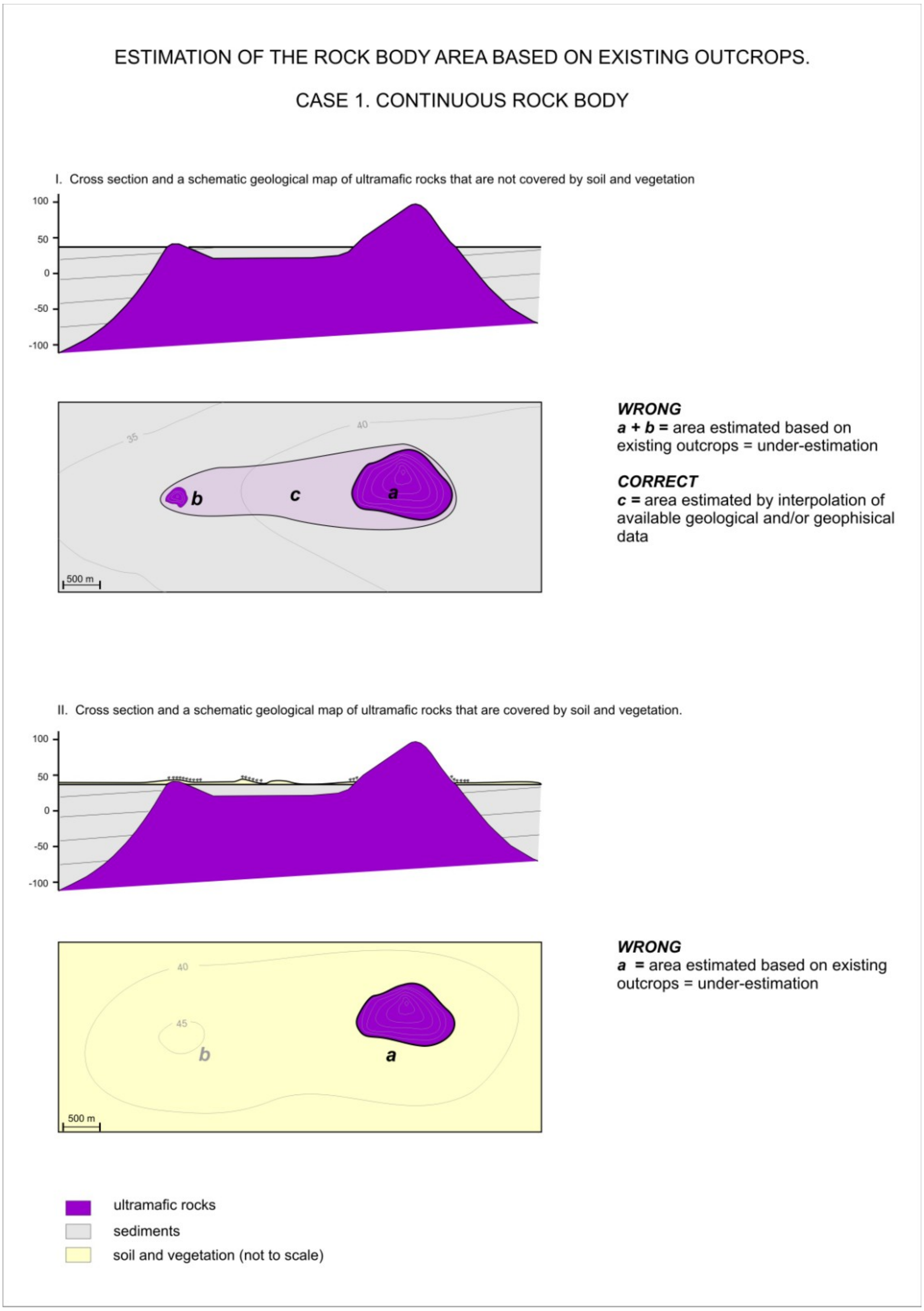


Figure 12 A schematic geological cross section and map showing possible interpretations of the geology and resource estimation. [Copyright BGS, NERC]

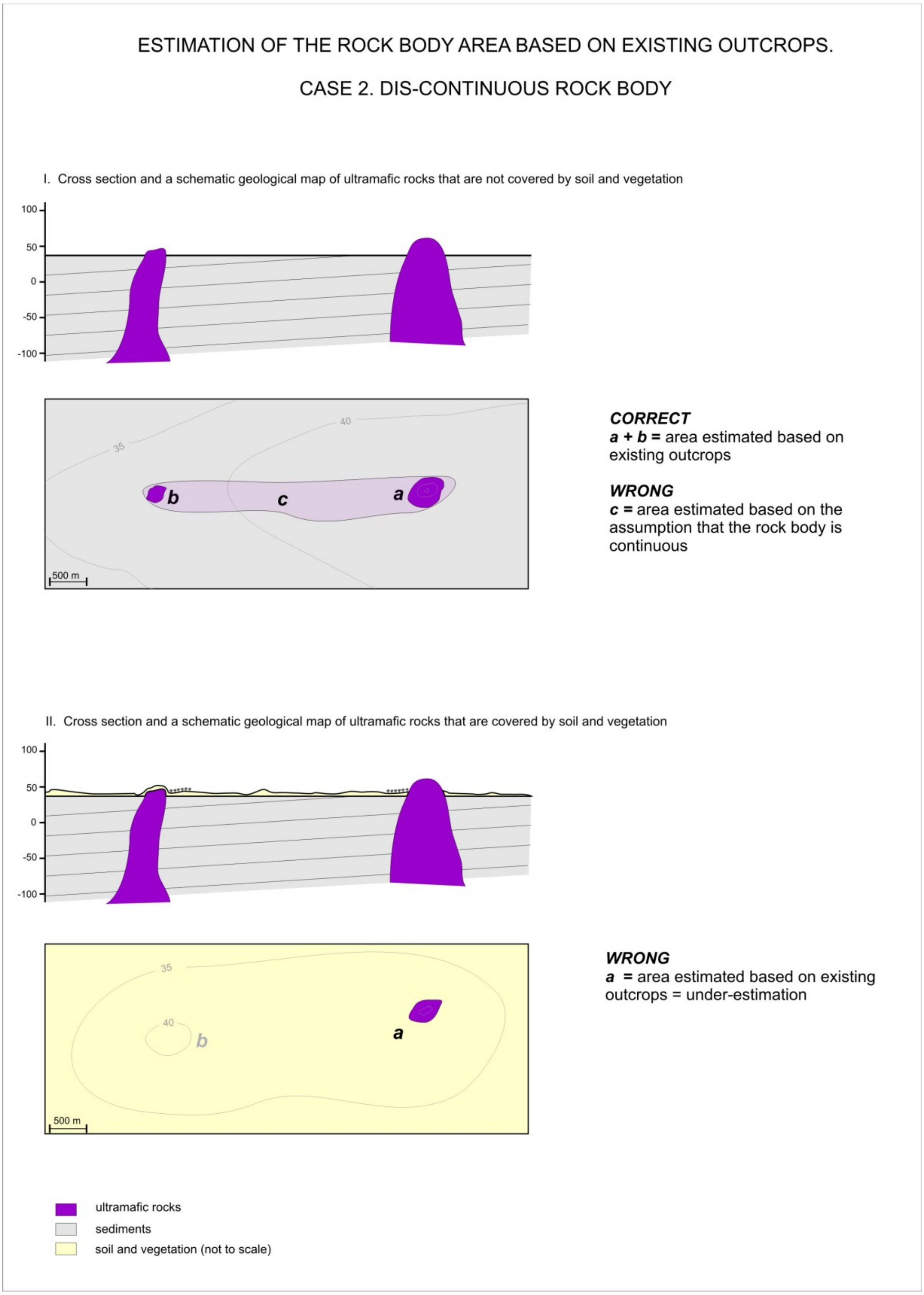


Figure 13 A schematic geological cross section and map showing alternative interpretations of the geology and resource estimation. [Copyright BGS, NERC]

These examples are given to demonstrate that existing geological maps are the best starting point for the location of possible source rocks and the initial estimation of resources. They are *not*, however, the final answer, and must be treated with caution. For the estimates used here, only the exposed area of rock has been used, which gives a reliable but minimum estimate. There may be alternative sources of information (such as geophysical data) that can considerably improve the estimation of the size of bodies of ultramafic rock. Serpentinites often have a strong magnetic signature, and fresh ultramafic rocks are denser than normal sedimentary rocks and clearly show up on gravity surveys. Examination of additional sources of data is envisaged for Phase 2 on a small number of selected sites that should enable a more reliable and probably larger estimate. However, once sites have been chosen as possible source areas, a proper mineral exploration programme will be required to accurately determine the size and quality of the resource. This might involve detailed surface sampling, trenching, drilling boreholes and geophysical surveys. This has to be done properly, as the investment required to open a large quarry is tens of millions of pounds.

3.2.2 Selection criteria

The digital geology map has been used to identify areas of ultramafic rocks that are larger than 0.5km^2. The BGS Memoirs that accompany the published maps and other BGS reports, along with published papers, have been used to build up information about the composition of the rocks at each location.

The proportions and compositions of the constituent minerals are used to classify the rocks according to the scheme described in section 2.2.1 and shown in Figure 5. This gives an initial indication of the likely suitability of the rock; only those rocks that plot in or close to fields 1 and 5 are considered suitable. The degree of serpentinisation is an important feature, as increasing amounts of non-serpentine silicate minerals decrease the suitability for CCSM. This feature has rarely been a point of interest in previous studies, often being referred to in vague terms, and will need to be investigated in greater detail for any areas targeted during Stage 2.

The location of the rock bodies has been examined using 1:50,000 Ordnance Survey datasets, paying particular attention to proximity to features that are likely to preclude exploitation of the body e.g. those that are located in, or very close to, towns and villages. Other factors that will considerably affect the cost of working a body have also been considered. These include:

- Remoteness – long distances greatly increase cost of infrastructure requirements and transport costs.
- Topography – location on tops of rugged mountains will make quarrying more difficult.
- Transport links – existing major roads could be used for transporting large amounts of rock, but small narrow roads could be very impractical and thus need upgrading.
- Coastal location – transport by ship is much cheaper, hence, a location at or very close to the coast (particularly existing harbours) could greatly reduce transport costs and enable usage of rock at any other coastal locations.
- Amount of resource – this has been calculated, firstly, on the area of rock actually shown on the map and, secondly, on a larger area if a greater extent of continuous rock can reasonably be assumed

Finally, the combination of all these features has been used to arrive at an overall suitability rating. Suitable rocks with a coastal location or with very good transport links are rated A.

Suitable rocks with inferior location are rated B, whereas less suitable rocks or those with very poor locations are rated C. Only those with an A rating are likely to be considered further in Phase 2.

3.3 UK RESOURCES

The examination of the digital geological maps showed that there were 276 polygons designated as ultramafic rock (see **Error! Reference source not found.**). This shows that ultramafic rocks are widespread in Scotland, and are present at a few locations in Southwest England and on Anglesey, North Wales.

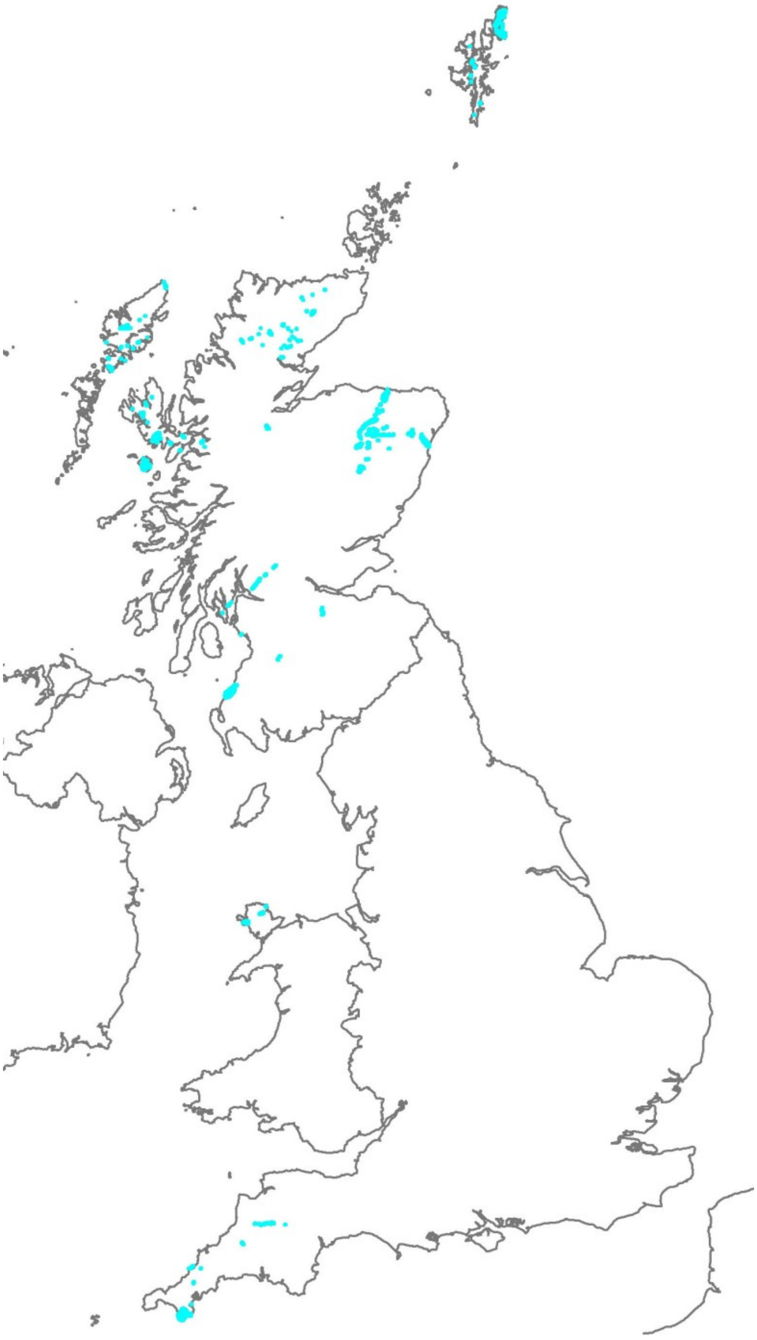


Figure 14 All polygons of ultramafic rocks in the UK. [Copyright BGS, NERC]

When we apply the area cut-off criterion at 0.5km^2, and eliminate those that are clearly unsuitable rock types (such as those with abundant amphibole), the number of bodies reduces to 27. These 27 bodies have a total surface area of 206km^2, nearly ***10 times*** the resource target of 22km^2. The locations of these 27 bodies are shown on Figure 15, but to make the data more informative the size of the symbol reflects the amount of resource at each location.

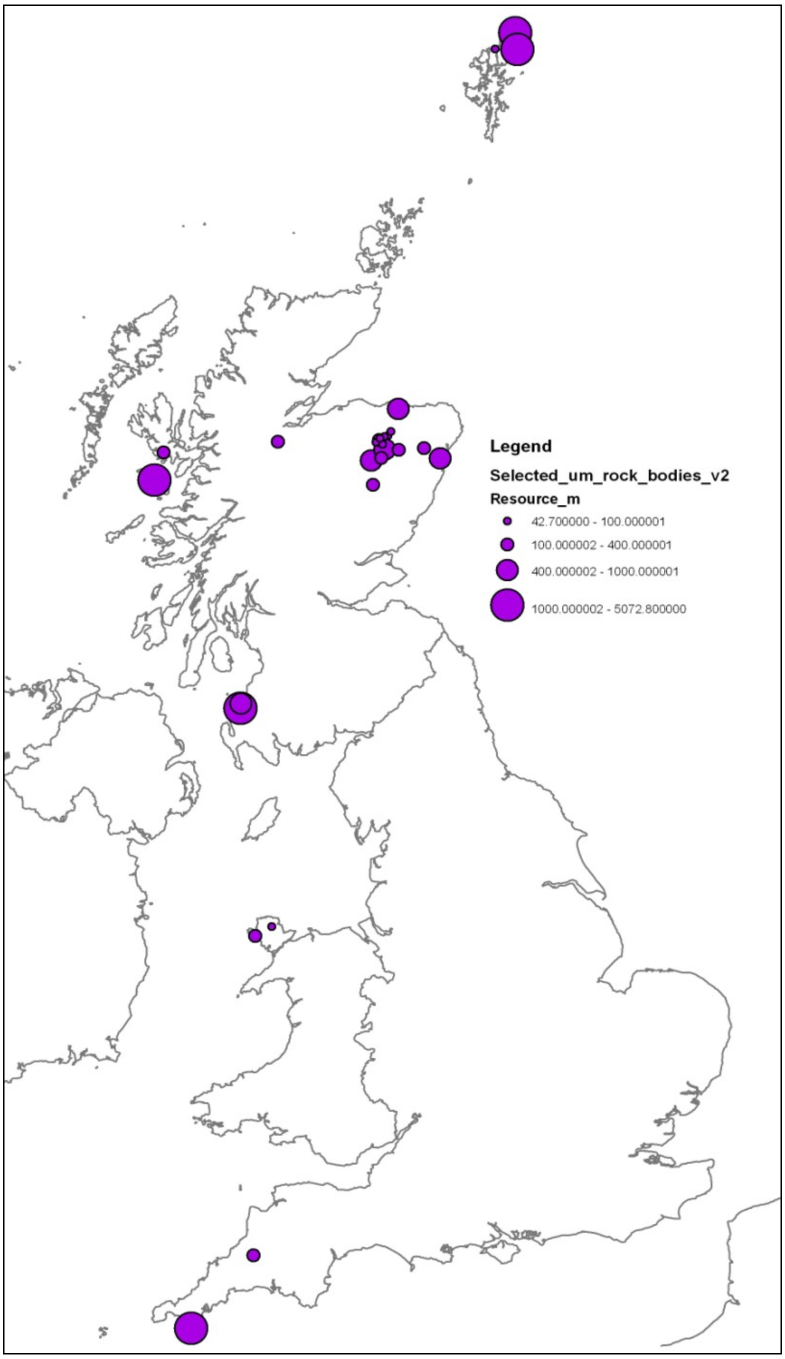


Figure 15 The locations of all ultramafic rocks rock bodies with area greater than 0.5km^2 with the size of symbol related to the magnitude of the resource in Mt. [Copyright BGS, NERC]

The bodies are shown in Table 2, being listed, firstly, in order of overall rating and then by decreasing resource size. A full description of each of the bodies is given in Appendix 2, but in the following section, a summary of the features of the highest rated bodies (A or A/B) will be described.

Location	Area sq km	Rock type	Rock Clasification	Resource MT	Rating
Lizard Peninsula, Cornwall	53.7	Meta-peridotite, serpentinite	5 & 4	5073	**A**
Shetland Isles (Unst)	38.2	Serpentinite, meta-peridotite	5	3500	**A**
Ballantrae South	16.6	Serpentinite	5	1540	**A**
Shetland Isles (Feltar)	16.4	Serpentinite, meta-peridotite	5	1499	**A**
Belhelvie	10.3	Meta-peridotite, serpentinite	4&5	951	**A**
Ballantrae North	9.5	Serpentinite	5	881	**A**
				13444	**Total**
Portsoy	4.7	Serpentinite	4 & 5	439	**A/B**
Anglesey-Holy Island	1.1	Serpentinite	4 & 5	100	**A/B**
Shetland Isles (Cunningsburgh)	0.9	Serpentinite	5	83	**A/B**
				14065	**Total**
Isle of Rhum	22.1	Peridotite and melatroctolite	6 with Plg	2325	**B**
Glen Nochty	5.9	Serpentinite, meta-peridotite	5	549	**B**
South Boganclogh	4.9	Serpentinite	3 & 4	454	**B**
Isle of Skye	2.8	Peridotite and troctolite	6 & 1 with Plg	295	**B**
Glen Urquhart	2.0	Serpentinite, meta-peridotite	5 & 10	182	**B**
Kindie Burn	1.4	Meta-harzburgite, serpentinite	5	127	**B**
Upper Deveron NE sector	1.0	Serpentinite	5	93	**B**
Huntly-Knock intrusion	0.9	Ultramafic rock	7	90	**B**
Blackwater intrusion	0.8	Serpentinite, meta-peridotite	5 & 10	74	**B**
Upper Deveron SW sector	0.6	Serpentinite	5	56	**B**
				18310	**Total**
North Anglesey	0.5	Picrite	9 & 4	43	**B/C**
Oldmeldrum	2.6	Serpentinite and tremolite schist	4 & 5	261	**B/C**
South Inch	1.5	Serpentinite	5	141	**B/C**
Polyphant	1.2	Meta-peridotite, serpentinite	4 & 5	113	**B/C**
Kelman Hill metaultramafites	2.8	Metaultramafite	15	274	**C**
Coyles of Muick	1.4	Meta-pyroxenite, serpentinite	9	143	**C**
North Boganclogh (Mount of Haddoch)	1.0	Serpentinite, meta-peridotite	5	89	**C**
Upper DeveronCentral sector	0.7	Meta-pyroxenite, serpentinite	13	70	**C**
	205.3			**19444**	**Total**

Table 2 The properties of the main resources of ultramafic rocks in the UK. [Copyright BGS, NERC]

3.3.1 Lizard Cornwall

The Lizard peninsula in Cornwall is largely composed of serpentinite and constitutes the largest single resource of ultramafic rocks in the UK, around 5Gt; this is twice the project target. The body has both a coastal location and an established quarrying industry for aggregate and armourstone (most of the quarried material is transported away from the area by sea). The scale of quarrying is, however, on a very much smaller scale than envisaged for a CCSM resource quarry. From a technical point of view, the Lizard is an ideal source area, but it is an area of outstanding natural beauty, a popular holiday destination and there could well be difficulties with areas having special designations and planning restrictions that will need to be investigated further.

3.3.2 Shetland Islands

The Shetland Islands have several resources with the largest, Unst, having 3.5Gt, the second largest single body in the UK. Neighbouring Fetlar, with 1.5Gt, is another large resource. There is a smaller but still significant deposit (0.8Gt) on Mainland. The rocks are largely serpentinite and hence very suitable. The deposits actually occur by the coast on relatively small islands and are eminently suitable for transport by sea. Unst has a small existing quarrying industry, largely for the working of talc, and several industrial installations connected with the oil industry. The Shetland Islands are very promising from a technical point of view and merit further investigation.

3.3.3 Ballantrae

The Ballantrae bodies are on the Ayrshire coast about 40km south west of Ayr and 90km from Glasgow. The two adjacent bodies have a combined resource of 2.4Gt and are serpentinite, a suitable rock type. These bodies alone could fulfil the project target. The bodies are at a coastal location suitable for sea transport and not close to major towns or villages. Ballantrae is very promising from a technical point of view and merits further investigation.

3.3.4 Belhelvie

Belhelvie is on the coast just north of Aberdeen. It has a resource largely of serpentinite, a suitable rock type, that comprises nearly 1Gt. Quarrying for granite is well established in the Aberdeen area and the location is suitable for sea transport. Belhelvie is very promising from a technical point of view and merits further investigation.

3.3.5 Portsoy

Ultramafic rocks, largely serpentinite, occur on the coast and in a group of bodies located inland from Portsoy, on the Banffshire coast, about 60km northwest of Aberdeen and 90km east of Inverness. The rock type is very suitable and a location near the coast makes sea transport feasible. Estimating the size of the resource is difficult as there is virtually no rock exposed except at the coast. The resource estimate of 0.4Gt is based on the sum of the actual polygons on the map, but if there were some subsurface continuity between them then it could be much greater. The setting in a tectonic fault zone makes estimation of the true extent particularly difficult. The Portsoy area has several good points from a technical point of view and merits further investigation.

3.3.6 Anglesey

There is a body of serpentinite on Holy Island, itself located on the northwest side of Anglesey Island, in North Wales. The resource is 100Mt and is located on the coast and hence suitable for sea transport. The bodies are, however, relatively close to small villages, which might make exploitation difficult.

3.3.7 Locations with B rating

Ten locations were given a B rating, and these fall into two distinct categories. Firstly, the rocks described from Portsoy in section 3.2.5 are located at the northern end of a long chain of km-sized ultramafic rock bodies that extend southwards for 150km. Those further south are mostly composed of very suitable serpentinite, but due to their smaller size and increasingly remote locations they are ranked as B. Their more remote locations do, however, give them one more positive feature in that they are mostly in uninhabited areas, utilised for forestry or rough grazing, and therefore much more likely to get planning permission for quarrying operations.

The other category includes the rocks on the Inner Hebridean islands of Rum and Skye. Rum has a substantial deposit of olivine-rich rocks, that are interlayer with feldspar-bearing rocks, that probably forms a resource of over 2Gt, and the coastal location is convenient for sea transport. Critically, though, the whole island is a nature reserve owned by Scottish Natural Heritage and it is a National Nature Reserve with no development permitted. It is highly unlikely that permission would be given for quarrying on a large scale. The rocks on Skye, in the Cuillin Mountains, are also a mixture of mafic and ultramafic rocks. The rocks are probably less suitable and the location in rugged mountains makes quarrying less attractive .

3.4 SUMMARY

The BGS digital geology maps have been used to identify all the bodies of ultramafic rock in the UK. There are 276 such bodies, but many are very small and when the data were filtered to remove those areas covering less than $0.5km^2$, the number of suitable bodies was shown to be 27. This indicates a resource of around 20Gt, roughly 10 times the project target of 2.2Gt. A more detailed examination of the data enabled the rating of these possible resources based on rock type and location. The top six areas, rated as A, give a possible resource of 13.5Gt – roughly six times the project target.

This section also outlined the possible inaccuracy of the estimates based on the current geological maps. In lowland areas of the UK where surface exposures of rock are rare, these are more likely to be underestimates rather than overestimates, but this should be explored further in Phase 2.

The information from this survey suggests that there is sufficient rock source material in the UK for CCSM to be a viable proposition.

3.5 CONCLUSIONS

- a resource of around 20Gt, roughly 10 times the project target of 2.2Gt
- areas rated as A, give a possible resource of 13.5Gt – ~six times the project target
- these are more likely to be underestimates rather than overestimates
- there is sufficient rock source material in the UK for CCSM to be a viable proposition

4 Waste materials

The waste streams of calcium oxides that can be used for mineral carbonation are: Recycled concrete aggregate (RCA), steel slag (SS), blast furnace slag (BFS), pulverised fuel ash (PFA), secondary steel slag such as argon-oxygen decarburisation (AOD), desulphurisation slag and ladle slag, incinerator bottom ash (IBA), air pollution control (APC) residue, cement kiln dust (CKD), incinerator sewage sludge ash (ISSA), paper sludge ash (PSA), biomass ash (BA), clinical waste ash (CW) and quarry waste and fines.

Some of the potential resources identified, such as cement kiln dust, pulverised fuel ash or steel slag, enjoy the benefit of being co-located with the emitter to which they could be applied. However, the high variability of their volumes and chemical composition represent a major obstacle to the deployment of these materials in CCSM. In particular, the presence of contaminants might affect the efficiency of CO_2 sequestration and the possibility to produce some valuable products.

4.1 INTRODUCTION

Waste materials from a wide range of industrial processes are rich in the oxides and hydroxides of calcium and magnesium, which are good source materials for CCSM. However, the consideration of waste is in many ways more complex than natural rocks. Rocks are a finite resource in a specific location that stay essentially unchanged for long periods and could act as a resource for hundreds of years. In contrast, a material previously considered as waste may find a use due to developments in technology. A second factor that can radically change things is legislation that imposes penalties on disposal of waste and creates markets for low value by-products. The use of waste products is a constantly moving target with a very unpredictable future.

A variety of waste materials that could generally be called mineral waste provides sources of the useful oxides that are readily available and reactive. Even through their total amounts are far smaller than silicate rocks, the fact that they may not need expensive pre-treatment and react comparatively quickly with CO_2 due to their chemical instability means that they represent a valuable raw material for accelerated carbonation. Also, mineral wastes such as cement kiln dust, pulverised fuel ash or steel slag are often located close to CO_2 emitters, therefore eliminating the issue of transport over long distances (IPCC, 2005; Teir et al, 2007; Huijgen, et al, 2007).

The waste streams of calcium oxides that can be used for mineral carbonation are: Recycled concrete aggregate (RCA), steel slag (SS), blast furnace slag (BFS), pulverised fuel ash (PFA), secondary steel slag such as argon-oxygen decarburisation (AOD), desulphurisation slag and ladle slag, incinerator bottom ash (IBA), air pollution control (APC) residue, cement kiln dust (CKD), incinerator sewage sludge ash (ISSA), paper sludge ash (PSA), biomass ash (BA), clinical waste ash (CW), and quarry waste and fines. Carbon dioxide sequestration by mineralisation using the above materials has been demonstrated in recent studies (Gunning, et al 2009 and 2010; Li et al, 2007, Teir et al. a, 2007; Doucet, 2010; Huijgen et al, 2007; Iizuka et al, 2004).

The inorganic materials that represent a potential resource for the carbon capture and storage by mineralisation must be available in large volumes and provide sources of oxides for the carbonation reactions. Instead, the materials that are already reused in other ‘environmental friendly applications' represent a future potential resource for the CCSM technology that might be used as an intermediate step before the final application.

4.2 RECYCLED CONCRETE AGGREGATE

Recycled concrete aggregate (RCA) results from the processing of inorganic material previously used in construction and principally comprising crushed concrete. The cement paste component of RCA consists of a series of calcium silicate hydrate and calcium aluminate hydrate compounds, including calcium hydroxide, which is highly alkaline. The alkalinity of RCA can decrease due to age-related natural carbonation. Chloride ions from the application of de-icing salts to roadway surfaces or sulphates from contact with sulphate-rich soils can also be present (FHWA, 2008). The maximum theoretical CO_2 uptake (Rx%) is 30, based on the oxide content (cement). However, the current RCA RCO_2 and Rx%/RCO_2 are 2 and 15, respectively (Kashef-Haghighi and Ghoshal, 2010). In many places, this material is no longer considered as waste and now re-used by the construction industry for engineering rock-fill or as hardcore beneath foundations and roadways. However, it might be feasible to enhance its properties by processing it using CCSM technology producing an intermediate product that might be access different low and high-end markets.

4.3 PULVERISED FUEL ASH AND FURNACE BOTTOM ASH

Pulverized-fuel ash (PFA), also known as coal fly ash (FA) is extracted by electrostatic precipitation from the flue gases of modern coal-burning power stations and is similar in grain size to cement. PFA is a fine powder made up of individual fused ash spheres with a diameter of about 10–15µm. A certain proportion of PFA is formed as cenospheres, which are hollow glass spheres. Furnace bottom ash (FBA) is the coarser fraction of ash produced in coal burning power stations resulting from the fusion of pulverized-fuel ash particles which fall to the bottom of the furnace. It varies in size from fine sand to coarse gravel and has a porous nature. FBA accounts for approximately 20% of the annual coal-fired power station ash production (WRAP a 2010; WRAP and EA, 2009). The principal components of bituminous coal fly ash are silica, alumina, iron, and calcium (5-30%), with varying amounts of carbon. The chemical properties of fly ash are influenced largely by those of the coal burned and the techniques used for handling and storage. Calcium and magnesium oxide content varies according to the type of coal utilized in the power plants. The global production of fly ash is far larger than the potential uses and only 30% is used as construction material; therefore, new applications are needed. Taking into account the volumes available worldwide, PFA can be considered a potential resource even though, at the current state of the art, the maximum amount of CO_2 that can be sequestrated by PFA is only about 5% by weight (Rx%/RCO_2) (Li et al, 2007). However, it is not one of the more attractive types of waste material.

4.4 STEEL AND BLAST FURNACE SLAGS

Steel slag is the by-product of the manufacture of steel from pig iron. There are two types: basic oxygen furnace slag (BOF) and electric arc furnace slag (EAF). The steel slag can be subdivided in Basic Oxygen Furnace slag (62%), Electric Arc Furnace slag (29%), and secondary metallurgical slag (9%) (Gahan et al, 2009).

EAF slag generally has lower free lime and magnesia contents than BOF. Blast furnace slag is a by-product from the production of iron, resulting from the fusion of fluxing stone (fluorspar) with coke, ash and the siliceous and aluminous residues remaining after the reduction and separation of iron from the ore (WRAP b, 2010). The chemical composition of slag is usually expressed in terms of simple oxides calculated from elemental analysis determined by X-ray fluorescence. Steel slag usually presents about 40-50% of calcium oxide. The predominant compounds are dicalcium silicate, tricalcium silicate, dicalcium ferrite, merwinite, calcium aluminate, calcium-magnesium, iron oxide, and some free lime and free magnesia.

BFS is a non-metallic by-product produced in the process and typically contains calcium oxide in the range of 34-43% and magnesium oxide content ranging from 7 to 15%. It consists primarily of silicates, alumino-silicates, and calcium-alumino-silicates. The molten slag, which absorbs much of the sulphur from the charge, comprises about 20wt% of iron production (FHWA, 2008). Averagely, these materials show RCO_2, Rx% and Rx/RCO_2 of 3, 76 and 25, respectively (Teir et al. b, 2007; Doucet, 2010).

4.5 INCINERATOR BOTTOM ASH

Incinerator bottom ash aggregate (IBA) is processed from the material discharged into the burning grate of municipal solid waste (MSW) incinerators and comprises 80 to 90% of the total MSW ash production (WRAP b, 2010). The most abundant elements in municipal waste combustor ash are silica, calcium, and iron. Although ash composition can be expected to vary from facility to facility, these elements are present within relatively predictable ranges. Generally, about 35-50% of CaO and 3-4% of MgO are available in IBA (FHWA, 2008). The use of processed bottom ash in engineering applications is in its infancy in the UK and CCSM may be more attractive as a use for this material than production of aggregate, due to the high content of the desirable Ca and Mg. IBA present RCO_2 and Rx% of 4, 20.

4.6 AIR POLLUTION CONTROL RESIDUE

Air pollution control residue consists of particulates that originate in the primary combustion zone area and are subsequently entrained in the combustion gas stream and carried into the boiler and air pollution control system. The entrained particulates stick to the boiler tubes and walls or are collected in the air pollution control equipment, which consists of the scrubber, electrostatic precipitator, or bag house. Ash extracted from the combustion gas consists of very fine particles, with a significant fraction measuring less than 0.1mm in diameter (FHVA, 2008). Calcium and chloride are by far the major constituents, accounting for more than 50% of the total ash mass, consistent with the large $Ca(OH)_2$ at 38% and CaClOH at 29%, totalling 67%. These compounds are used in excess for acid gas abatement (Baciocchi et al, 2009). Therefore, carbonates derived from APC residue might not be suitable for construction due to their high level of chlorine. However, APC residue is a hazardous waste that can be reclassified by CCSM to not hazardous by decreasing its metal leaching.

4.7 CEMENT KILN DUST

Cement Kiln dust (CKD) is a fine by-product of Portland cement and lime high-temperature rotary kiln production that is captured in the air pollution control dust collection system (e.g., cyclones, electrostatic precipitators). The chemical and physical characteristics of CKD mainly depend on the method of dust collection employed at the facility. The concentration of free lime in CKD is typically highest in the coarser particles captured closest to the kiln, while fine particles tend to exhibit higher concentrations of sulphates and alkalis. About 75% of the kiln dust particles are finer than 0.030mm. CKD from wet-process kilns tends to be lower in calcium content and richer in salts than dust from dry-process kilns. Chemically, CKD has a composition similar to conventional Portland cement. The principal constituents are compounds of lime, iron, silica, and alumina. CaO usually varies between 31 to 44% and MgO between 1 and 1.7% (FHWA, 2008). The experimental sequestration capacity (Rx/RCO_2) was evaluated as about 11% (i.e. every kg of CKD has potential to capture 0.11kg of CO_2) (Huntzinger et al, 2009).

4.8 OTHER RESOURCES FOR CARBONATION

A number of other inorganic materials such as argon oxygen decarburization slag (AOD), ladle slag, desulphurisation slag, incineration sewage sludge ash (ISSA), paper and biomass sludge ash can be considered as a secondary resource for carbonation in the UK and might be of primary importance in other countries based on their availability. Secondary processes for further refinement of stainless steel through reduction of carbon content and pollutants such as sulphur also produce slag. To further refine the steel after coming out of the BOF or EAF, fluxes are added to the molten steel while in a ladle. The slag from this process is usually called ladle slag. The chemical composition of ladle slag is significantly different from that of steel furnace slag in that the former has a very low FeO content and a higher Al_2O_3 content. In addition, a mixture of argon and oxygen with addition of cleaning agents to eliminate impurities is added to the molten to decrease its carbon content. The oxygen combines with carbon in the unrefined steel to reduce the carbon level. The presence of argon enhances the affinity of carbon for oxygen and thus facilitates the removal of carbon forming argon oxygen decarburization slag (AOD) (Shi, 2002). Sewage sludge ash is the by-product produced during the combustion of dewatered sewage sludge in an incinerator. It contains between 3 and 37% of CaO (FHWA, 2008). Paper sludge incineration ash (PS) is the residue from incineration of the wastewater sludge from papermaking. It contains residual fibres, fillers and chemicals and contains about 50% of CaO (Gunning et al, 2010). Biomass ash (BA) is the by-product produced during the combustion of the pressed plant fibre residue (rape-cake) after oil extraction. Wood ash (WA) is generated from combined electricity and heat generation plants using wood sources. BA and WA contain about 25% and 45% of CaO, respectively (Gunning et al, 2010). These wastes have high contents of desirable elements but are only produced in low volumes in the UK.

4.9 QUARRY WASTE AS POTENTIAL RESOURCE

Processing of crushed stone for use as construction aggregate consists of blasting, primary, and secondary crushing, washing, screening, and stockpiling. These operations produce significant amounts of waste, often referred to as quarry waste and fines. Usually sand and gravel workings do not produce permanent waste, while hard-rock quarries produce variable amounts of quarry waste and fines. Quarry fines are the inherent fraction of an aggregate below 63µm, as defined by BS EN standards. However, more commonly, quarry fines are defined as the < 4mm ‘sand’ fraction that is the undersize from screening coarse aggregate and the 63µm fraction as the airborne dust collected in dust extraction filters. Following the conclusions of section 2.2, only waste and fines from operations processing ultramafic rocks should be considered as potential resources (Mitchell, 2009).

4.10 WORLD POTENTIAL RESOURCES

The potential for developing waste recovery and recycling, the increasing pressure of environmental issues and the future scarcity of natural resource will force a rising number of countries to develop genuine recovery strategies for their waste, opening a new market for secondary raw materials obtained from waste. Under this scenario, CCSM might play an important role in converting steel slag, CKD, RCA, and other mineral wastes into low/high end materials (Veolia, 2009). Only the first three resources would be potentially able to sequester about 220 Mt/year of carbon dioxide worldwide considering the current experimental efficiency (Gunning et al, 2009 and 2010; Huntzinger et al, 2009; Kashef-Haghighi and Ghoshal, 2010; Amutha Rani et al, 2008).

The Veolia survey indicates that the way in which waste is treated at the production and collection stage depends on the approach of the different societies and can be summarised in uncontrolled landfill sites, disposal into controlled landfills, recovered by biogas or energy production, incineration with or without energy recovery and material recovery ranging from composting to recycling.

Generally, the choice of incinerated municipal solid waste corresponds to high urban population densities and a relative shortage of space such as for Japan or Northern Europe. About 200 million tonnes of MSW (1.7B tonnes re produced worldwide every year) is treated through energy recovery incineration (Veolia, 2009). Therefore, about 40Mt of Incineration Bottom Ash (IBA) would be potentially employable in CCSM assuming a mean ash yield of 20wt% and an efficiency in weight of 25% (1 tonne IBA sequestrates 0.25 tonne CO_2). This amount would sequester 10 Mt CO_2/y.

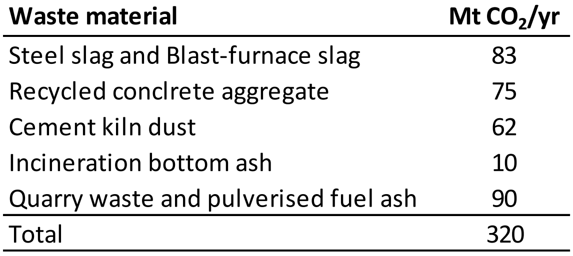
Waste landfilling is preferred where there is a large space available (e.g. Australia, USA) or clay soils (e.g. UK). About 1Bt of construction and demolition (C&D) waste are produced every year mainly in the developed countries, Europe (570Mt) and USA (260Mt) (Veolia, 2009). The global production of RCA has the potential to store 75Mt of CO_2 per year, based on 50 wt% of C&D waste being Recycled Concrete Aggregate (RCA) (DEFRA a, 2007) and an experimental efficiency in weight of 15% (1 tonne RCA stores 0.15 tonne CO_2) (Kashef-Haghighi and Ghoshal, 2010).

Steel and blast-furnace slag production data for the rest of the world are unavailable, but it is estimated that annual world iron and steel slag output is of the order 220 to 420Mt (330Mt in average), based on typical ratios of slag to crude iron and steel output (USGS, 2006). The global potential of the steel and blast furnace slag resource, if used in the CCSM process, would be about 83Mt CO_2 stored.

The world cement production was 2.77Bt in 2007 (Cembureau, 2009) and about 0.15 tonnes of cement kiln dust (CKD) are generally produced for each tonne of clinker or cement produced, of which about half is generally sent to landfill. Therefore, approximately 208 Mt might be available for CCSM and this amount would be able to sequestrate 62Mt CO_2/y. This calculation takes into account that only a few manufacturing facilities recycle all or a portion of their CKD into the raw material line entering the kiln as happens in the UK (Huntzinger et al, 2009).

Finally, the world production of mining industrial (quarry waste) and electricity waste (pulverised fuel ash) in 2006 was about 6Bt (600Mt of PFA) distributed as follow: Russia (2.5Bt), EU27 (0.92Mt), China (0.9Mt) (Doucet, 2010; Marxsen, 2001; Veolia, 2009). Potentially, this waste might capture and store about 90Mt of CO_2 per year based on 5% conversion efficiency in weight and assuming that 30% of the 6Bt would be usable (see Section 2.1.8).

Table 3 summarises the global mineral waste potential that could be employed in CCSM technology. The sum of the different wastes would be able to sequester about 320Mt CO_2/year, based on the assumption and calculations reported here.



Waste material	Mt CO_2/yr
Steel slag and Blast-furnace slag	83
Recycled conclrete aggregate	75
Cement kiln dust	62
Incineration bottom ash	10
Quarry waste and pulverised fuel ash	90
Total	320

Table 3 Global potential CO_2 uptake of waste materials. [Copyright University of Nottingham]

5 Assessment of UK waste material resources for CCSM

The current state of the art for mineralisation technology indicates that only about 2-15% of the annual CO_2 reduction target set for this project can be achieved using the main industrial wastes and by-products as feedstock alone. However, mineral waste usage presents significant drawbacks such as high chemical variability and presence of contaminants and for these reasons it does not represent a preferential option at this stage of the programme.

5.1 INTRODUCTION

The objective of the overall project is to demonstrate the potential to capture, as a minimum, 11Mt of CO_2 per year for 100yrs totalling 1.1Gt. This section assesses the potential of UK waste streams to contribute to this total. The assessment of the inorganic waste utilizable as resource material for CCSM technology has been carried out considering the annual volumes available in the UK, their chemical composition, their location and the annual tonnage estimated in a lifespan of 20yrs (from 1990 to 2010) to minimise the waste production variability. The lifespan of 20yrs was chosen because of:

1. Difficulties in retrieving long-term data for past production that even when available are often inaccurate and too site-specific compared to the permanent availability and access of silicate rocks suitable for CCSM, and
2. The unpredictable nature of future sources and availability of waste. Clearly, it is too ambitious to estimate the availability of the mineral waste materials 70-100 years ahead.

A discussion on the future availability of the waste resource and the possibility to employ the CCSM technology as an intermediate process towards the re-use of the mineral wastes has been included in this section. The parameters used to assess the current and the future potential of the mineral wastes as resource for the CCSM were:

1. Volumes available and future trend
2. Presence of calcium and magnesium

5.2 RECYCLED CONCRETE AGGREGATE

Recycled concrete aggregate is increasingly being seen as a valuable source of engineering materials for the construction industry in the UK. Using RCA materials potentially reduces reliance on primary aggregates and lowers the environmental impact of construction. On average, the data indicate that about 46Mt of RCA is generated annually in the UK (WRAP c, 2006; Lawson at al, 2001).

All available RCA is currently used in construction applications as aggregate, mainly for low-end applications such as building products and land reclamation hereby reducing the amount of material that is sent to landfill and reducing the need for virgin materials in new constructions (WRAP b, 2010). In 2006, RCA was generally used in the construction of road-bases - a low-value application that often yields less than the cost of crushing it (Harvey, 2006).

Economic and legislative developments driven by increasing emphasis on energy and water consumption, recycling and waste generation and disposal issues will influence the future aggregate production trends, driving a radical change in the extraction and processing aggregates industry. The wide distribution of the RCA production facilities might be an advantage for the integration of a mineralisation plants reducing costs of moving materials for long distances. Several local aggregate recycling plants are present in the UK because the businesses are profitable only if the material movements are limited to a local area (30-50 miles). These materials might economically be transported to the local CO_2 emitter (e.g. cement plant, incinerator, steel slag, coal power plant). RCA is generally produced using a commercial plant to produce crushed-rock aggregate, comprising primary jaw and secondary cone crushers and screens. The already-crushed material would not require the mining and grinding costs associated with rocks. Therefore, RCA might be successfully employed in inland locations where the CCSM by rocks in not economical.

The UK construction sector consumes about 380Mt of resources every year and is facing a number of fundamental changes over the next few years. The aim is to develop a sustainable construction industry capable of delivering a low carbon future and to meet the current carbon, water and waste reduction targets Figure 16 shows the distribution of C&D waste in the UK from 1999 to 2005. The data suggest that in the future there will be a significant amount of recycled concrete aggregate even if is difficult to extend this assumption for a lifespan of 100yrs.

The above considerations are reflected in the increased fraction of C&D waste that has been recycled in the recent years and indicate that RCA tonnage that reached 50% of C&D waste in 2010 will increase in future. The publication of the Quality Protocol, the European Standard for Aggregates and BS8500-1:2006 on the production of recycled aggregates demonstrates the full recovery and quality of the product and will increase confidence in the product and indicates that concrete from RCA can also be used for high value applications such as structural concrete opening a new profitable market.

Cost for crushing the C&D waste is approximately £7/tonne while the RCA selling price for low-end applications (e.g. road sub-base aggregate) is 2-4£/tonne (WRAP. 2010; Soutsos et al, 2010). CCSM might be used as intermediate step after the recycling process to further improve the properties of the RCA. Potentially, CCSM technology would be able to produce materials with higher purity for high-end applications and less pure products to use for low-end applications (e.g. silica). The process would not require transport of feed material for long distances if the RCA is close to the emission site and also, the CCSM products can be used locally as nowadays happens for RCA. CCSM might contribute to increase the overall RCA selling price enough to cover all the cost of crushing it. For example, the recovery of ‘pure` silica sand would guarantee an extra value to the demolition companies that process RCA.

It has been proposed that the production of aggregates and construction products could possibly be modified to enable easier recycling and improve the properties of recycled aggregate, for example by the separation of the cement from the natural aggregate enabling the production of a recycled aggregate with properties much closer to those of natural aggregate (Goodquarry, 2010). The CCSM might help this by enhancing the ‘purity’ of the different product streams of the RCA by multistage processes downstream from the RCA grinding and screening steps.

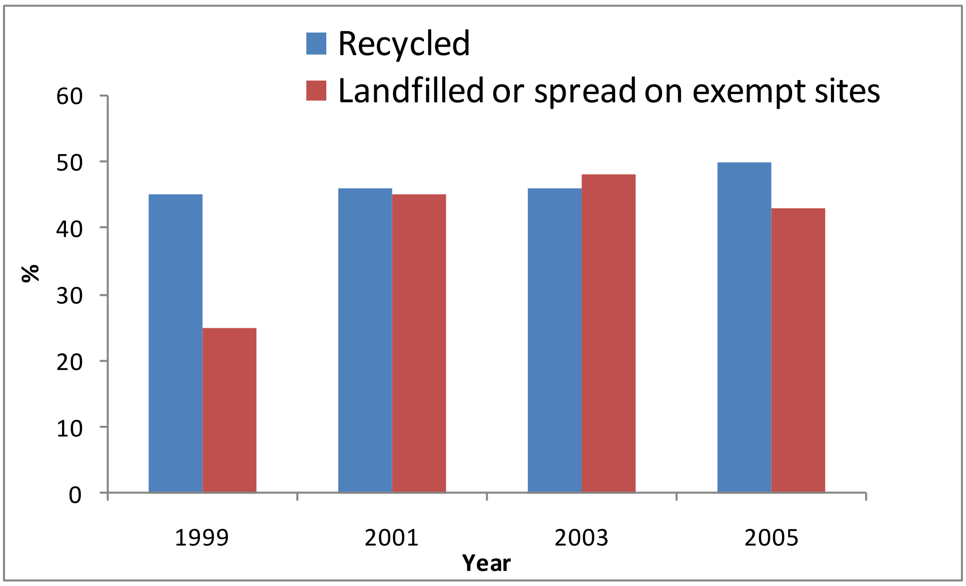


Figure 16 Construction and demolition waste management from 1999 to 2005 [Communities and Local Government, 2007].

5.3 PULVERISED FUEL ASH AND FURNACE BOTTOM ASH

About 5.6Mt of PFA and 1Mt of FBA are produced every year in England and Scotland. About 50% of PFA and FBA is sold for varied applications including concrete production, asphalt, hydraulically bound mixtures, uses without any binding agent (e.g. fill material in embankments and as capping layers) or as grouts, where the material is hydraulically pumped or injected into the ground to fill void space. The remaining 50% of PFA is normally sent to landfill as conditioned ash in either a monofill or a lagoon. FBA and PFA come from coal-fired power stations that are mainly located in the North West, Yorkshire and the Humber, West Midlands, East Midlands, South East of England and Scotland. Stockpiles depend on regional demands for the material in relation to local power station output and large volumes are being sent to landfill in Scotland, Yorkshire, the North West, and the Midlands (WRAP b, 2010; WRAP and EA, 2009).

It is very likely that coal power stations will continue to generate electricity for the predictable future in the UK and due to the environmental issues the new 'clean coal' power stations will adopt carbon capture and storage technologies such as mineralization. Therefore, the production of fly ash in the UK is expected to likely remain unvaried and available for the construction industry. In addition, concrete made with 50% fly ash denote poor performance and are not recommended (Berndt, 2009).

There is more fly ash produced annually than is used, and when it is used to extend CEM I cement, it can save about 20-30% tonnes of CO_2 per tonne of concrete with equal 28 day strength (Sustainable Concrete, 2010). Under this scenario, CCSM might play an important role helping the sector to fully re-use the fly ash and in the same time adding them a higher value converting at the power plant the ashes into silica sand and carbonate powders. However, the low PFA reactivity (5% in weight) would require moving larger volumes of products compared to the original feedstock and the potential CO_2 sequestration in the bigger coal fired power plants results quite low ranging from 0.05 to 0.1% of the CO_2 emitted.

Therefore, big emitters would not significantly benefit from the use of their wastes in terms of CO_2 reduction and large amount of silicate rocks would be required if CCSM was adopted.

5.4 STEEL AND BLAST FURNACE SLAGS

A total of 1.25Mt/year of steel slag is produced in England and Wales. This slag would be able to sequester about 1.5% (17% in theory) of the annual steel works CO_2 emissions (about 21Mt/yr). BOF and EAF account for 0.99Mt (2001) and 0.26Mt (2005), respectively. Currently, the total production is mostly used as aggregates. About 3Mt of blast furnace slag is generated in England and Wales. At present, about 75% of the slag is processed to produce ground granulated blast furnace slag (GGBS), which is used by the concrete industry as a cement replacement material. The remaining fraction (25%) is air-cooled and is used as an aggregate. The split between the two uses is dictated by production choices, economics and demand (WRAP b, 2010; DEFRA d, 2010). Overall, 100% of the steel slag and 25% of the blast-furnace slag could potentially be converted into carbonates by CCSM that may possibly enhance the value of the products. However, all is currently used as aggregate. Therefore, SS and BFS might be considered as a potential CCSM's feed material in the near future only if the mineralisation technology is used to produce an intermediate product with enhanced properties compared to the raw slag.

Steel slag and, to a lesser extent, blast-furnace slag are very promising candidates to be used as feedstock in the CCSM technology for a series of reasons:

- They are directly located at large emission plants,
- Their calcium oxide content is quite large and guarantee a CO_2 uptake of 25-30% in weight
- They are mainly used in low-end applications for the production of aggregates and CCSM would not diminish this end use but also could open new market increasing the slag value.

CCSM would increase the amount of product at the end of the process to a reasonable extent due to the high efficiency compared to other mineral wastes such as pulverised fuel ash that require a larger amount of materials. In addition, the high iron oxide content in the slag can further increase its value where the CCSM technology employed is able to separate it from the other products stream. The production of crude steel and steel slag in the UK is shown in Figure 17. The production of steel slag varied from 0.9 to 1.2Mt in the last 20 years when the production of steel decreased about 30% in the same period.

The future availability of steel slag might flatten out considering that the production of electric arc furnace (EAF) slag is expected to rise in the South East and can balance the decline of the basic oxygen furnace (BOF) slag. The latter is used for aggregate use and considering that the demand is expected to continue, there is little necessity to find alternative uses (DCLG, 2007). However, CCSM might become attractive due to the possibility of separation and recovery of the iron oxide and the silica products, adding value to the slag. In addition, the blast-furnace fraction not currently used for GGBS (25%) could be converted by CCSM technology.

It is believed that the global steel market will rise from 1.4Bt in 2010 to 1.6Bt in 2014 and the iron market will rise by 0.2Bt in the same period (MEPS, 2010)

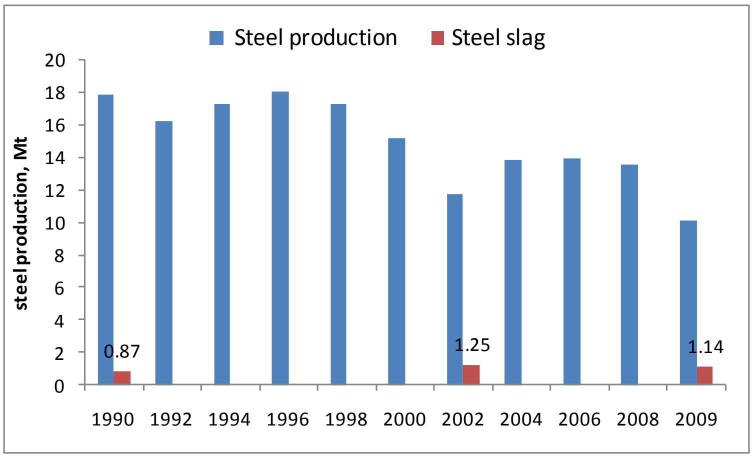


Figure 17 UK crude steel production from 1990 to 2009 and steel slag production in 1990, 2002 and 2009 [Iron and Steel Statistics Bureau, 2010]

BOF steel (8Mt) is mainly produced by Corus in South Wales (Port Talbot), Humberside (South Teesside), and Yorkshire (Scunthorpe). Instead, Electric Arc Furnace (EAF) steel (2.1Mt) is produced in Rotherham (Corus), Sheffield (Forgemasters, Outokumpu), Cardiff (Celsa, Forgemasters), and Sheerness, Kent (Thamesteel). Celsa alone produces 1.2Mt/year. The distribution of the steel slag is limited to few areas in the country and the majority of the works are close to port facilities that would facilitate the movement of materials in and out. The steel slag would be able to sequester only a small fraction of the CO_2 emitted by the steel works and additional materials (e.g. silicate rocks, RCA) would be necessary to sequestrate all the CO_2 emitted in the steel works.

5.5 INCINERATOR BOTTOM ASH AND AIR POLLUTION CONTROL RESIDUE

The annual tonnage of incinerator bottom ash (IBA) produced in England is 0.7Mt of which 0.4Mt (55%) is currently used to produce aggregates. Previously, from 1996 to 2000, about 90% of the ash produced in the UK was sent to landfill but due to the strict EU landfill directive the space used for these hazardous wastes has significantly decreased and alternatives such as CCSM would be necessary (Li et al., 2007). The Waste Strategy 2000 predicted a rise of waste-to-energy of about 25% of municipal solid waste by 2020. This is likely to result in significant increases in IBA available for mineralisation (WRAP b, 2010). Table 4 shows the annual emissions and potential CO_2 uptake of IBA of a selection of MSW incineration plants. It is noticeable that a high proportion of CO_2 might be captured by the IBA produced in the same plant. This indicates that CCSM using the waste produced in the same plant seems more beneficial for small/medium emitters compared to big industrial emitters that would require movement of large amounts of external feedstock.

waste incinerators	CO2 emissions, Mt/y	IBA potential, CO2 Mt/y	potential, %
Tysesley	0.25	0.08	30.7
Stockton-on-Tees	0.23	0.05	23.2
Coventry	0.15	0.05	35.0
Wolverhampton	0.15	0.04	28.4
Dudley	0.12	0.02	16.4

Table 4 Potential CO_2 emission reduction in a selection of waste incinerators. [Copyright University of Nottingham]

However, overall IBA represents a small resource for CCSM because the majority of MSW is currently sent to landfill in the UK (DEFRA b, 2009). This resource would be much larger if the incineration would be preferred in the future due to diminishing space available for new landfill.

Air pollution control (APC) residues produced from cleaning gaseous emissions generated during combustion of wastes at incineration plants had an annual tonnage of 128,000 tonnes/yr in the UK in 2008 and 85% was landfill as hazardous waste. These residues are often transported for long distances for treatment and disposal and alternative sustainable treatments would be beneficial (Amutha Rani et al, 2008). APC residues are generated in the same locations as IBA and might be used together increasing the uptake of CO_2 in the incineration plant.

5.6 CEMENT KILN DUST

The UK cement industry disposes of about 46,000 tonnes/year of cement kiln dust (CKD), and an additional 5,000 tonnes of CKD was returned to manufacture in 2008 compared to 2007. The total annual tonnage of CKD being disposed of has fallen significantly since 1998. In that year, some 289,207 tonnes went to landfill. The CKD produced in the UK per tonne of cement produced is very low (< 1%) because the CKD is mainly recycled in the kiln during the production process. However, this small amount alone would be able to sequestrate 0.5-1% of the CO_2 emitted in each of the selected cement works shown in Appendix 3. This low value is mainly due to the very low CKD volumes produced in the UK.

The production of CKD decreased considerably from 1999 to 2008 but it is expected to rise again in the near future as shown in Figure 18. Before 2007, CKD together with sewage sludge could be used to create fertile soil in land reclamation projects, but changes to legislation now preclude this use. Therefore, the CKD sent to landfill is expected to rise to 75,000 tonnes and remain at this level from 2010 to 2015 (Mineral Products Association, 2009). It is difficult to estimate the amount of CKD that will be available in the future as global cement consumption continues to rise.

However, the cement industry might decline in the UK due to the expected rise of the cost of producing cement because of EU regulations (EU ETS, climate change agreements, carbon reduction commitments and a carbon levy) and this could worsen if the UK government added its own tax. There is a risk of dispersal overseas considering that often it is cheaper to import cement from other countries and the main industries are owned by foreign firms. Currently, Tarmac is the only British firm and has only one cement production site. The UK was a leading cement producer just 50 years ago but since then it declined to reach only 0.5% of the world output in 2005, therefore, the availability of CKD in 50-100yrs is unpredictable (Merlin-Jones D., 2010). The emissions of the cement industry might be reduced by CCSM technology. In addition, this technology might enhance the CKD value producing valuable products. Therefore, even if the resource is not available in significant quantities it could play an important role in the CCSM demonstration stage where they could integrate the rock resources in tackling the cement plant emissions even if their potential in selected cement plant was estimated to be less than 1% of the emissions. This would allow detailed investigation of the possible effect(s) of waste resource contaminants on the mineralisation process, and the influence of mixtures of different rocks and waste materials on the reaction efficiency.

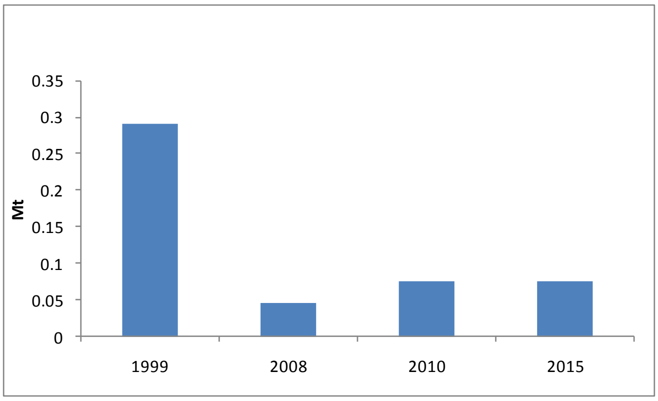


Figure 18 CKD production and forecast for 2010 and 2015 [Mineral Products Association, 2009]

5.7 RESOURCES ASSESSMENT

This section presents an assessment of the potential resource for CCSM, based on waste materials that are not currently being reused. Table 5 reports the yield of the waste materials that were assessed as primary resources for CCSM in the UK, their theoretical and experimental efficiency and the CO_2 uptake in regards to the established target, taking into account the indications given in the definition section 2 for a material to be considered as resource. The values were calculated considering the average of the annual tonnage available for CCSM (materials sent to landfill) in a lifespan of 20yrs, between 1990 and 2010. The same performance parameters of the rocks assessment were used to allow a comparison between the fresh minerals and the waste materials. As for Section 2.2.3, the efficiency parameters were:

- RCO_2 Theoretical mass ratio of the waste necessary to carbonate unit mass of CO_2 (the theoretical capture capacity, a small number is good)
- $Rx_{\%}$ Reaction efficiency, % stoichiometric conversion of Ca and Mg cations in waste feed to carbonate (a large number is good), but this is dependent on the experimental procedure used
- $Rx_{\%}$ / RCO_2 Combination of the two parameters to give an indication of the overall sustainability as a feed material (a large number is good)

Pulverised fuel ash (PFA), air pollution control (APC) residue, incinerator bottom ash (IBA) and cement kiln dust (CKD) are the current potential resource available for CCSM in the UK due to their available volumes and/or the reaction efficiencies. Table 5 presents average annual amounts of PFA, APC, IBA, and CKD available, based on information for the period of 1990 – 2010. Over this period annual production varied by ± 30%. The $Rx\%/RCO_2$ of the selected resources, based on the CaO content differs for different resources, ranging from 25 for APC to 5 for PFA and IBA (Gunning et al, 2009 and 2010; Huntzinger et al, 2009; Kashef-Haghighi and Ghoshal, 2010; Amutha Rani et al, 2008). Furthermore, in practice the theoretical uptake is not achieved (see Chemical composition of inorganic waste resources in Appendix 2). It is important to highlight that the theoretical efficiency represents the efficiency given by the amount of alkali available for the carbonation, while the experimental efficiency is the measured efficiency of the technologies investigated. It is affected by several parameters such as contact surface between CO_2 and the alkali metals, kinetics of reaction under the process conditions etc. As mineralisation technologies are developed, performance may be enhanced towards the theoretical maximum by controlling the reaction parameters.

In addition, the chemical variability of the waste resources can affect the process efficiency mainly because it changes the percentage of reactive alkali metals. For example, PFA from bituminous, sub-bituminous, and lignite coal has different proportion of CaO, MgO, silica etc. The fraction of the reactive alkali decreases proportionally to the increase of coal's quality, where bituminous has up to 17% of CaO/MgO, sub-bituminous has up to 36% CaO/MgO and finally lignite can reach 50% of Ca and Mg oxides. Therefore, the different type of the same resource can strongly affect the efficiency of mineralisation process.

Current resource	Tonnage Mt/yr	RCO_2 t_{waste}/t_{CO2}	Rx% %conv.$_{Mg/Ca}$	Rx/RCO_2 $\%_{weight}$	theoretical CO_2 uptake, Mt	theoretical target CO_2, %	experimental CO_2 uptake, Mt	experimental target CO_2, %
Pulverised Fuel Ash	2.0	20.0	100.0	5.0	0.10	0.9	0.10	0.9
Air Pollution Control Residue	0.1	1.5	38.5	25.0	0.07	0.6	0.03	0.2
Incinerator Bottom Ash	0.8	4.0	20.0	5.0	0.18	1.6	0.04	0.3
Cement Kiln Dust	0.2	3.4	33.3	10.0	0.05	0.5	0.02	0.1
Total	3.0				0.4	3.6	0.2	**1.6**

Table 5 Mineral waste resources available for carbonation in the UK, considering the annual tonnage of wastes that are currently sent to landfill and not re-used. These values represent the average considering the variability of the volumes produced from 1990 to 2010. [Copyright University of Nottingham]

Currently, the inorganic waste resources identified here have a theoretical potential to capture 0.4Mt of CO_2/year, which represents about 4% of the target. However, considering the experimental efficiency reported in previous studies and state–of-the art published research this figure is closer to 2%.

5.8 CCSM AS INTERMEDIATE PROCESS TOWARDS A FINAL ENVIRONMENTALLY-FRIENDLY REUSE

The section presents a total potential estimation of the mineral waste resource available in the UK for the CCSM assuming that 100% of the RCA and steel/blast furnace slag will be used for carbonation technology in a intermediate step before its final re-use (e.g. as recycled road filler)

Table 6 reports the yield of the waste materials that could be considered as primary resources, their theoretical and experimental efficiency, and the CO_2 uptake. Recycled concrete aggregate (RCA), steel slag (SS), blast furnace slag (BFS), pulverised fuel ash (PFA), air pollution control (APC) residue, incinerator bottom ash (IBA) and cement kiln dust (CKD) would be the potentially primary resource for accelerated carbonation in the UK.

Future potential resource	Tonnage Mt/yr	RCO_2 t_{waste}/t_{CO2}	Rx% %conv.$_{Mg/Ca}$	Rx/RCO_2 $\%_{weight}$	theoretical CO_2 uptake, Mt	theoretical target CO_2, %	experimental CO_2 uptake, Mt	experimental target CO_2, %
Recycled Concrete Aggregate	6.4	2.0	30.0	15.0	3.20	29.0	0.95	8.6
Steel Slag	1.2	3.0	75.8	25.0	0.39	3.5	0.30	2.7
Blas Furnace Slag	0.8	3.0	75.8	25.0	0.25	2.3	0.19	1.7
Pulverised Fuel Ash	2.0	20.0	100.0	5.0	0.10	0.9	0.10	0.9
Air Pollution Control Residue	0.1	1.5	38.5	25.0	0.07	0.6	0.03	0.2
Incinerator Bottom Ash	0.8	4.0	20.0	5.0	0.18	1.6	0.04	0.3
Cement Kiln Dust	0.2	3.4	33.3	10.0	0.05	0.5	0.02	0.1
Total	11.3				4.2	38.4	1.6	**14.6**

Table 6 Primary potential waste resources for carbonation in the UK, expressed in tonnes per year and diversification of the current materials reuse. These values represent the theoretical sum achievable considering the variability of the volumes produced from 1990 to 2010. [Copyright University of Nottingham]

Under this scenario, it can be seen that inorganic waste has a theoretical potential to capture 4.2Mt of CO_2/year that represents about 39% of the target or just about 15% of the target at the experimental efficiency reported in previous studies. If the CCS by mineralisation process is integrated into the already existing aggregate recycling process, it will not be in competition with the current alternative re-use. For this to be practical, the recycling centres would need to be close to emission sites.

The efficiency of the majority of the waste resources (excluding PFA and ISSA) expressed as ratio 'waste' to CO_2, are comparable with those of olivine and serpentine rocks, showing a RCO_2 between 2 and 4. Furthermore, the index $Rx_{\%}/RCO_2$ indicates that the experimental efficiency of steel slag, BFS, APC, paper sludge and RCA are comparable to those of fresh rocks, ranging from 15 to 25 while the others resources show an index below 10.

In addition, SS and BFS that have a ratio of 'waste' to CO_2 comparable to fresh rocks and an advantageous location could represent the 'perfect' candidate for the introduction of the carbonation technology.

Figure 19 shows the distribution of all the waste resources vs. the main CO_2 emitters in the UK, including potential future resources such as steel and blast furnace slag. The location of the mineral waste is widely distributed across the UK, and in many of the cases, the waste resource is co-located with the CO_2 emission source. This means that the fixation of CO_2 on-site would be advantageous and economical. In particular, the Southeast, South Wales, East Midlands, and the Northeast seem to be regions with higher potential for CCSM, considering the wastes available. Indeed, steel and cement works, incinerators, and crude-oil refineries of small and medium dimension represent the `ideal match' for the application of the technology.

RCA, steel slag, CKD results the best candidate for the application of this technology in the UK contest.

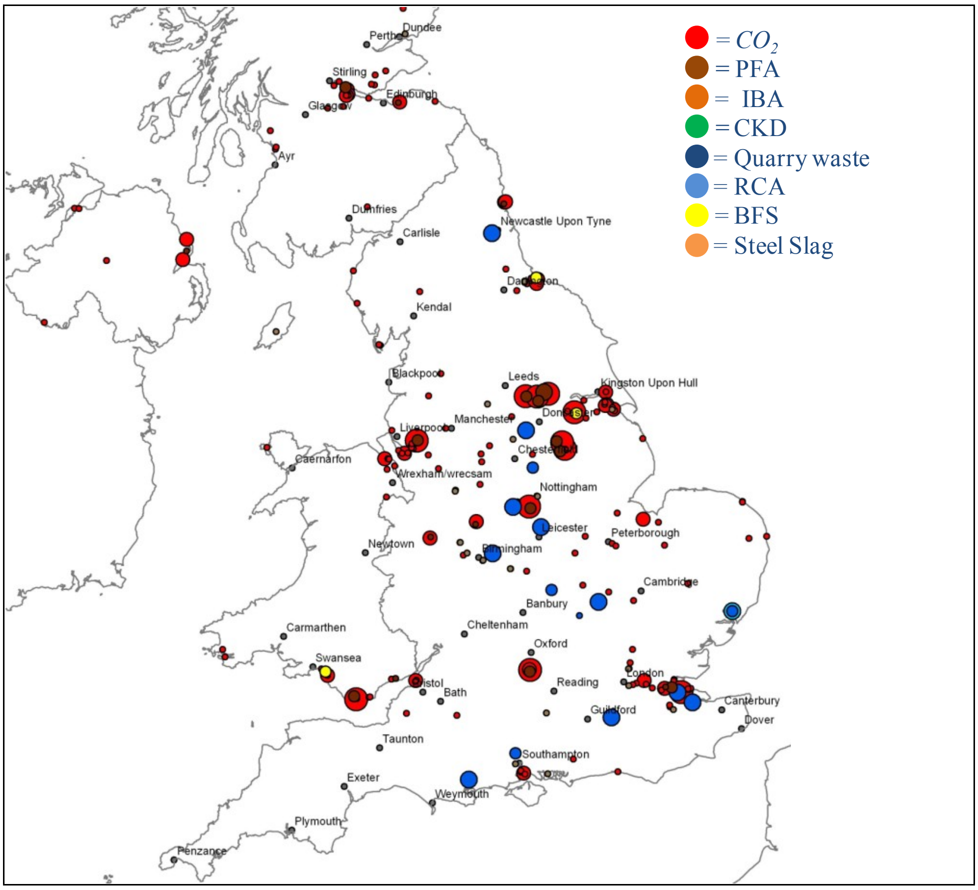


Figure 19 Waste resources and CO_2 emitter locations considering a lifespan of 20 years and a future use for CCSM. [Copyright BGS, NERC]

5.9 CONCLUSIONS

Waste resources have the theoretical potential to capture between 4 and 39% of the annual CO_2 target. 4% represents the current CO_2 uptake achievable, based on waste streams that are currently not being re-used, and 39% indicates a theoretical maximum, if all useable waste products are turned over to CCSM before their current applications and the maximum theoretical efficiency could be achieved. However, the current state of the art for mineralisation technology indicates that only about 2-15% of the annual CO_2 target can be achieved. Whilst the cumulative waste resource represents a 'complimentary resource' for CCSM in comparison to the silicate rocks, this is offset by the significant advantage of co-location with the major CO_2 emitters such as iron and steel works, cement manufacture, and power generation.

A wide array of comparatively small quantity waste and industrial by-product resources was identified. Their composition could be suitable for mineralisation, with SS, BFS, APC and RCA being the most reactive, but the extent and influence of variability needs to be further quantified.

This investigation indicates that RCA and PFA would likely be available in a life span of 100yrs. The accessibility of steel slag, BFS, IBA, and APC, however, is highly uncertain over the next 40-100yrs due to market and environmental issues. From the chemical composition of the inorganic wastes, it emerged that the wide range of contaminants that they can contain (e.g. chlorides, sulphates, iron oxides) can affect both the mineralisation process and the possible post-processing applications.

Overall, even though some advantages were identified such as using waste resources requiring less energy for the pre-treatment, co-location with CO_2 emitters, and the facilitation of waste reclassification, significant drawbacks of high chemical variability, high variability of the available volumes, and contaminants represent a major threat to their use in CCSM. Furthermore, any CCSM technology based on waste would need to be very flexible to cope with the variable feedstock whilst still achieving high levels of capture: indeed, to ensure robustness it would probably need to be able to work with new mineral also increasing both CAPEX and OPEX. These circumstances indicate that the level of uncertainty is too high compared to silicate rocks resources and it is proposed to drop this option for the present programme.

However, their uses might be considered as introductory feed material at the demonstration stage of the technology (e.g. CKD in a cement plant) when small volumes are needed and in the context where there do already exist infrastructures for the recycling and reuse of these materials. The current available volumes of CKD and SS/BFS would be able to sequester only a small fraction of the CO_2 emitted in a cement/steel works (<1.5%). These values might increase to 10-15% if all the already re-used SS and BFS would be employed in CCSM. Hence, the production of aggregates and construction products that represent the largest potential waste resource in the UK could possibly be modified to enable easier recycling and improve the properties of recycled aggregate, for example by the separation of the cement from the natural aggregate, enabling the production of a recycled cement more appropriate for CCSM technology and decreasing the possible effect of contaminants. Also, because the cost for crushing the C&D waste is higher than the price for low-end applications (e.g. road sub-base aggregate) CCSM might be used as intermediate step after the recycling process to further improve the properties of the RCA producing materials with higher purity for high-end applications (e.g. micro-silica). The post-processing products can be used locally as nowadays happens for RCA decreasing the transport costs contributing to increase the RCA selling price enough to cover all the cost of crushing it.

6 UK industrial point sources of CO_2

The UK's National Atmospheric Emissions Inventory[1] (NAEI) compiles estimates of emissions to the atmosphere from large facilities (described here as industrial point sources) such as power stations, steel works, and other industrial plants. The NAEI inventory of emissions is compiled using the following sources (Bush et al. 2008):

1. The Environment Agency's 'Pollution Inventory' (PI), the Scottish Environment Protection Agency's 'Scottish Pollutant Release Inventory' (SPRI), and the Inventory of Sources and Releases (ISR) produced by the Department of the Environment (Northern Ireland)
2. Direct from process operators or trade associations.
3. Point sources registered with and trading emission credits under the EU-Emissions Trading Scheme (EU-ETS)
4. AEA Energy and Environment, who produce estimates of emissions data from point sources regulated by Local Authority Pollution Control/Air Pollution Control (LAPC/APC) in England and Wales, and in Scotland respectively, based on site-specific data collected from these regulators.
5. Point sources where emissions are modelled by distributing national emission estimates over the known sources based on capacity or other 'surrogate' statistics.

All major industrial point sources of CO_2 in England, Wales, Scotland, and Northern Ireland that are regulated under the Integrated Pollution Control (IPC) or Integrated Pollution Prevention and Control (IPPC) regulatory regimes and produce more than 10,000 tonnes of CO_2 per year are required to report their emissions to their respective environmental protection agency.

The NAEI inventory data from 2006 were collated to produce a CO_2 point source database containing 190 records for this project (Figure 20). This was the latest data available at the time of collation. The database only lists sources that emit >100,000 tonnes per year because the amount of CO_2 captured from plants below this threshold would be small on an individual basis. If the scalability of the mineralisation is shown to be suitable for emitters smaller than this, a more comprehensive database can be explored in Phase 2.

In 2006, the UK emitted approximately 555Mt of CO_2 (NAEI website) of which 269Mt came from reporting industrial plants. Power plants account for approximately 70% (187Mt) of the total reported industrial emissions in 2006 (Figure 21). The 50 largest sources comprise 36 power plants, 9 refineries, 4 integrated steel plants and 2 aluminium smelters, with total emissions of 212Mt of CO_2 per year, which is almost 79% of emissions from reporting sites. The largest sites contain relatively low percentages of CO_2 in their waste streams and would need to be fitted for CO_2 capture. UK emissions could be significantly reduced even if CCS was implemented using only a few of these larger sources.

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[1] The UK National Atmospheric Emissions Inventory is maintained by AEA on behalf of Defra and the Devolved Administrations © Crown copyright 2006

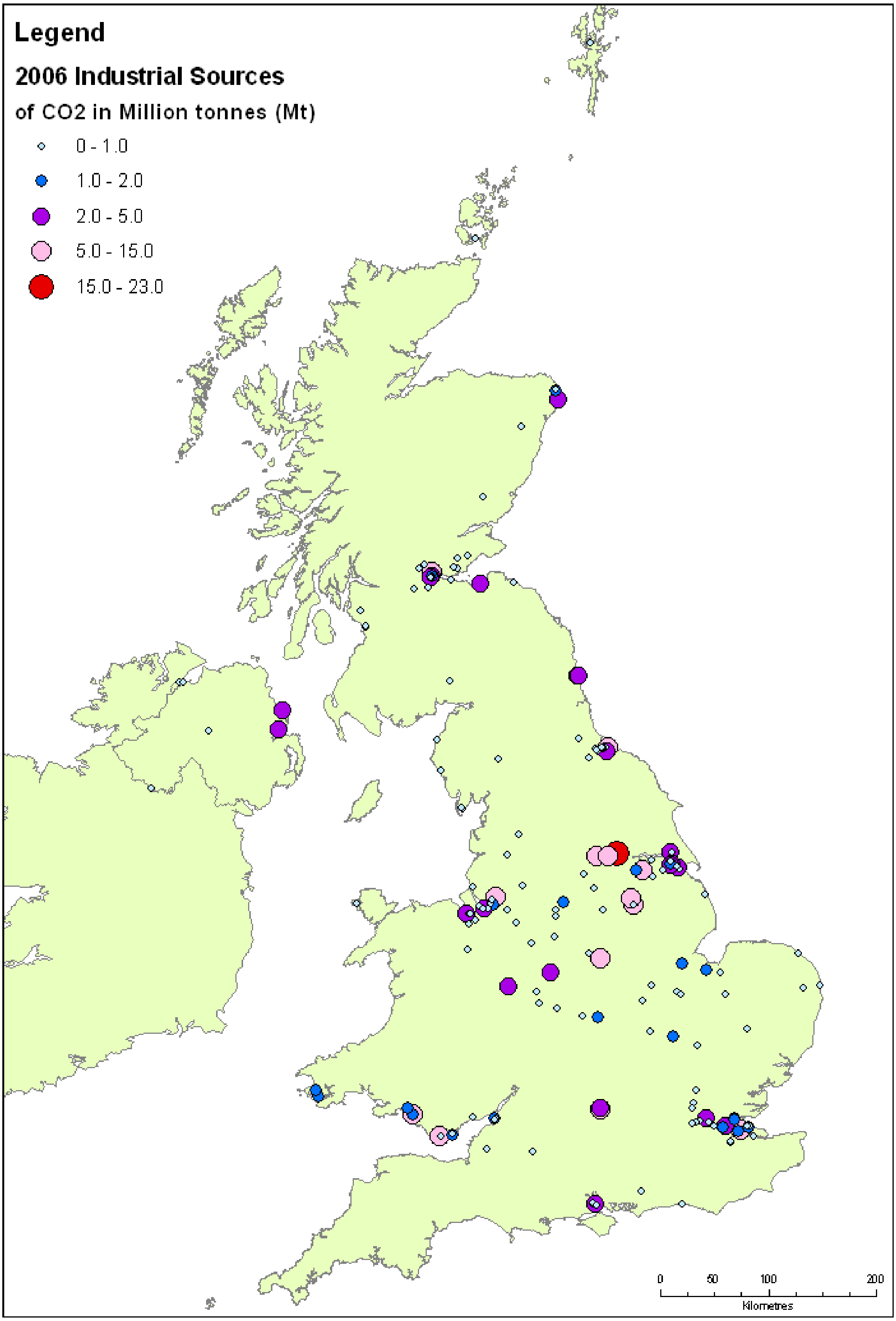


Figure 20 Map of UK industrial sources of carbon dioxide. [Copyright BGS, NERC]

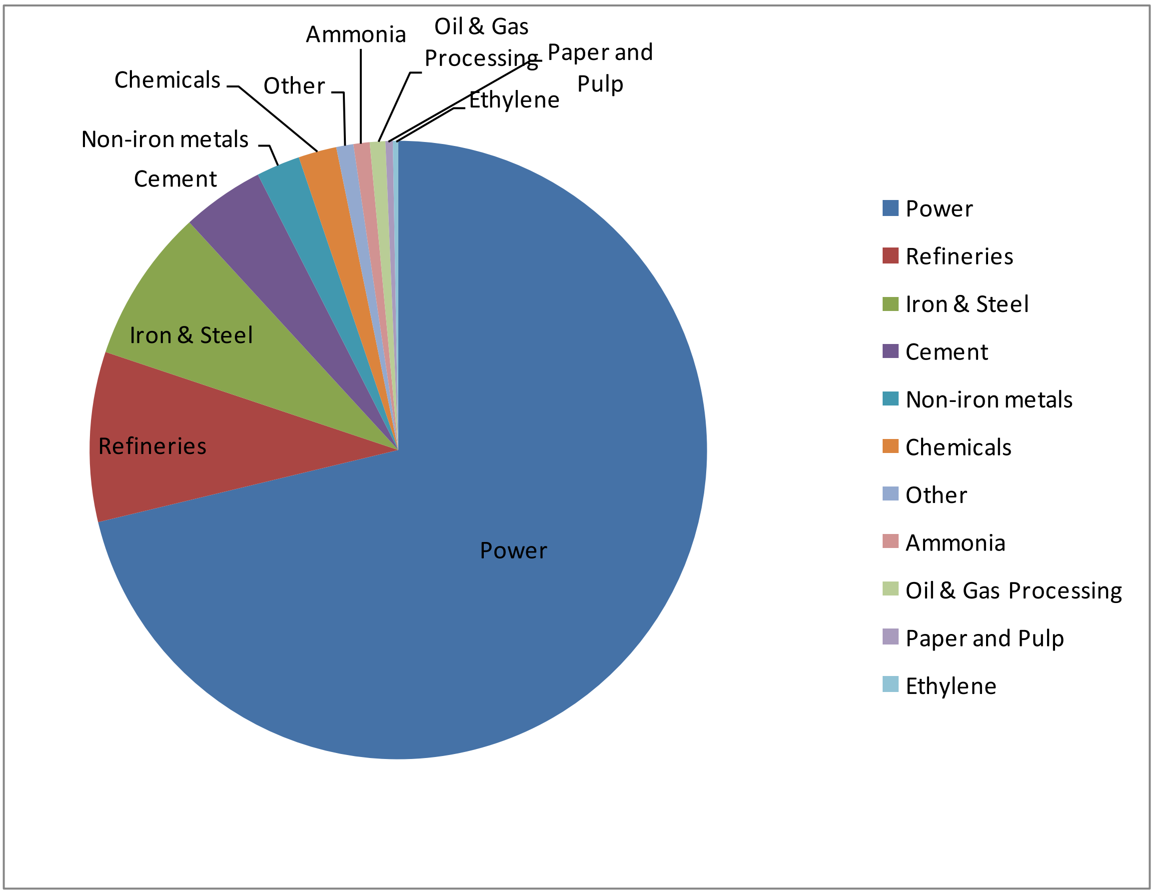


Figure 21 CO_2 emissions from industrial point sources in the UK [data from NAEI]

7 The relationship between resources and emitters

For moving large volumes of material, the ideal situation is a coastal quarry, where the material can be loaded directly onto ships, and the ships travel to a coastal CO_2 emitter. Information is presented illustrating the high number of intermediate and small emitters located within 2km of the coast, a situation where direct transport by ship is feasible. This means that a coastal mineral resource in a remote location such as Shetland could be utilised for CCSM in a wide range of emitter locations.

7.1 THE LOCATIONS OF ROCK RESOURCES AND CO_2 EMITTERS

The section of this report dealing with UK waste streams (Section 5) showed that these might make a minor contribution to a UK CCSM programme and that the waste to be used was, in general, generated at or close to points of CO_2 emission. The principal contribution of feed material for CCSM must, however, come from ultramafic rock resources. The locations of the UK rock resources and CO_2 emitters are shown in Figure 22.

Figure 22 shows that there is no close co-location and that the main rock resources are found a considerable distance from the main emitters (concentrated in the Humber–Trent region in central and eastern England). This, however, is not a significant drawback when the nature of the CCSM process is considered. The close proximity of the large emitters in eastern England is potentially an ideal situation for underground disposal of CO_2 where a large infrastructure is required. CCSM is envisaged as being complementary to underground storage rather than a direct competitor. It is anticipated that the process can be scaled for use with intermediate and small emitters, and used in places where underground storage is not possible or is uneconomic. Figure 35 also shows that the resources are not closely co-located with any smaller emitters, which means that either the rock or processed rock must be transported to a site, probably the emitter location, for mineralisation. Transportation costs will be a significant factor, far outweighing the quarrying cost of around £2 per tonne. There are two possible scenarios at the extraction site. The rock could either be crushed to a size convenient for transport (perhaps > 50mm), or, since the feed is likely to be serpentinite, the rock could be activated at the production site and then transported as fine dry powder. The latter would be analogous to a cement plant where fine rock powder is heated in large kilns.

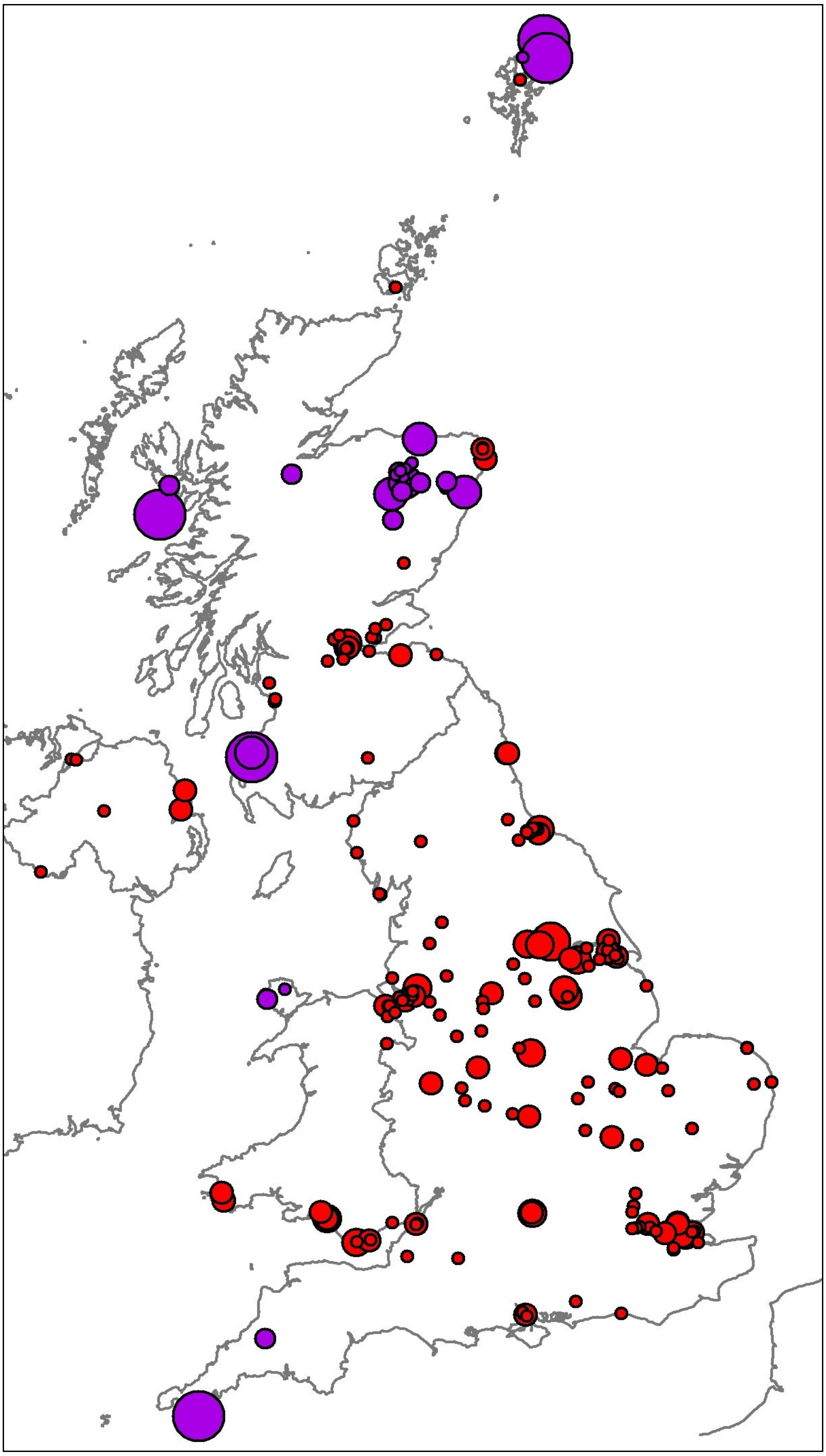


Figure 22 The locations of rock resources (purple) rated A or A/B and the CO_2 emitters (red) shown as graduated symbols according to their size. [Copyright BGS, NERC]

Transport method	**Cost 1^{st} mile**	**Next 30 miles per mile**	**Anywhere in UK Total additional cost**
Road	1.2	0.12	10
Rail	2	0.04	0.25
Sea big ship 90,000 tonnes			3
Sea small ship 15,000 tonnes			5
Interchange	1		

Table 7 The outline cost of transporting rock in £/tonne. [Copyright BGS, NERC]

General indicative costs for transportation have been provided by Lafarge Aggregates and Concrete UK (pers comm. 2010) and are shown in Table 7. Table 7 shows that rail and sea transport are much cheaper than road transport for distances greater than 50 miles and, if very large quarries are envisaged, they will have considerable advantages in terms of environmental impact. A further factor is the cost of interchange between one mode of transport and another, several changes add considerably to the cost. If the material is transported as activated powder rather than crushed rock the costs will be slightly higher.

For moving large volumes of material, the ideal situation is a coastal quarry, where the resource can be loaded directly onto ships and the ships travel to an emitter with a coastal location. Figure 23 is similar to Figure 22 but shows the emitters colour-coded to indicate their proximity to the coast. This shows that there are many intermediate and small emitters within 2km of the coast, a situation enabling direct transport by ship. This means that a coastal resource in a remote location such as Shetland could be utilised for CCSM in a wide range of locations.

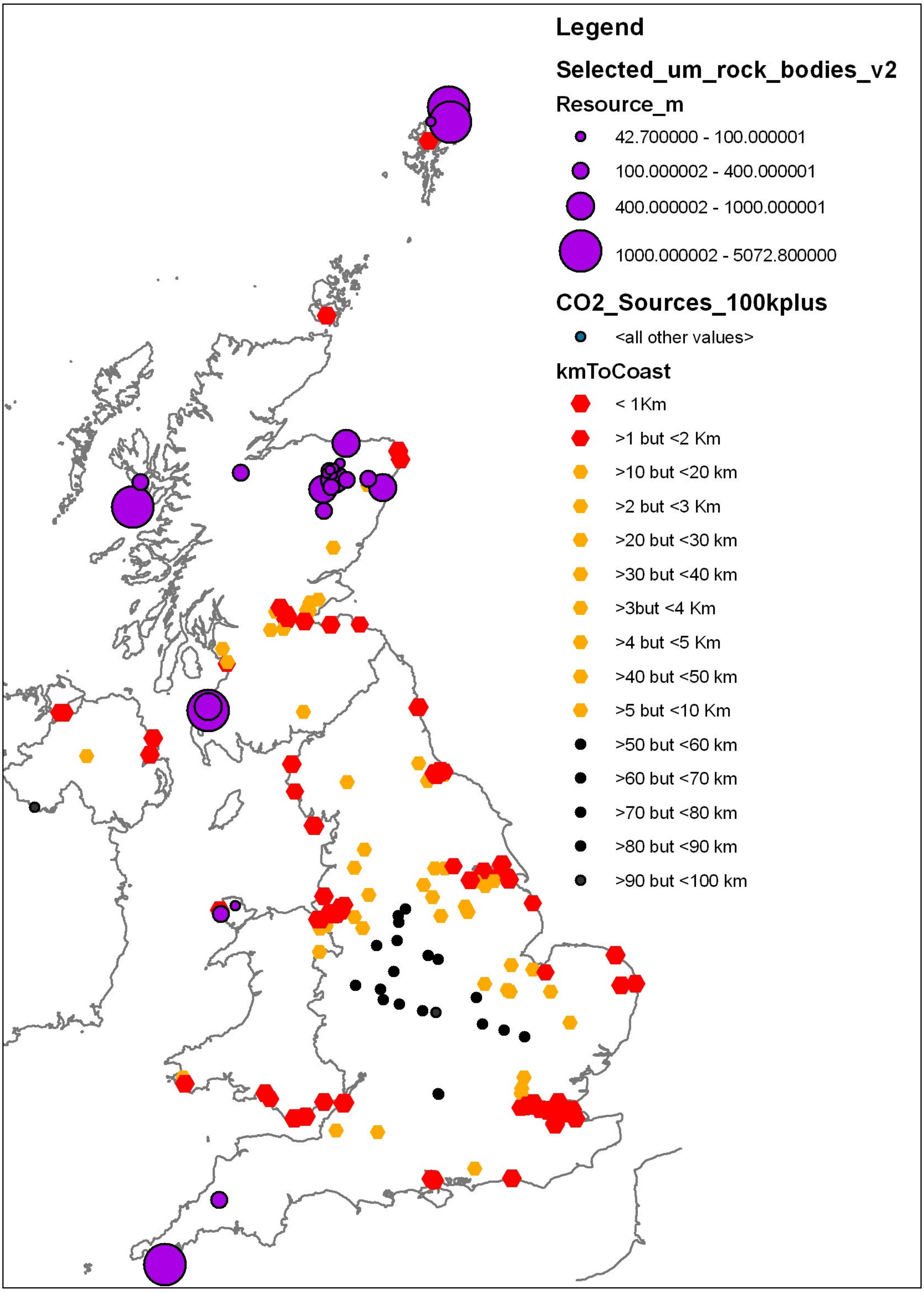


Figure 23 The locations of rock resources (purple) and the CO_2 emitters, where the distance to the coast is indicated according to the colour, less than 2km is red. [Copyright BGS, NERC]

8 Global resources of ultramafic rocks for CCSM

The maps of the different types of ultramafic rock resources show that many are in places where potential for underground geological storage is limited or impractical. These include substantial resources in northern Europe (Finland and Sweden), Japan, India, South Africa, Australia, and parts of North America. There is potential for implementation in many more countries. The high level review shows that there are huge resources of ultramafic rocks in the world that could be used for CCSM. The estimates here use only shallow quarrying depths, but it is still around **250 years** capture for total global emissions at 2006 levels.

8.1 INTRODUCTION

This section gives a very broad, high-level review of the global distribution of ultramafic rocks, thus providing an indication of the possible implementation of CCSM on a global scale. It is not possible to explain the geology in simple terms in a brief overview but the overall patterns and possibilities should be clear.

8.2 TYPES OF ULTRAMAFIC ROCKS AND THEIR GEOLOGICAL CONTROLS

The most common occurrences of ultramafic rocks are located in mountain building zones where the Earth's tectonic plates collide (Figure 24). Here, two general types of ultramafic rocks are found: (i) alpine-type ultramafics (ophiolites) and; (ii) ultramafic volcanic-arc plutons. Ultramafic bodies are also located in extensional zones (rifts) within continental plates, and include layered intrusions and smaller sills and dykes (Wyllie, 1967). In addition, ultramafic rocks can be found in continental margin settings associated with continental break-up. These include sills and dykes as well as ultramafic lavas. Finally, in some of the oldest parts of continental plates (cratons), metamorphosed ultramafic lava flows (komatiites) and related sub-volcanic intrusions are found locally. All of these rocks have distinct geological histories and show differences in location, mineralogy, and mineralogical distribution (Table 8).

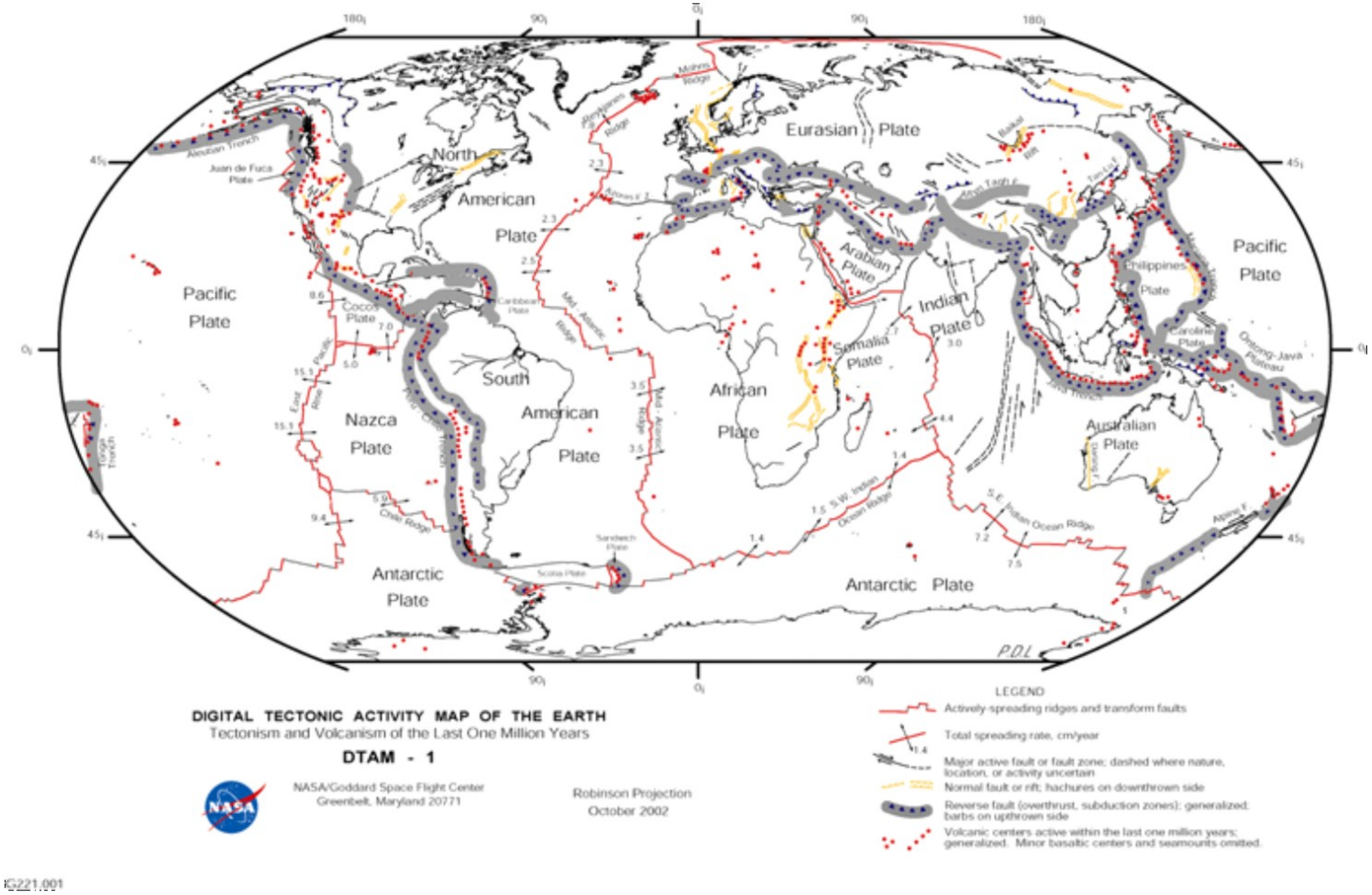


Figure 24 Map of the world showing the Earth's tectonic plates [map available from http://denali.gsfc.nasa.gov/dtam [June 2010]]. The grey zones with blue triangles represent areas of active mountain building where there is potential to locate ophiolites and hence a range of ultramafic rocks.

Geological setting	Complex type	Description	Distribution of ultramafic minerals	Examples
Orogenic	Alpine-type	The basal section of the oceanic crust has been thrust onto continental crust	Tectonised part contains harzburgite and lherzolite hosting pods of dunite. Cumulate part contains layers of dunite. Rocks are often highly serpentinised, but some are fresh and can represent significant sources of olivine	Troodos, Cyprus; Semail, Oman/UAE
	Volcanic arc plutons	Intrusion formed in an island-arc complex accreted onto continental crust	Concentrically zoned distribution of minerals comprising a core of dunite with zones of clino and ortho pyroxenite	Union Bay, Alaska, USA, Nizhny-Tagil, Russia (also a Pt deposit)
Intra cratonic	Layered intrusions	Large intrusions formed under or in continental crust	Layers of peridotite and pyroxenite can extend laterally over the whole intrusion. Serpentinisation is variable with alteration being concentrated along faults and shear zones. Though ultramafic layers occur, mafic layers predominate	Bushveld, South Africa; Great Dyke, Zimbabwe; Duluth, Canada; Stillwater, Montana, USA
	Komatiitic metavolcanic rocks	Differentiated flows and sub-volcanic intrusions in Archaean or Proterozoic mafic volcanic complexes	The basal parts of lava flows and sills are generally peridotitic. Degree of serpentinisation is highly variable	Central Lapland Greenstone Belt, Finland; Kambalda Greenstone Belt, Australia

Table 8 Ultramafic complex types [modified from Krevor et al. 2009]

8.2.1 Ophiolitic (Alpine-type) ultramafic complexes

Most of the world’s ultramafic rocks are located in ophiolites. These are stratified igneous rock complexes (comprising an upper basalt member, a middle gabbroic member and a lower peridotite member; Figure 25), which represent sections of ancient oceanic crust and the subjacent upper mantle that have been emplaced onto continental crustal rocks. It is considered that ophiolites will be the major source of ultramafic rocks for CCSM.

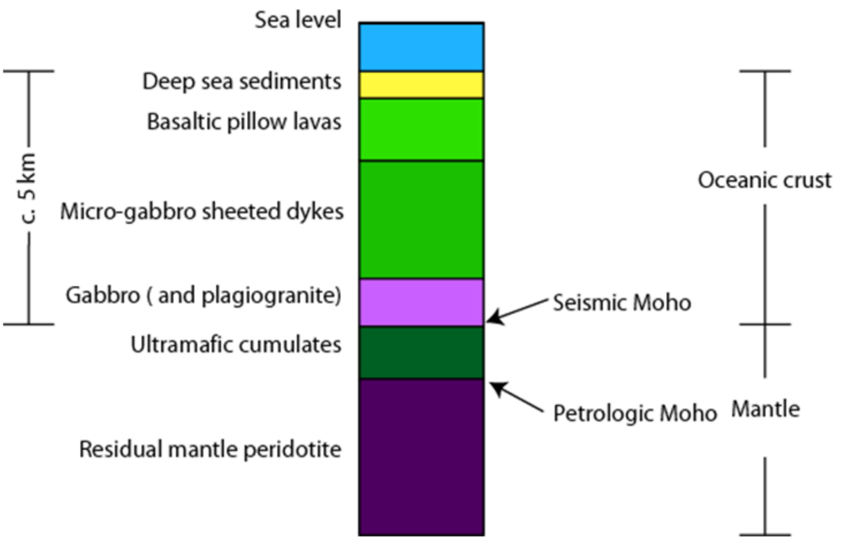


Figure 25 Generalised section through an ophiolite. Note residual mantle peridotite and ultra mafic cumulates are the zones with composition suitable for serpentinisation. [Copyright BGS, NERC]

Ophiolites are generally considered on-land fragments of oceanic lithosphere either generated at palaeo-spreading centres (mid ocean ridges) (e.g. Gass 1990) or in supra subduction zone environments at convergent plate boundaries (island arcs) (e.g. Pearce et al., 1984) that have been tectonically emplaced onto continental crust (Figure 26). The Cedar Hill and SW Oregon serpentinites referred to in section 2.2.5 would be in this category.

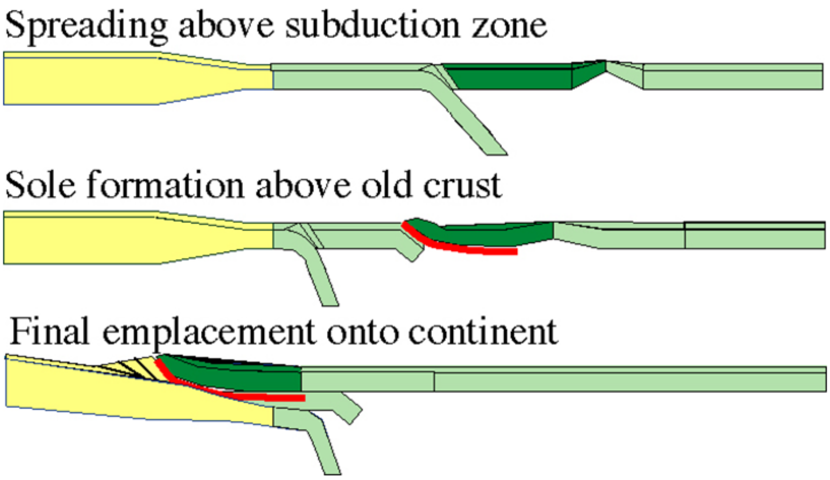


Figure 26 Schematic diagram showing the emplacement of oceanic crust (ophiolite) onto continental rocks, oceanic crust shown in green, continental crust in yellow. [Copyright BGS, NERC]

8.2.2 Volcanic-arc (Alaskan-type) ultramafic complexes

In addition to ophiolites, which are tectonically emplaced, a suite of intrusive magmatic ultramafic rocks can also occur in environments prone to collision. Generally, these ultramafic rocks are not as highly serpentinised as their ophiolitic counterparts and comprise a range of pyroxene and olivine-rich rocks. Their type locality is in Alaska (e.g. Himmelberg and Loney, 1995). Alaskan-type complexes are characteristically zoned, with wehrlite, clinopyroxenite, and hornblende-rich rocks surrounding a dunite core (Irvine, 1987). This series is idealised and any one of these zones may be missing or discontinuous (Nixon, 1990). Massive dunite cores, consisting primarily of forsteritic olivine (Irvine, 1987), may be exposed over large areas, and in many cases, dunite is well preserved. The Twin Sisters dunite referred to previously would be in this category.

8.2.3 Intracratonic layered intrusives

Layered mafic-ultramafic intrusions are either sill-like (e.g. Stillwater) or funnel shaped bodies (e.g. Great Dyke). They may be associated with tholeiitic flood basalt provinces and are commonly intruded into rifted cratons. The cyclically layered sequences form as magma crystallizes and differentiates. In the ideal sequence, dunite is at the base and is followed upward by a harzburgite and an uppermost orthopyroxene layer (Naslund and McBirney, 1996). The units vary in thickness. For example, in the Bushveld complex they are present on a millimetre scale (Eales and Cawthorn, 1996), in the Great Dyke on a centimetre scale (Naslund and McBirney, 1996) and at Muskox intrusion on a metre scale (Irvine and Smith, 1967). Olivine composition in a typical layered ultramafic intrusion trends from forsterite-rich olivine towards fayalitic olivine upwards in succession. Olivine composition changes from Mg-rich (forsterite) to Fe-rich (fayalite) from lower to upper zones within layered intrusive complexes. The layering is commonly laterally continuous for hundreds of square kilometres (Eales and Cawthorn, 1996) and the ultramafic sequence can be up to several kilometres in thickness. For example, the Windimurra Complex has a 0.5km thick ultramafic section (Mathison and Ahmat, 1996), the Muskox Intrusion has ultramafic layers that total 1.5km in thickness (Irvine and Smith, 1967), and the Great Dyke has an ultramafic sequence several kilometres in thickness (Wilson, 1996), 550km long, and several kilometres wide with a potential resource of 3,000Gt (Figure 27).

Figure 27 Landsat image of the Great Dyke, Zimbabwe. [Copyright BGS, NERC]

8.2.4 Intracratonic komatiitic metavolcanic rocks

The final major ultramafic rock type is related to Archaean rocks (older than 2.5B yrs). These are komatiitic metavolcanic rocks and accompanying subvolcanic intrusions (Arndt, 1994). Peridotite and minor amounts of dunite cumulates form by crystal settling from thick basaltic, pyroxenitic, and peridotitic lava flows and subvolcanic sills. Serpentine minerals, talc, chlorite, magnesite, anthophyllite, and tremolite often form in the basal parts during metamorphism. These lava flows and sills are commonly a few meters to 0.5km thick and may be exposed over 1–5km. They are typically associated spatially with thick submarine tholeiitic basalt sequences. Their tectonic environment of formation remains controversial, ranging from ocean floor volcanism related to mantle plumes to compression and tension arc environments. However, their occurrence is almost completely restricted to volcanic sequences in Archaean cratonic rocks that form the stable heartlands to continents (Figure 28). The Hitura serpentinite referred to in section 2.2.5 would be in this category.

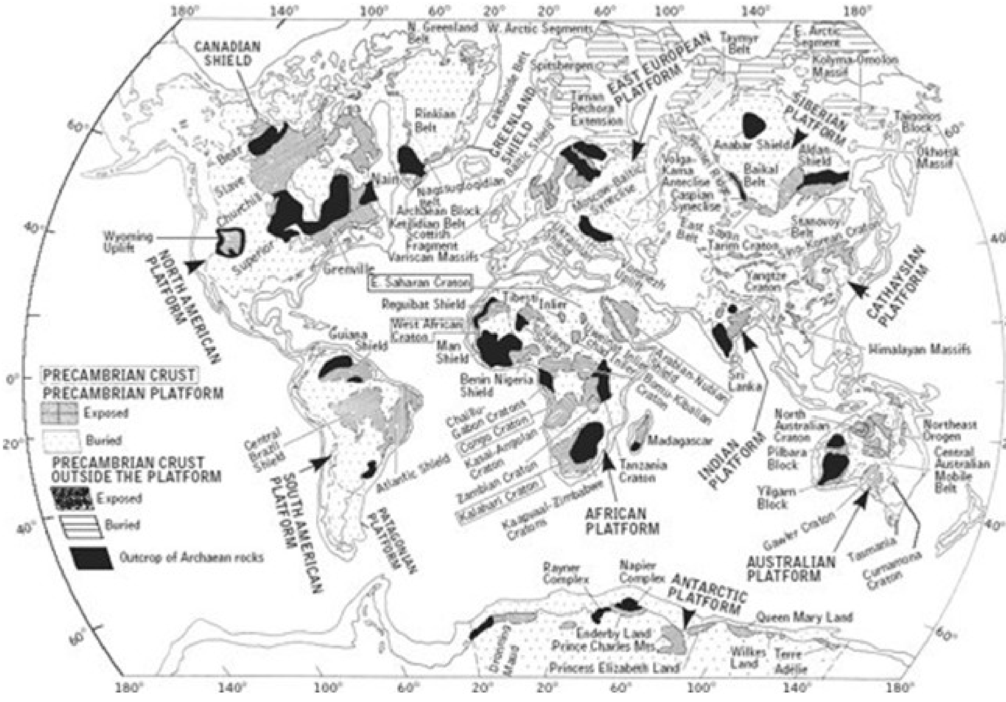


Figure 28 Global distribution of Archaean rocks showing the possible locations for ultra basic rocks associated with komatiites [image available from http://science.jrank.org/pages/47317/Archaean-eon.html [June 2010]]

8.3 COUNTRY SPECIFIC STUDIES IN THE LITERATURE

A few government organisations have conducted inventories and assessments of ultramafic rocks with a view to assessing their potential as a source material for CO_2 mineralisation. These include the United States Geological Survey (USGS), Bureau de Recherches Géologiques et Minières (BRGM) in France, the British Columbia Ministry of Energy and Mines in Canada and the National Geophysical Research Institute, India (Krevor et al., 2009; Marechal and Lachassagne, 2004; Voormeij and Simandl, 2004; Mani et al., 2008)

8.3.1 United States

Researchers at Columbia University and the U.S. Geological Survey have developed a digital geological database of ultramafic rocks in the conterminous United States (Krevor et al., 2009). Data were compiled from varied-scale geologic maps of magnesium-silicate ultramafic rocks. The focus of the national-scale map is entirely on ultramafic rock types, potentially suitable as source material for mineral CO_2 sequestration. The map produced by Krevor et al., 2009 is shown in Figure 29. The land area of the United States is 8,143,121km^2 and the area of outcropping ultra basic rocks is around 0.2%. Furthermore, the distribution is uneven. The majority of outcropping ultra mafic rocks are ophiolitic and restricted to two linear belts: one running down the western seaboard and the other corresponding to the Appalachian Mountains. This emphasises the importance of major geological control on the global distribution of ultramafic rocks.

Figure 29 Distribution of ultramafic rocks in the USA [from Krevor et al., 2009]

8.3.2 British Columbia

Compared to the UK and the other regions and countries discussed in this section, British Columbia has favourable geology and excellent exploration potential to host the raw materials suitable for CO_2 mineral carbonation. It has been located on the active, west-facing Pacific margin of continental North America for at least the last 530M yrs, and subjected to a subduction zone (accretionary) tectonic setting for the last 390M yrs. Due to its tectonic history, British Columbia contains numerous Alpine-type and several Alaskan-type complexes. The study of Voormeij and Simandl, 2004, draws relevant information and utilizes a database originally designed to evaluate mineral potential for the province. From this database, a map depicting dunite- and serpentinite-bearing ultramafic rocks has been produced (Figure 30).

British Columbia has a land area of 944,735 square kilometres and based on the Voormeij and Simandl, 2004 map, around 3% of BC's surface is underlain by ultramafic rocks containing dunite and/or serpentinite. Again, this shows the importance of tectonic environment for controlling the distribution of ultramafic rocks.

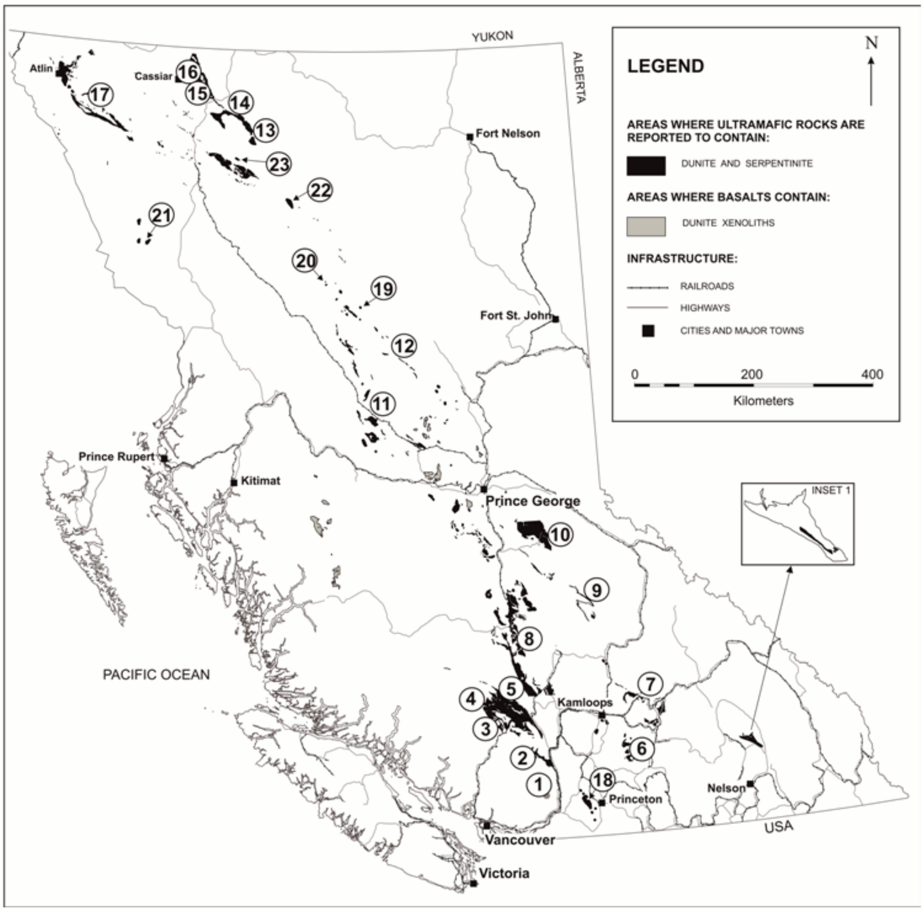


Figure 30 Distribution of ultramafic rocks (serpentinite and dunite) in British Columbia and Canada. Distribution of dunite and serpentinite-bearing rocks in British Columbia. Alpine-type/ophiolite ultramafic complexes include: 1. Cogburn Emory Zone; 2. Coquihalla Serpentine Belt; 3. Bralorne-East Liza; 4. Bridge River Complex; 5. Shulaps; 6. Chapperon Group; 7. Mount Ida Assemblage; 8. Southern Cache Creek Complex; 9. Crooked Amphibolite; 10. Antler Formation; 11. Central Cache Creek Complex; 12. Manson Lake Complex; 13. Blue Dome Fault Zone; 14. Sylvester Allochthon; 15. Cassiar and McDame; 16. Zus Mountain; 17. Northern Cache Creek Complex (includes Atlin and Nahlin complexes). Alaskan-type ultramafic complexes include: 18. Tulameen; 19. Polaris; 20. Wrede; 21. Hickman; 22. Lunar Creek; 23. Turnagain. The Land area of BC is nearly double that of France.

8.3.3 France

There are two studies on the efficacy of ultramafic rocks for mineral carbonation (Marechal and Lachassagne, 2004; Bailly, 2004). Bailly, 2004 has produced a GIS of the distribution of basic and ultramafic rocks in France. This estimates that 1.71 % of the surface area of France (544,435km^2) is covered by basic and ultramafic rocks of which mantle and ophiolite peridotites occupy 0.06 % (317km^2)

8.3.4 India

Aside from the Himalaya and the Andaman Islands, which are geographically remote, India has no significant resources of ophiolite-hosted ultramafic rocks. However, in southern India there is a significant Archaean craton – the Dharwar Craton—which has the potential to host intracratonic komatiitic metavolcanic rocks. Mani et al. 2008 conducted a study on the carbon dioxide sequestration potential of ultramafic rocks in the greenstone belts of southern India (Figure 31). They recognise two zones, the Kola and Chitradurga belts. The real extent of the Kola belt is about 320km^2, with an average width of ~6km, while that of the Chitradurga belt is 6,000km^2 and maximum depth of up to 10km. Estimates show that an ultramafic portion of 1km^3 in the Kolar belt can store ~2.94Mt of CO_2 and that in the Chitradurga belt ~4.7Mt, accounting for about 0.6% of annual CO_2 production in India.

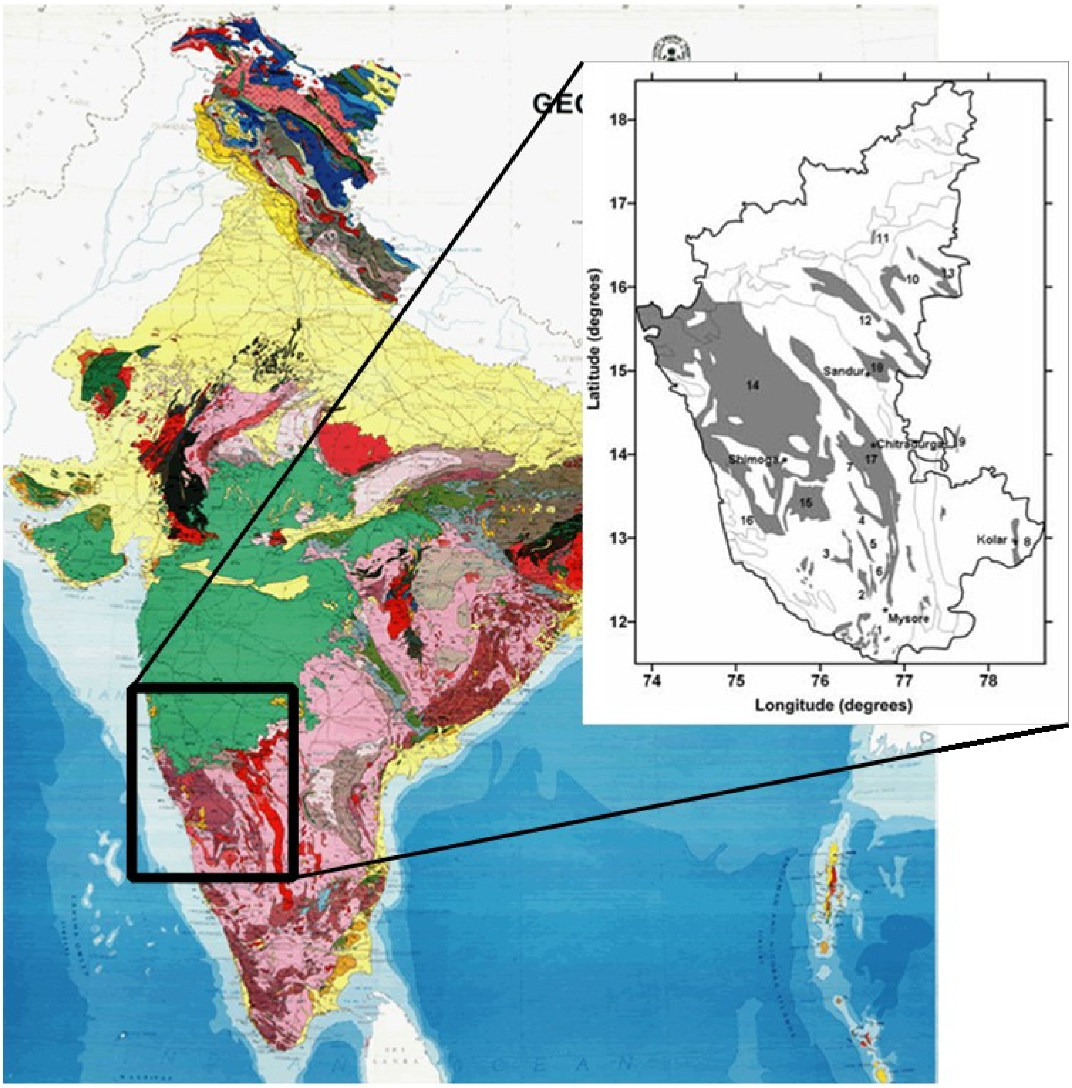


Figure 31 Distribution of Archaean greenstone belts in southern India—Greenstone belts contain ultramafic rocks. Inset is from Mani et al., 2008 and show areas with the potential for ultramafic rocks in grey. Geological map is from Geological Survey of India web site portal of maps covering all of India http://www.portal.gsi.gov.in/portal/page?_pageid=108,721665&_dad=portal&_schema=PORTAL [Jun 2010]

8.4 GLOBAL DISTRIBUTION OF ULTRAMAFIC ROCKS

8.4.1 Ophiolites

Ophiolites represent the most important geological setting for the location of ultramafic rocks. In terms of their global distribution, there are major episodes of ophiolite formation during phases of tectonism and mountain building at various times in Earth history. These have geographically restricted extents and occur in semi-continuous curvilinear belts (Figure 32) that reflect their origin at subduction zones along continental margins or continental collision zones.

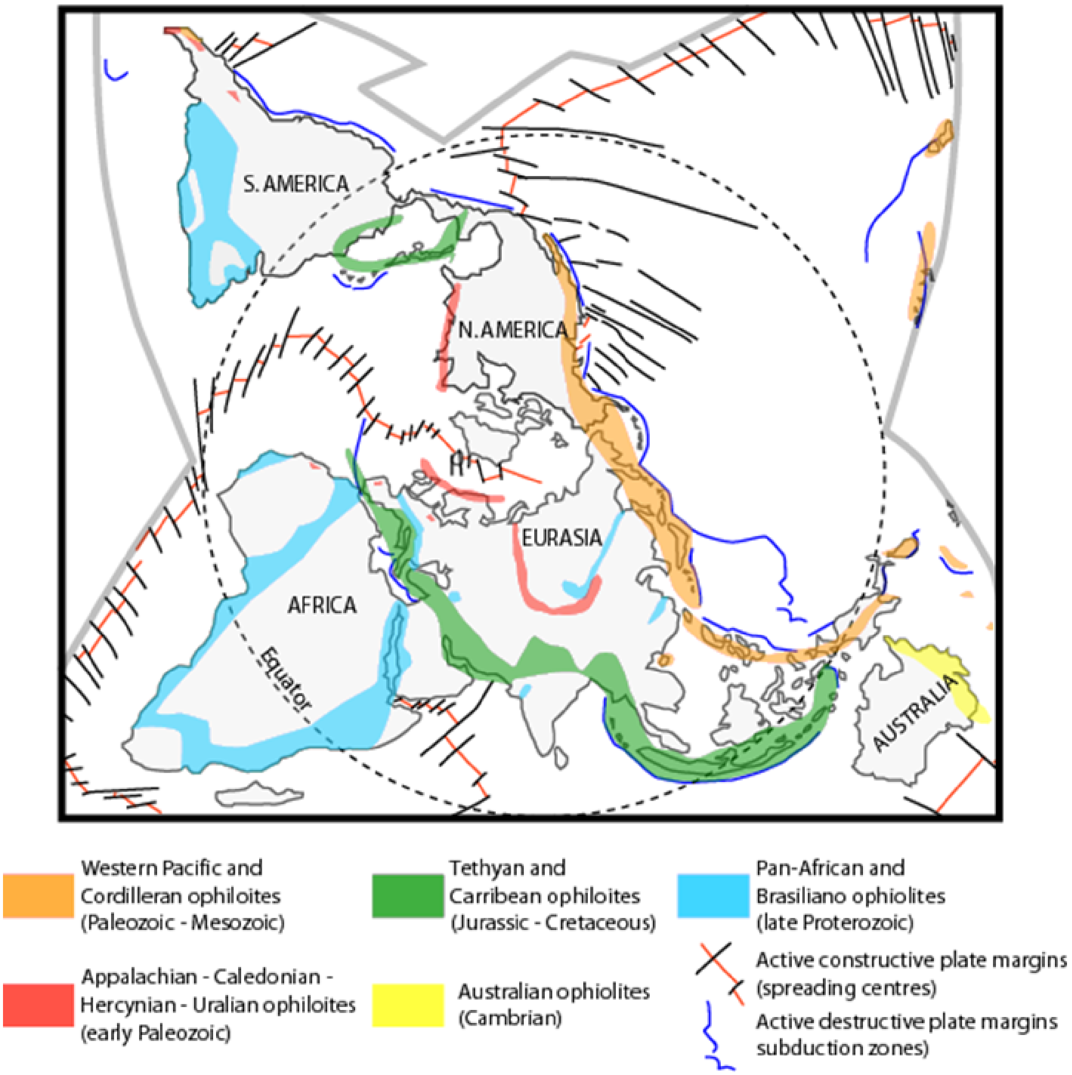


Figure 32 Polar projection of the world showing generalised global distribution of ophiolites on a North polar projection map [modified from Dilek, 2003]

These belts have been divided into five geological regimes (Dilek, 2003):

- Pan-African and Brasiliano ophiolites—These are Late Proterozoic in age (< 860 Ma) and are mainly located in South America, Africa, and Arabia with localised occurrences in Europe (Cadomian belts [NW France] the Rhodope massif [Balkan Peninsula]), the Lesser Caucasus (Transcaucasian massif), and central Asia

(Agardagh, Tes Chem, Songshugou and Jiangxi ophiolites) (Figure 32—blue ornament).

- Eastern Australian ophiolites—These formed in the early Palaeozoic (530–485 Ma) and are part of the Tasmanide orogenic belt that occurs along the eastern margin of Australia (Figure 32—yellow ornament)
- Appalachian, Caledonian, Hercynian, and Uralian ophiolites—These occur associated with the orogenic belts that extend from eastern North America thorough Scotland, northern Europe (including Iberia) and Scandinavia to polar-central Russia and central Asia (Figure 32—red ornament).
- Tethyan–Caribbean ophiolites—Jurassic to Cretaceous (230–90 Ma) Tethyan ophiolites are located in Betic–Rif (S. Spain–N Africa), Pyrenees, Alpine–Apennine mountain systems (Corsica, Sardinia, Eastern Alps, Internal and External Ligurides), Carpathians (Apuseni, Bodva), Dinaride–Albanide–Hellenide mountain belt, Lesser Caucasus, Intra Pontide and Izmir–Ankara–Erzincan suture zone (N. Turkey), Tauride and Zagros mountain belts (S. Turkey and Iran), Himalayan and Tibet orogenic systems and the Andaman Sea–Indonesian region (Figure 32—green ornament)
- Western Pacific and Cordilleran ophiolites—These range in age from Palaeozoic to Cenozoic (545–20 Ma). Typical examples occur in the Indonesia–New Guinea region Philippines, Japan, Koryak–Kamchatka orogenic belt, Verkhoyansk–Chukota fold belt, Alaska and North America Cordillera (Figure 32—orange ornament).

Within the curvilinear belts illustrated in Figure 31, ophiolites will occupy a small proportion of the indicated zone and in turn, ultramafic rocks will occupy an even smaller aerial extent. For example, within the Tethyan and Caribbean ophiolite belt, a well-preserved section of ophiolite, the Troodos Ophiolite, occurs on the island of Cyprus in the Mediterranean. It is roughly rectangular in shape, approximately 75km long by 35km wide, and has a surface exposure of around 2,000km^2. The mantle sequence, i.e. the part of the ophiolite that comprises ultramafic rocks with the potential to be suitable for CO_2 mineralisation, is about 100km^2, representing ~5% of the exposed ophiolite. Within the Tethyan and Caribbean ophiolite belt, according to the Exxon Tectonic Map of the World (Exxon, 1994), there are 50+ similar sized and larger ophiolites. It should be noted that that the Cyprus ophiolite is dominated by the upper part of the sequence, whereas other complexes are predominantly mantle rocks. In contrast, the large Oman-UAE ophiolite has a thick mantle section, severalkm, with a possible reserve of 34,000Gt.

Figure 33 Google Earth image showing the Oman-UAE ophiolite, dark coloured rocks.

It is very difficult to estimate an average, but mantle rocks perhaps represent around 35% of an ophiolitic terrain. Overall, this is a substantial resource when compared to other bulk commodities such as coal and iron ore.

8.4.2 Volcanic-arc (Alaskan-type) ultramafic complexes

In addition to Alaska (and British Columbia), these complexes are also known to occur in the Lachlan fold-belt in SE Australia and in a chain of zoned mafic-ultramafic complexes extending over 900km from the Central to the Northern Urals. The latter have a strong association with platinum group elements (Pt, Pd, Rh, Ru and Os).

8.4.3 Intracratonic layered intrusives

Intracratonic layered intrusives are rare, but have a worldwide distribution. There are known examples on nearly all continents. Though they are rare, they tend to be large. Stillwater, in Montana, USA has an outcropping area of 4,400km^2 and its ultramafic series is 1.4km thick. The Bushveld, South Africa, intrusion has an area of 65,000km^2, and is up to 9km thick in total. The critical zone, which is predominantly ultramafic (pyroxenites, chromitite, harzburgites, through to norites and anorthosites), is up to 1.5km thick. Other examples include:

- Duluth, Minnesota, USA
- Greak Dyke, Zimbabwe
- Muskox Northwest Territories, Canada

- Giles complex, central Australia
- Windimurra intrusion , western Australia
- Rincon del Tigre, Bolivia
- Lukkulaisvaara, Russia
- Xianjie layered intrusion, Sichaun Province, SW China

Though large, these intrusive bodies do not necessarily contain significant amounts of peridotite and serpentinite. However, they are commonly the loci for a range of metals (Ni, Cu, Au and PGM), which are commonly exploited. There is thus the potential for resources of waste, already crushed, rock with the potential to act as source material for CO_2 sequestration.

8.4.4 Intracratonic komatiitic metavolcanic rocks

These are associated with belts of mafic rocks in very ancient areas of the Earth's crust and are found on most continents (Figure 28). Within these ancient cratons, the komatitites are restricted to the belts of mafic volcanic rocks separating the granitic bodies that make up most of the cratons. In terms of a global resource of ultramafic rock, komatiitic rocks are likely to be a small proportion. However, this rock type is commonly associated with nickel mines. Thus, there is the potential for an already mined and crushed resource to be exploited. Examples of this would be Hitura Mine in Finland and Kambalda mine in Australia.

8.5 ESTIMATION OF GLOBAL RESOURCES

Our estimate of ultramafic rock resources in the UK is around 20Gt (Section 3.3). The UK is not particularly well endowed with ultramafic rocks and the surface area of outcropping ultramafic rocks represents less than 0.09% of the land area of the UK. An example of a favourable region would be British Columbia, Canada. Here, the geological terrain is almost entirely represented by rock formations associated with collision tectonics, and hence favourable for the location of ultramafic rocks that comprise around 3% of the land area (Voormeij and Simandl, 2004). In the USA, there are two large orogens (Cascades and the Appalachians) plus a number of intracratonic layered intrusives. There are, however, large tracts of the country that are devoid of ultramafic rocks. Here, the percentage of outcropping ultramafic bodies is around 0.2%, approximately double that of the UK but less than a third of British Columbia. France, the largest country in Western Europe, has a relatively low percentage of ultramafic rocks, comprising 0.06% of the total area of outcropping rocks (Bailly, 2004)

In an extremely crude manner, which is probably only correct to one or even two orders of magnitude, it is possible to upscale the above information to get a global estimate of the total amount of available ultramafic rock. The above figures, plus the following assumptions: (i) that each deposit is 35 m thick and (ii) that only 10% of outcropping ultramafic rocks will be suitable for CO_2 sequestration, can be used to estimate global resources. The results of this estimate are illustrated in Table 8. This shows that for good to favourable geology (as in British Columbia), where ultramafic rock represents around 3% all geological formations, ultramafic rock resources are around 21,500,000Mt (21.5T tonnes). This could sequester annual CO_2 emissions, at 2006 levels, for over 750yrs. For less optimistic estimations, where ultramafic rocks comprise 1% and 0.2% of all geological formations, **the global**

sequestration potential is between 250 and 50yrs (Table 9). However, the assumption about mining depth could easily be increased from the very conservative depth of 35m to say 100m giving a threefold increase in resource estimated.

Place	Favourable geology	Surface area (km^2)	% ultrabasic rock	Estimated resource (Mt)	CO_2 mineralising potential (Mt)[3]	Years of global CO_2 production[4]	Source for resource estimate
United Kingdom	very low	242,900	0.09	1,992	996	0.04	This study
British Columbia	good to high	944,735	3.00	272,792	136,396	4.8	Voormeij and Simandl (2004)
United States of America[1]	low	8,143,121	0.20	156,755	78,378	2.8	Krevor et al (2009)
France[2]	very low	543,965	0.06	3,141	1,571	0.06	Bailly (2004)
World	good to high	148,940,000	3.00%	43,006,425	21,503,213	757.2	This study
	intermediate		1.00%	14,335,475	7,167,738	252.4	
	low		0.20%	2,867,095	1,433,548	50.5	

[1]Not including Alaska

[2]Not including French dependent territories

[3]1 t rock sequesters 0.5 t CO_2

[4]2006 global CO_2 emissions @ 28.4Gt

depth of deposit	35 m
amount of minable ultra basic rock	10%

Table 9 Ultramafic rock resource estimates for the UK; British Columbia, Canada; USA; France; and the World. [Copyright BGS, NERC]

To provide a more robust estimate it would be necessary to reproduce the work undertaken in the report concerning UK resources on a more global scale using a range of geological maps at scales of between 1:500,000 and 1:100,000. This is a large task for the whole globe, but a reasonably reliable figure could be produced by concentrating on a few key countries to see the variability of outcropping ultramafic rocks with broad-scale geology and tectonics. This is planned as a part of the Phase 2 activities. This will place emphasis on areas with limited scope for underground storage.

8.6 SUMMARY

The high level review shows that there are huge resources of ultramafic rocks in the world that could be used for CCSM. The estimates here use only shallow quarrying depths, but it is still around **250yrs** capture for total global emissions at 2006 levels.

The maps of the different types of ultramafic rock resources show that many are in places where potential for underground geological storage is limited or impractical. These include substantial resources in northern Europe (Finland and Sweden), Japan, India, South Africa, Australia, and parts of North America. There is potential for implementation in many more countries.

Acknowledgements

We would like to thank Kathryn Goodenough of BGS for a thorough and helpful review of this section of the report and Emma Hines of Lafarge Aggregates and Concrete UK for informative discussions and the provision of indicative transport costs.

Part 2 – CCS Mineralisation Technologies

9 Introduction to CCSM Systems

Mineral carbonation is an accelerated form of the natural weathering process, one of our planet's major CO_2 mitigation options (Seifritz, 1990). Ex-situ carbon dioxide mineralization is defined as the reaction of Divalent Metal Cations (Mg^{2+}, Ca^{2+}) from the feedstock with CO_2 to form a carbonate product stream:

$$\text{Divalent Metal Cation} + CO_2 \rightarrow \text{Carbonate} + \text{Heat out}$$

For serpentine the reaction is:

$$Mg_3Si_2O_5(OH)_4 + 3CO_2 \rightarrow 3MgCO_3 + 2SiO_2 + 2H_2O + 64 \text{ kJ/mol } CO_2$$

Hence, any deployed CCSM system would consist of three main steps:

1. Feedstock identification
2. Mineralisation technology application
3. Product application

The mineralisation technologies themselves consist of 3 processes:

1. Pretreatment of the mineral through grinding and chemical or thermal activation
2. Carbonation where the mineral or leached cations are reacted with carbon dioxide to produce mainly carbonate and silica
3. Post processing to separate and upgrade the carbonate and silica to a suitable quality and state for disposal or sale to an appropriate market

The upstream part in terms of feedstock nature (naturally occurring minerals, industrial residues), availability, and distribution has been addressed in detail in Sections 1 – 8 of Work Package 1.

There is a variety of mineral carbonation technologies, using or able to use different feedstock, their CO_2 "feedstock" suitability (pure CO_2, flue gas), product, or products purity, and at a different Technical Readiness Level. These carbonation technologies can be grouped as shown in Figure 34. These fall into two basic types:

- **Direct carbonation of mineral/mineral slurry**: The simplest carbonation process that involves a direct reaction of CO_2 with Calcium- or Magnesium-silicate minerals (simple design and easier to apply the reaction heat produced during carbonation than in a multistage indirect process; e.g. Caterpillar and Shell Processes).

- **Indirect carbonation of extracted divalent cations**: The reactive fraction of silicates is first extracted by dissolution and then reacted with CO_2. As a result, carbonation proceeds much faster.
- **Gas-solid**: Gaseous carbon dioxide reacts with Calcium- or Magnesium-silicate powder in a dry environment (e.g. Åbo Akademi uses an indirect gas-solid dry process where the $Mg(OH)_2$ is first extracted from minerals and then carbonated in a Fluidized Bed Reactor). The advantages of this approach is the simplicity of the reactor design and that it is easier to apply the reaction heat produced during carbonation.
- **Aqueous**: The presence of water considerably enhances the reaction rate in carbonation process (e.g. the ARC process directly mineralises an aqueous Ca/Mg-silicate slurry at high temperature and pressure or UoN, which indirectly carbonates a Ca/Mg-silicate aqueous slurry in a multistep process).

These basic types can be further divided into the following 6 categories:

- Direct Carbonation
  - Gas Solid…………… (1)
  - Aqueous
    - Single Step, No Addditives…. (2)
    - Additive Enhanced……(3)
- Indirect Carbonation
  - Gas Solid…………… (4)
  - Aqueous Additive Enhanced
    - Double Step… (5)
    - Multi-Step….. (6)

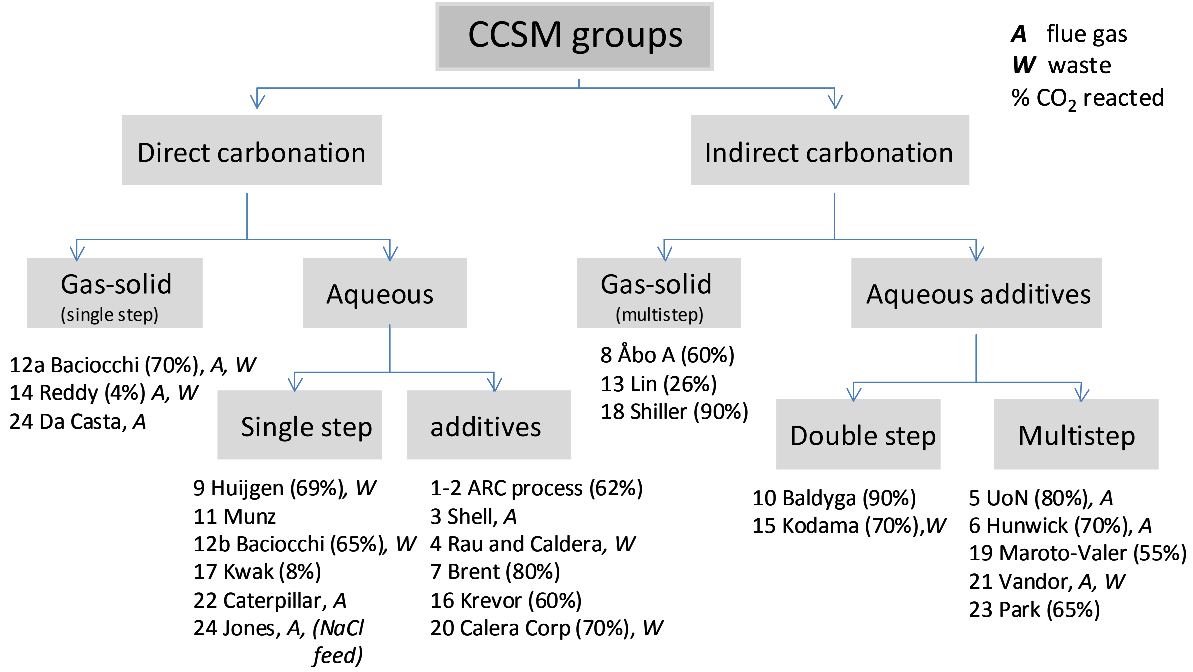


Figure 34 CCS Mineralisation Carbonation Process Categories. [Copyright University of Nottingham]

The carbonation processes identified by the consortium and discussed in detail in Chapter 14 are shown against the category in which they fall.

On the downstream side, there are varieties of potential product applications that result in requirements for the mineral carbonation product stream and/or for the post-processing step.

Simplification and integration over the complete technology and value chain is essential to arrive at a CCSM system with minimal abatement cost. So far, the CCSM system pieces largely have been studied individually.

A sound interplay between 'technology push' and 'market pull' is needed. To give an example, providing land protection measures can be performed using mineralization product slurry whilst other product applications require it to be in powder or aggregate form.

Work Package 2 aims to provide guidance for the later phases of this project to ultimately recommend CCSM systems to be further assessed for development towards demonstration phase in a (preferably) UK context and clarify the ETI's possible role in that development.

To start with, the interplay between the individual pieces of the CCSM system on the mineral carbonation technology and on the product side needs to be assessed. This is not straightforward because the available amount of information strongly varies. This ties to the differing TRL status. The combination of the assessment method used (technology grouping) with a TRL estimate yields an initial ranking of technologies.

Some of the identified gaps will be filled in phase 2 of the project by carrying out an experimental programme before conducting a detailed Pugh analysis. Along with the identified development needs, this analysis will form the input for the techno-economic assessment by Foster Wheeler.

10 Initial Assessment Methodology for CCSM System Technologies

A Pugh-type assessment method has been used by the consortium to assess the relative capabilities of the CCSM system technologies identified, based on their current levels of development. The 5 criteria used are: energy needs, ratio of mineral to carbon dioxide sequestered, potential product revenues vs. chemicals used, apparent simplicity and apparent feasibility.

10.1 INTRODUCTION

An initial ranking of mineral carbonation technologies will be made by combination of a Pugh-type assessment method, with a Technical Readiness Level estimate. Both the identified mineral carbonation technologies and the most promising ones according to the initial ranking will be grouped. This creates common ground for the section Appendix 10 on scenarios and economics, and gaps and development needs, respectively.

10.2 ASSESSMENT METHOD USED

The study reported here aims at identifying promising concepts and especially those that are near or in a stage of scale-up and demonstration.

Therefore, to carry out the performance comparison analysis, five essential assessment criteria were used. Each criterion was transformed into an assessment scale of A (very good) to E (very bad). The first three criteria were based on quantitative information while the last two are more subjective and consider the processes as an overall system. This was done on purpose since a large amount of available data and information was incomplete, inconsistent or simply did not allow any quantitative evaluation. While the first three criteria are based on specific data for CCSM process routes the last two are more general and consider the CCSM process as chemical processing plant that should have certain features that result in good practice and operation within certain margins and ranges of uncertainties, problems, costs, complexity and impact on resources and the environment. Depending on location and the size and character of the CO_2 producing process a certain CCSM may appear most suitable or promising.

Criterion 1. Energy usage, CO_2 fixation efficiency

The fixation efficiency of CO_2 by mineral carbonation can be measured by considering the use of power and heat by the process. Energy factored in the analysis includes: pre-treatment energy (mechanical and thermal), energy to heat up reactants to reaction temperature, heat released from reaction and energy for capture and compressing CO_2, are expressed in kWh/tonne of CO_2 (1kWh ~ ½ kg CO_2). Therefore, input energy utilised may have resulted in CO_2 emissions at a power utility and should be accounted for. In this work, heat and power used in carbonation were clearly distinguished. The CO_2 produced during generation of the necessary amounts of heat and power was charged according to earlier work by Rubin *et al.*(2004). CO_2 fixation efficiency is thus defined as the ratio of CO_2 avoided to CO_2 sequestered, expressed as a percentage:

$$CO_2 \text{ F. E.} = 100\% \times (CO_2 \text{ sequested} - CO_2 \text{ equivalent of energy usage})/CO_2 \text{ sequested}$$

A	≥ 90% CO_2 fixation efficiency *
B	≥ 70% CO_2 fixation efficiency
C	≥ 50% CO_2 fixation efficiency
D	≥30% CO_2 fixation efficiency
E	< 30% CO_2 fixation efficiency

* Less than 100kg CO_2 formed during fixation of 1,000kg

Criterion 2. Mineral input and products output streams per t CO_2

In this criterion, the amount of mineral used in sequestering a unit amount of CO_2 and the order of production and consumption of water in the process were quantified. Measuring parameter used is the R_{CO2} value as defined by Goff and Lackner (1998) during early work in the USA. It is defined as a theoretical mass of a given input mineral necessary to convert a unit mass of CO_2 into mineral carbonate. For serpentine the minimum amount needed is R_{CO2} = 2.10kg/kg CO_2, for olivine R_{CO2} = 1.60kg/kg CO_2. In addition, water use is considered here since at many locations a considerable consumption of water cannot be allowed, while at the same time a production of water (here serpentine has a benefit when compared to olivine) is considered a bonus here.

A*	Mineral input $R_{real} < R_{CO2} \times 1.1$
B	Mineral input $R_{real} < R_{CO2} \times 1.5$
C	Mineral input $R_{real} < R_{CO2} \times 2.5$
D	Mineral input $R_{real} < R_{CO2} \times 4$
E	Mineral input $R_{real} \geq R_{CO2} \times 4$

* In case of significant water production, one rating up. In case of large water consumption, one rating down (unless it is a once through process using seawater).

Criterion 3. Valuable products *versus* not-recovered chemical additives

In this criterion, potential revenue to be earned from sale of valuable products (goethite, building material) will be compared to the cost of additional chemical additives lost during CO_2 mineralisation process. (A implies significant profit; E implies significant loss).

A	Potential revenues products >> costs chemicals
B	Potential revenues products > costs chemicals
C	Potential revenues products ~ costs chemicals
D	Potential revenues products < costs chemicals
E	Potential revenues products << costs chemicals

Criterion 4. Apparent simplicity

In this criterion, the layout of the process as a system of process units, the complexity of these units, and specific details that may cause complications (e.g., long distances between units or operations), is assessed. This gives a qualitative ranking with a slight pitch towards costs. Note that long residence times (hours versus minutes or seconds) and/or very high pressures add to both “capex" and “opex”. This criterion also gives indications on scalability, as many processes or process steps might not be feasible at the large scale needed for significant CCS (> 0.1Mt CO_2/year).

A	Combination of simple proven technology, little risk (low capex, low opex)
B	A few tricky components, otherwise conventional and simple (reasonable capex, low opex)
C	A few tricky components, reasonable complexity (reasonable capex, reasonable opex)
D	A few tricky components, somewhat complex as a whole (reasonable capex, high opex)
E	A complex mix of uncommon process units (high capex, high opex)

Criterion 5. Apparent feasibility: proven by demonstration in a continuous process? (Demonstrated viability)

This is a general, yet important, criterion that assesses the process as a whole. It covers features that cannot be addressed under criteria 1-4, and it includes the level of success that has been obtained so far. In addition, here, scalability is covered.

A	It works, it is being demonstrated.
B	It may work and be successful. Needs some improvement and investment, advanced R&D needed
C	This may be developed into a success but many factors can make it or break it (location, local market)
D	This will need much improvement, starting level R&D needed.
E	This will fail if not heavily subsidized (special cases like asbestos waste).

10.3 TECHNICAL READINESS LEVEL (TRL)

The following is a list of the technology readiness level (TRL) status definitions used for this project. The detailed explanation can be found in the Appendix.

Level 1: Basic principles observed and reported
Level 2: Technology concept and/or application formulated
Level 3: Analytical and experimental critical functions and/or characteristic proof-of-concept
Level 4: Component and/or bench configured subsystem validation in laboratory environment
Level 5: Component and/or bench configured subsystem validation in relevant environment
Level 6: System/subsystem model or prototype demonstration in a relevant environment
Level 7: System prototype or system demonstration in an operational environment
Level 8: Actual system completed and qualified through test and demonstration
Level 9: Actual system proven through successful mission operation

11 Pretreatment

Pretreatment (or activation) step is used to transform relatively inert raw silicate minerals into highly reactive materials for CCSM processes. The objective of the mineral activation concept is to promote and accelerate carbonation reaction rates and efficiencies through surface activation. There are four types of pretreatment processes: mechanical activation, thermal activation, chemical activation, and mechano-chemical activation. Mechanical activation is focused on increasing surface area to volume ratio through crushing and grinding and carries an increasing energy penalty with reducing particle size. Thermal activation yields an amorphous phase by dehydroxylation. Chemical activation is focused on the extraction (leaching) and separation of valuable components by using chemical additives . In the mechano-chemical process, the chemical reactions occur at the interface of the particles and these are continuously re-generated during milling or grinding.

11.1 INTRODUCTION

The purpose of the pretreatment (or activation) step is to transform relatively inert raw silicate minerals into highly reactive materials for CCSM processes. The objective of the mineral activation concept is to promote and accelerate carbonation reaction rates and efficiencies through surface activation. Research on mineral activation was initiated because it became apparent that the slow reaction kinetics for some potentially attractive Ca/Mg-silicates, particularly serpentine, could not be enhanced sufficiently by careful selection of a process route and process conditions only. Two major methods are used: high energy mechanical grinding and chemical leaching, although other important methods (heat treatment, mechano-chemical, thermo-mechanical, etc.) are known. High-energy mechanical activation results in particle size reduction and “amorphization” of the solids due to the distortion of mineral crystal structure. Chemical activation (or mineral dissolution) produces aqueous solutions enriched with highly reactive chemical species (such as $[Mg^{2+}]aq$) required for CCSM processes. It was shown in several studies that serpentines are not susceptible to the mechanical activation; therefore, heat treatment method was applied. In this specific case, the dehydroxylation takes place during high temperature treatment and could be considered as high temperature chemical activation.

11.2 MECHANICAL ACTIVATION

11.2.1 Mechanical Mineral Processing Review: Industrial Equipment

In contrast to Geological Sequestration where processing of supercritical compressed CO_2 stream requires significant R&D of novel materials as well as novel tooling & equipment, the mining and processing of silicate minerals for mineralisation utilizes standard industrial machinery and processes well established in mining industry. The field of mineral processing has also been given other titles such as *mineral dressing*, *mineral extraction*, *mineral beneficiation*, and *mineral engineering*. Generally, mineral processing begins when an ore is delivered from a mine, to a processing facility. At this point, the ore is called *run-of-mine material* because there has been no treatment performed on it.

The process of size reduction is called c*omminution*. Comminution in the mineral processing plant is carried out in a sequential manner using *crushers* and *screens* followed by *grinding* *mills* and *classifiers*. The comminution process is shown in Fig. 38 and detailed description of various large-scale equipment and cost can be found in Appendix 4.

It should be mentioned that based on the economic analysis by O'Connor *et al*. (2004) approximately 2,500 tonnes/h of olivine mineral would be required to treat ~1,100 tonnes CO_2/h generated by ~1GW coal power plant. This mineral consumption is at least an order of magnitude higher than the capacities of various mineral processing equipment described in the literature, which in turn makes the cost estimation of large scale capital equipment as well as its application for large coal power plant uncertain. On the other hand, CO_2 emissions generated by Caterpillar manufacturing plant (common energy intensive facility) and various Distributed Energy Resources fall in the range of 1-5 tonnes CO_2/h, which requires 2-10 tonnes/hr of mineral processing and can be easily accomplished by utilization of standard mineral processing equipment described above.

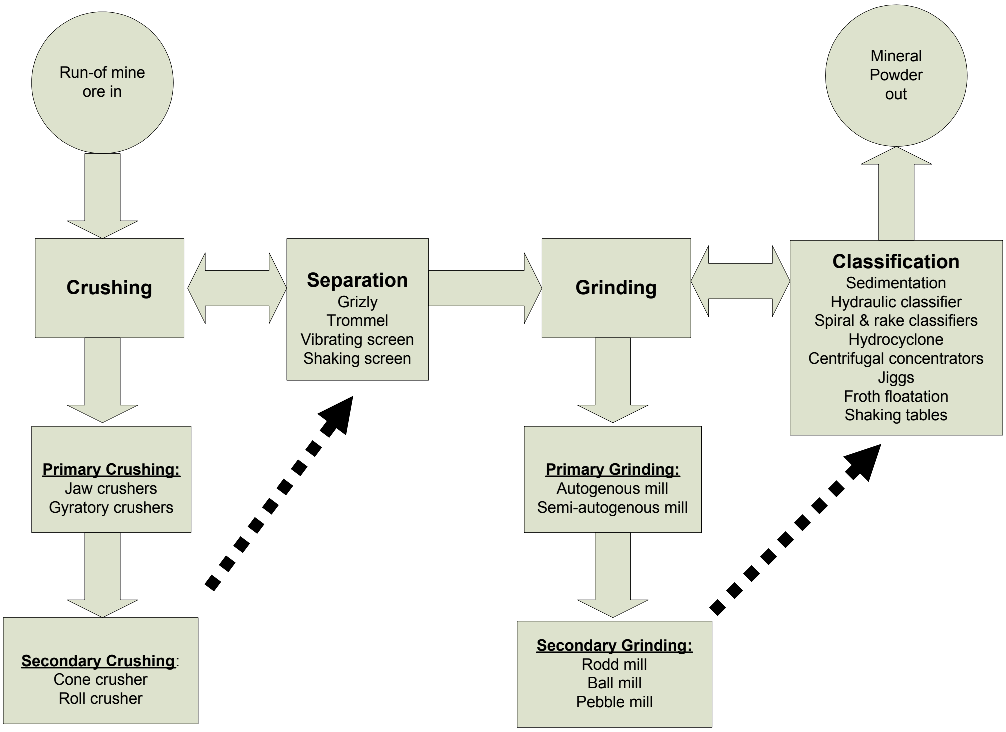


Figure 35 Mechanical mineral processing flow chart. [Copyright Caterpillar Inc.]

11.2.2 Mechanical Mineral Processing Review: Energy Requirements

Various pre-treatment options such as ultrasonic treatment and wet grinding in a caustic solution have been tested that did not result in a higher reactivity of silicate minerals (O'Connor *et al*., 2001). The major problem with many other pre-treatment options has been (or still is) the high energy input requirement, and it was recently concluded that, for select minerals, only conventional grinding has been proven both energetically and potentially economically feasible (Huigen & Comans, 2005). The mechanical grinding approach aims at destruction or disordering of the mineral lattice and thus an increase of the specific Surface Area (SA). Extensive studies in mechanical activation of silicates were performed at the Albany Research Centre (O'Connor *et al*., 2004; Gerdemann *et al*., 2002) and were later reviewed by Huijgen & Comans (2005) and Zevenhoven and co-workers (Sipila *et al*., 2008). The major conclusions made were that high-energy attrition grinding of silicates resulted in a higher conversion rates but consumed too much energy.

The fact that the pre-treatment of the mineral source is energy consuming can be further seen in Table 10 as given by O'Connor *et al.* (2002)**.** In the study, several levels of mechanical pre-treatments were considered, a) initial crushing, b) grinding to < 75µm, c) grinding to < 38µm and d) high intensity grinding in a so-called SMD (stirred media detritor) mill, to < 10µm (D_{50} ~ 5µm). The required energy input for these were a) 2kWh/tonne, b) 11kWh/tonne, c) 70kWh/tonne, and d) 150kWh/tonne. Besides this, after the initial crushing beneficiation (e.g. gravity separation) may be used for materials of less than 100% purity. Noted below as mechanical pre-treatment beneficiation, this would require additional 2kWh/tonne for a 70% pure olivine, and 4kWh/tonne for a 50% pure wollastonite. Table 10 lists the energy requirements of three different grinding alternatives and shows that the energy consumption does not depend on type of mineral, but rather (a) mineral grade and (b) desired particle size. The initial crushing and beneficiation step consumes only marginal amounts of energy, but the energy demand increases steeply as particle size is reduced. Overall, it was estimated that 75% of total mineralisation process energy consumed by mineral pre-treatment. Therefore, O'Connor *et al.* (2002) concluded that except for wollastonite, the increased reaction rates achieved with Stirred Media Detritor® (SMD) mills cannot fully compensate for the associated high-energy costs.

Ore mineral and grade	Pretreatment methodology	Crushing, kW-h/ton	Beneficiation, kW-h/ton	Grinding, St 1, kW-h/ton	Grinding, St 2, kW-h/ton	Grinding, St 3, kW-h/ton	Total, kW-h/ton
Lizardite, 100%	ball mill, 75 micron	2		11			13
Antagorite, 100%	ball mill, 75 micron	2		11			13
Olivine, 100%	ball mill, 75 micron	2		11			13
	ball mill, 38 micron	2		11	70		83
	SMD	2		11	70	150	233
Olivine, 70%	ball mill, 75 micron	2	2	15			19
	ball mill, 38 micron	2	2	15	70		89
	SMD	2	2	15	70	150	239
Wollastonite, 50%	ball mill, 38 micron	2	4	21	70		97
	SMD	2	4	21	70	70	167

Table 10 Energy consumption of different mechanical pre-treatment alternatives for various minerals [1-10]. The reported energy for crushing includes all the energy costs including mining and transportation up to and including the crushing stage [O'Connor *et al,* 2002]

As it was mentioned above, the mechanical activation by grinding aims for destruction or disordering of the crystal structure of minerals and increase of surface area. Recent study by Balaz *et al.* (2008) evaluates the structural changes in olivine $(Mg,Fe)_2SiO_4$ generated by its mechanical activation. After the first stage where the increase in Surface Area (SA) is almost proportional to the milling time, the second stage is observed where the surface area levels off. This effect is most pronounced when using a planetary mill, and in literature is attributed to particle enlargement (aggregation and/or agglomeration). A special effect has been observed by milling of olivine in nutating mill in the presence of water. The less water is applied, the higher the values for SA have been obtained.

The summary of the milling results is given in Table 11. Milling in an attritor seemed to be very promising from the point of view of induced physico-chemical changes: both surface area (SA) and crystallinity (X, %) values are the most different in comparison with as-received sample (SA=35.2m^2/g vs. 0.25m^2/g and X=12% vs.100%).

Type of mill	**RPM**	**Time, min.**	**SA, m^2/g**	**Crystalline phase, %**	**Milling energy, kWh/kg**
As-received	-	-	0.25	100	-
Attritor	1500	10	7.3	45	0.19
		30	18.1	26	0.58
		120	35.2	12	2.31
Planetary	450	10	4.8	37	2.01
		30	5.2	17	6.03
Nutating	900	10	3.0	57	0.64

Table 11 The milling parameters and physico-chemical properties of the olivine samples [Balaz et al., 2008]

It should be mentioned that energy consumption varies significantly and depends on the type of mill. The lack of particle size data along with the surface area makes it difficult to accurately compare the energy consumption results shown in Table 10 and Table 11. Our internal preliminary study on olivine material (Green Mountain, NC) showed the following correlation between SA and particle size: ~75µm/3.18m^2/g, ~15µm/6.19m^2/g, ~2µ/45.28m^2/g. Therefore, the attrition for 10 minutes required 190kWh/tonne and produced powder with SA of 7.3m^2/g and approximate particle size ~10-15µm. This result could be compared to data in Table 11 for 100% olivine ball milled plus SMD-treated down to ~ 10µm with energy consumption of ~233kWh/tonne. In another study by Fabian *et al.* (2010), the CO_2 absorption capacity of olivine mechanically activated in different conditions was studied and the results are summarized in Table 12.

Time, min	**Energy, kWh/g**	**SA, m^2/g**	**CO_2 Abs, µmol/g**
0	0	0.25	1.9
10	0.17×10^{-3}	7.3	13.9
30	0.52×10^{-3}	18.1	30.2
60	1.04×10^{-3}	27.7	49.7
120	2.08×10^{-3}	35.2	72.9

Table 12 Time and energy of milling, surface area (SA) and CO_2 subsequent absorption capacity of olivine mechanically activated for different times (attrition mill, 1500 rpm, steel balls, 1:20:1 = mineral: ball media: water). [Copyright Caterpillar Inc.]

It can be seen that 10 minute grinding requires 170kWh/tonne energy and produces powder with a surface area of 7.3m^2/g and ~10µm particle size (based on a Caterpillar internal correlation study). This energy consumption is lower than the 190kWh/tonne (Table 11) and

233kWh/tonne (Table 10) values and may be attributed to the “wet grinding” performed in this study. Meanwhile, it can be seen that the total CO_2 absorption capacity of activated olivine was still very low.

A recent study conducted by Haug [1-35], included over sixty olivine samples prepared by milling. The dissolution rates were studied in 0.1M HCl and pressured CO_2/H_2O, and the carbonation rates were studied at 128ºC-150bar and 115ºC-185bar. The results were correlated to mechanical activation under various conditions (wet-dry, planetary, attritor and nutating mills). The following major conclusions were made from the study:

- Mechanical activation with the addition of 10-wt% water resulted in a most significant increase of specific surface areas with milling time.
- Wet milled samples had smaller particles relative to the specific surface area than the dry milled samples.
- The crystallinity was observed to decrease with prolonged mechanical activation for both dry milling and wet milling. The dry milling was more efficient in reducing the crystallinity.
- Crystallinity as calculated from X-ray diffractograms was the material parameter with the best correlation with the measured dissolution rates.
- The relative importance of precipitation kinetics during direct olivine carbonation has implications for the choice of pre-treatment methods and the design of the carbonation process used for CO_2 sequestration.

11.2.3 Mechanical Pretreatment Conclusions and Recommendations

Based on the literature review presented, the following conclusions are made:

- No breakthrough mechanical activation methods were developed for silicate minerals during 2008-2010 timeframe.
- The standard mineral processing equipment and tooling are available and can be used for mechanical activation of the silicate minerals.
- Surface Area of mechanically ground powders increases with the duration and then flattens up at ~ $35m^2/g$ (for olivine).
- Mechanical activation results in structural disorder of minerals that can be observed by broadening of the characteristic peaks in XRD patterns as well as noticeable changes in FTIR absorption bands.
- Attrition milling as well as “wet milling” seems to be the most promising method for mechanical activation but the energy consumption is very high (~170kW-h/tonne to generate ~ 10-15μm powder with ~$7m^2/g$ surface area).

Therefore, additional mineral activation methods such as thermal and chemical activation are attractive options and are discussed in the following sections.

11.3 THERMAL ACTIVATION

As described in Work Package 1, the most plentiful feedstock is mineral rocks containing magnesium silicates such as serpentine and olivine. At quarries, the mineral rocks are crushed. Further pretreatment is required to make optimal use of the Mg^{2+} cations.

All mineral carbonation technologies have in common that cations are released under the influence of protons from the carbonic acid equilibrium. This will be detailed in Section 14.

In this context, Shell applies a simple method to assess the Mg^{2+} leaching behaviour for a variety of samples. Under ambient conditions, pure CO_2 is bubbled through aqueous slurry containing the solid sample. At regular times, the Mg^{2+} concentration is measured using ion chromatography. The analysis typically is concluded with a TGA-MS analysis of the remaining solid to ascertain that no solid precipitate was formed during the leaching test.

The graph below shows the leaching behaviour of samples of olivine (Mg_2SiO_4), serpentine ($Mg_3Si_2O_5(OH)_4$) and thermally activated serpentine, all with similar size range.

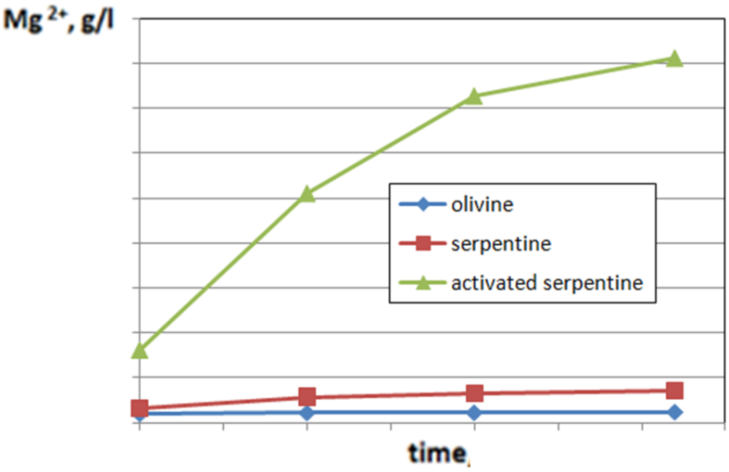


Figure 36 Comparison of leaching behaviour olivine, serpentine and thermally activated serpentine [© Shell Global Solutions]

One recognizes the strong improvement of leaching behaviour of serpentine by carrying out a thermal pretreatment step. Thermal activation (e.g. Chizmeshya *et al.*, 2002) yields an amorphous phase by dehydroxylation on a volumetric basis.

$$Mg_3Si_2O_5(OH)_4 \rightarrow (MgO)_3(SiO_2)_2 + 2\ H_2O$$

Shell has investigated the so-called T-τ window (in which T is temperature and τ duration of thermal pretreatment) for serpentine (patent pending). An optimal reactivity requires sufficient degree of dehydroxylation, but a constraint is that operating at elevated temperatures forms a larger proportion of less reactive or inert components such as forsterite (by recrystallization of the amorphous phase). A partial dehydroxylation of ca. 75% yields optimal reactivity.

As well, the tensile strength is reduced by a factor of ca. 3 which reduces energy requirements for the further size reduction of the feedstock (increase of specific surface). Mechanical pretreatment of serpentine, whilst generating specific surface, appears less efficient than thermal activation because the amorphous phase is formed on a surface basis.

The difference between the leaching behaviour of olivine and serpentine under these ambient conditions could be due to their crystal structure: orthosilicate vs. phyllo(sheet)silicate. We note that at elevated temperatures and CO_2 partial pressures this could be different.

Both thermal and mechanical pretreatment require energy. Energetic integration of thermal pretreatment in a CCSM system may offer more possibilities than mechanical pretreatment. This however needs to be assessed on a case-by-case basis.

11.4 CHEMICAL ACTIVATION

Chemical activation (or dissolution) of natural minerals for the purpose of extraction (leaching) and separation of valuable components (Al, Cu, Ag, Au, PGM, etc.) is a well-established large-scale industry. The dissolution behaviour of silicate minerals as a function of pH, DOC ("Dissolved Organic Carbon"), and atmospheric CO_2 has been the subject of numerous fundamental studies in the area of geochemistry of natural minerals. In accordance with the earliest study by Levenspiel (1972, **Figure 37**), the solid particle dissolution process is generally controlled by one of the following sequential steps:

(a) diffusion through a fluid film surrounding the particle,

(b) diffusion through a solid product layer on the particle surface (also called "ash" by the author), and/or

(c) chemical reaction at the particle surface.

The rate of the overall process is controlled by the slowest of these sequential steps. Based on this approach, both "particle shrinking" and "core shrinking" models were proposed, where the overall dissolution rate $\boldsymbol{r}$ can be described as a function of a specific surface area $\boldsymbol{S}$ of a solid sample:

$$\boldsymbol{r} \sim k\boldsymbol{S}^{p} \qquad (1)$$

Equation 1 is valid under the assumption of the existence of a power-law relationship between the total surface area $\boldsymbol{S}$ and total volume (or mass) of the solid sample ($\boldsymbol{S} \sim m^{p}$), constant T, P, pH, and mono-sized particle sample population. The particle dissolution model shows how the specific surface area $\boldsymbol{S}$ varies during the dissolution process. Parameter p is a function of the particle size distribution. Mono-sized convex particles with constant shape, have $p = 2/3$ (Jonckbloedt, 1998).

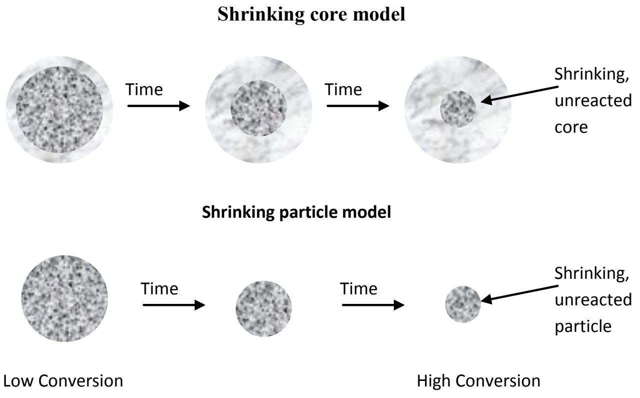


Figure 37 Schematic of a dissolution process using "shrinking particle" (SP) and "shrinking core" (SC) models [Levenspiel, 1972]

Dissolution kinetics for olivine and serpentine, the two main source silicate minerals for mineral carbonation, have been studied for several decades; especially, olivine has attracted noticeable interest, mainly due to its structural simplicity and high reactivity (Table 13). In an acidic media, it was shown that the dissolution rate of silicates increases almost two orders of magnitude as the pH deceases from neutral to pH=2. The dissolution rate is stoichiometric (congruent) with regard to Mg:Si ratio and follows the "particle shrinking" model.

The addition of complexing (bidentate) agents improves dissolution rates when the media is slightly acidic (pH=3-5), but shows negligible effect at lower pH levels. In this case, both stoichiometric and non-stoichiometric (incongruent, "core shrinking") scenarios were documented. The generic expression of the dissolution rate in acid and acid-complexing agent system at constant ambient P and T can be described as (Wogelius & Walther, 1991):

$$\boldsymbol{r}\ (\mathrm{mol\ cm^{-2}\ sec^{-1}}) = \mathrm{a} + \mathrm{b}\boldsymbol{a}_{\mathrm{H+}}{}^{\mathrm{n}} + \mathrm{c}\boldsymbol{C}^{\mathrm{m}} \qquad (2)$$

where $\boldsymbol{C}$ is the concentration of complexing agent and $\boldsymbol{a}_{\mathrm{H+}}$ is the acidity. Therefore, log $\boldsymbol{r}$ is approximately a linear function of concentrations of hydronium ions and complexing agent. At acid to neutral conditions (pH 2-6) and ambient temperature, the exponent, n, in the Eq. 2 has been found in many dissolution studies to be close to 0.5.

A very thorough study by Wogelius & Walther (1991) revealed that the presence of atmospheric CO_2 plays significant role in silicate dissolution at pH>7 due to CO_2 uptake by any alkaline media. Therefore, the data obtained in an ambient environment and in N_2 glove box gave different results. It was concluded that in alkaline conditions under N_2, both Mg and Si dissolution rates increase; the dissolution is stoichiometric at pH=8-10 and non-stoichiometric with Si preferential dissolution at pH=10-12. The presence of atmospheric CO_2 results in non-stoichiometric dissolution with preferential release of Si, and it is pH independent at pH = 8 – 12. Under these conditions, the Mg release is inhibited due to the reaction with atmospheric CO_2 and the formation of a carbonate layer on the solid particle surface.

Under the assumption that $\boldsymbol{a}_{\mathrm{H+}}$ (Eq. 2) is independent of temperature, the following correlation can be used to describe dissolution rates as a function of pH and T (Hänchen *et al*, 2006):

$$\boldsymbol{r} = \mathrm{A} \cdot \boldsymbol{a}^{\mathrm{n}}_{\mathrm{H+}} \cdot \exp(-\boldsymbol{E_a}/\mathrm{RT}) \qquad (3)$$

with $\boldsymbol{r}$ the dissolution rate [mol cm^{-2} s^{-1}], A the pre-exponential factor [mol cm^{-2} s^{-1}], $\boldsymbol{E_a}$ the activation energy [kJ mol^{-1}], T the temperature [K], R the universal gas constant = 8.3145 kJ mol^{-1} K^{-1}, $\boldsymbol{a}_{H+}$ the hydrogen ion activity, and n the reaction order with respect to hydronium ion concentration.

Using Equation 3 with the fitted parameters from various studies, the dissolution rate of olivine at 25°C and pH 2 is found to vary between $7.6\mathrm{x}10^{-13}$and $2.3\mathrm{x}10^{-12}$ [mol cm^{-2} s^{-1}] and 3 other values being between $1.1\mathrm{x}10^{-12}$ and $1.3\mathrm{x}10^{-12}$ [mol cm^{-2} s^{-1}] (see Table 13 for references). At higher pH values, the spread among the reported rates increases. Considering also extrapolated values from Rosso and Rimstidt (2000), the reported values at pH 6 and 25°C vary between $5\mathrm{x}10^{-15}$ and $2.3\mathrm{x}10^{-14}$ [mol cm^{-2} s^{-1}]. These differences stem both from the varying properties of natural minerals and from experimental difficulties, e.g., very low aqueous concentrations.

Activation energy is the other important parameter for characterization of the mineral dissolution process. The two lowest values found for olivine are 38.1 and 42.6kJ/mol, with the latter being based on the large data set from Rosso and Rimstidt (2000). Other studies report figures up to ~80kJ/mol with standard deviations between 2 and 17 kJ/mol.

Overall, it should be mentioned that the dissolution rates at ambient T and P are still low (-log ***r*** = 8-12, or ~10^{-6}-10^{-8}g/sec) to be of interest for development of a large-scale industrial process. Few studies reported dissolution rates at higher temperatures of up to 150°C, and the data are shown in Table 13.

Reference	pH	***r***, (25°C, pH 2) [mol cm^{-2} s^{-1}]	Temp, °C	E_a, [kJ mol^{-1}]	Model
Grandstaff, 1986	2.9-5	1.9x10^{-13}	1-49	38.1±1.7	PS
Blum, 1988	2-5, 9,11	1.1x10^{-12}	25	-	PS
Wogelius, 1992	2-12.4	7.6x10^{-13}	25-65	79.5±10	PS
Fouda, 1996	~2	1.15x10^{-4}	30-75	35.6 (H_2SO_4)	CS
				72.8 (HNO_3)	CS
Jonckbloedt, 1998	-0.7-2	3.9x10^{-11}	60-90	66.5±2	CS
Chen, 2000	2-5	-	65	126±17 (pH=0)	CS
Pokrovsky, 2000	1-12	2.3x10^{-12}	25	-	PS
Rosso, 2000	1.8-3.8	1.2x10^{-12}	25-45	42.6±0.8	PS
Oelkers, 2001	2	1.3x10^{-12}	25-65	63.8±17	PS
Hanchen, 2006	2-10.5	1.03x10^{-9}(120°C)	90-150	52.9±6.9	PS
		2.18x10^{-13}(pH12, 90°C)			CS
Tier, 2007	~2	~10^{-6}:10^{-7}**	30-70	68.1±7.3 (H_2SO_4) 74.3±5.8 (HNO_3)	CS CS
Haug, 2010	2-3	~10^{-6}:10^{-4}**	25	-	(*)

* see text.

** rate constants (instead of global dissolution rates) were reported and they are much higher than rate constant of 10^{-7} for the reference sample from Rosso & Rimstidt, 2000.

PS – particle shrinking, CS – core shrinking.

Table 13 Selected studies on dissolution of silicate minerals

In a study by Hänchen *et al* (2006), the dissolution rates were measured at the temperatures of 90°C, 120°C, and 150°C. It was found that the dependence of the dissolution rate on pH follows a trend found already at ambient temperature (Eq.2) up to about pH 8. For higher pH values, the dissolution rate only shows a very weak dependence on pH. The value for the coefficient *n,* describing the pH dependence, is within the range of those reported in the literature at lower temperature, namely n = 0.45, 0.45, and 0.48 at 90, 120, and 150°C, respectively and close to its theoretical value of n = 0.5. As in earlier studies, n does not appear to change significantly with temperature.

The dissolution was found to be stoichiometric throughout almost all experiments, within experimental uncertainty, except for a start-up period observed in the experiments under neutral to alkaline conditions and two experiments at high pH. In these cases, an initial preferential release of silica was observed, in accordance with earlier data from Rosso and Rimstidt (2000).

Figure 38 shows the summary of selected studies on olivine dissolution at temperatures from 25°C to 150°C and at ambient pressure, where HCl and NaOH or LiOH were used to obtain the desired pH (summary from Haug, 2010). It can be seen that the dissolution rate in acidic media increases almost 4 orders of magnitude as temperature increases from 25°C to 150°C.

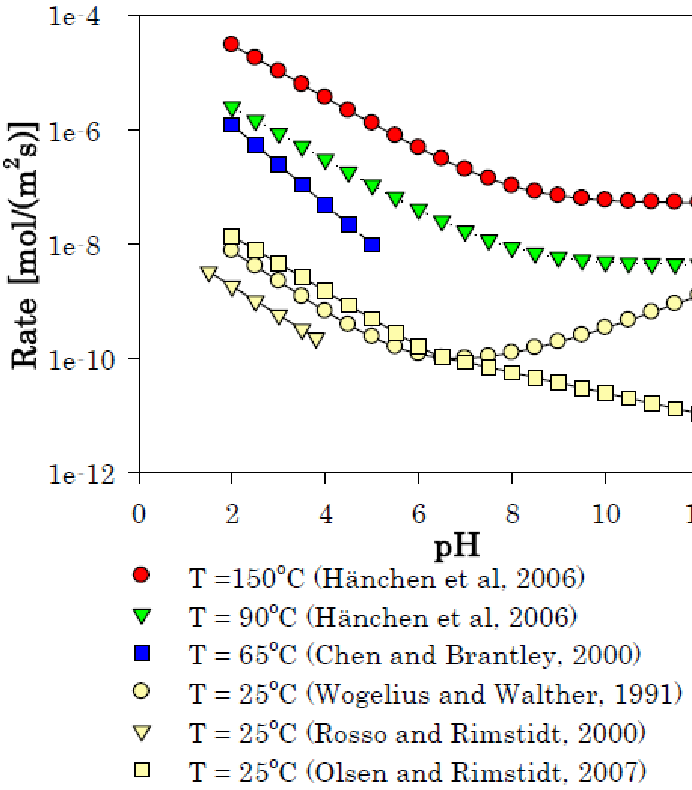


Figure 38 Dissolution rates of olivine at various pH and temperatures from selected studies [Haug A, 2010].

With regard to the development of CCSM technology, it was proposed to separate the process into two distinct phases; e.g. leaching of metal ions from the mineral/solid residue source followed by the carbonate formation. Sipilä *et al* (2008) concluded in their review that separating the mineral dissolution step from the carbonate precipitation step probably is the most promising approach, despite the additional investment costs, challenges with mass balance and equilibrium considerations. Various acids, bases, and complexing agents were tested (HCl, H_2SO_4, HNO_3, HCOOH, CH_3COOH, NaOH, KOH, NH_3, NH_4Cl, $(NH_4)_2SO_4$, NH_4NO_3, EDTA, terpineol). In the extraction experiments, sulfuric acid was found to be the best extraction agent of all the chemicals tested, but none of the acids was able to extract Mg selectively. For example, Cheng and Hsu (2006) showed that significant amounts of Mg (and Fe) could be extracted from serpentine leaving behind mainly SiO_2 using 5M H_2SO_4 at temperatures above 80°C. The significant effect of temperature on magnesium extraction can be seen in Table 14.

Composition%	SiO_2	MgO	Fe_2O_3	CaO	Al_2O_3
Raw serpentine	40.94	36.14	7.09	1.49	2.5
60°C	76.22	11.57	1.82	2.12	1.01
80°C	88.95	2.17	0.65	1.52	0.18
90°C	90.66	1.07	0.32	1.3	0.04

Table 14 Chemical composition of raw serpentine before and after treatment in an aqueous 5M H2SO4, L/S 10ml/g at different temperatures for 48h [Cheng and Hsu, 2006]

In summary, it was found that magnesium extraction improved with increasing acid concentration (1.5–5M) and decreasing particle size (median size: 163µm, 125µm and 63µm). Increasing the reaction times from 6h to 24h resulted in a 46% improvement of the magnesium extraction, and temperature increase improved the dissolution rate by 70%.

Further development of the dissolution model was done by implementing the so-called population balance approach. This involves polydispersed distributions of solid particles (instead of mono-sized) and allows for a better approximation of the dissolution rates of silicate minerals in real CCSM applications (Hänchen *et al*, 2007). For this purpose, the dissolution rate of olivine has been measured as a function of varying particle size with a pH between 2 and 4.75 and at 120°C. Three separate particle populations were used: <90µm, 90–180µm, and 180–355µm size fractions. Assuming particles with constant shape (defined by a surface shape factor k_s and a volume shape factor k_v), it is possible to describe the particle size evolution using one characteristic length, $\boldsymbol{L}$. The particle size distribution is then given by f($\boldsymbol{L}$, $\boldsymbol{t}$). The dissolution rate, $\boldsymbol{D}$, in this model is defined as the rate of change of the characteristic length $\boldsymbol{L}$ of a given particle over dissolution time t:

$$\mathrm{d}\boldsymbol{L}/\mathrm{dt} = -\boldsymbol{D} \qquad (5)$$

and the final population balance equation for this system is then:

$$(\delta \mathrm{f}/\delta \mathrm{t}) - \boldsymbol{D}(\delta \mathrm{f}/\delta \boldsymbol{L}) = 0 \qquad (6)$$

It was concluded that the previous models [Eq. 1 & 2] could be used as an approximation for particle population with narrow size distributions, while the improved model is capable of accommodating a much wider range of particle sizes.

Several studies on dissolution of serpentine (Teir *et al* (2007), Luce *et al* (1972), Apostolidis and Distin (1978)) showed that the rate limiting step for dissolution of serpentine in HCl, H_2SO_4, and HNO_3 is the product layer diffusion. However, the results showed that the process is temperature sensitive and the activation energy is of the order of 70kJ/mol, which is rather high for the diffusion-controlled process. It is possible that chemical reaction is rate limiting at the beginning of the reaction, with product layer diffusion gradually becoming rate limiting as the silica layer builds up and the unreacted surface area decreases.

In a recent study by Haug (2010), the dissolution of various mechanically activated samples of olivine was studied in a 0.01M HCl solution at room temperature and pressure. Three different high-energy milling methods were used: dry milling, wet milling (liquid: solid=5), and 10% water milling (or liquid: solid=0.1). Mechanical activation as a pretreatment method was found to enhance the initial dissolution rates by approximately 3 orders of magnitude. The specific surface area gave a nice correlation versus dissolution rate for samples milled wet and the samples milled with 10wt.% water, but it didn't follow the power-law relationship from Eq. 1. The measured particle size distributions could not explain the rate constants found, and the "shrinking core" model did not fit the specific surface area measurement of three differently milled and dissolved olivine samples. In this study the so-called direction dependent dissolution was observed for olivine (also documented previously by Awad *et al* (2000) and may have been enhanced by mechanical stress induced by milling. It was concluded that the "shrinking core" model was not suitable to describe changes in the specific surface areas for mechanically activated olivine, and this likely applies to other minerals as well.

The empirical Eq. 7 was proposed that better describes measured dissolution rates:

$$\boldsymbol{R_{emp}} = f_r \cdot [\boldsymbol{S_0} \cdot (100\text{-}b)/100] \cdot (N/N_0)^{fm} \cdot k \cdot (1\text{-}IAP/K_{fo}) \qquad (7)$$

This equation is composed of four parts: the initial surface area of olivine in the first brackets where $\boldsymbol{S_0}$ is the available surface area of the sample, and *b* is the degree of contamination in the sample. The second bracket implements a "shrinking core" model based on the initial moles of olivine (N_0) and the moles of olivine present (N). The third part is the reaction rate constant *k*. The last brackets express the reduction in reaction rate when approaching equilibrium. IAP is the ion activity product for olivine, and K_{fo} is the equilibrium constant. The power factor *p* from Eq. 1 was replaced with an empirical fitting factor f_m that has values between 6.9 and 20. The rate constant, *k*, was shown to vary and decrease as dissolution degree increased. The mineral powder crystallinity, calculated from X-ray diffractograms, was the parameter with the best fit for the observed changes in the specific rate constants.

An acid (HCl) extraction route technology assessment was performed by IEA GHG in 2000, concluding that the calculated cost of €179/tonne CO_2 avoided and the negative CO_2 balance makes this approach unattractive. A similar conclusion was reached by Teir *et al* (2007) for the process utilizing HNO_3 for leaching step and NH_4OH for carbonate precipitation step.

In order to improve the economics of an "acid extraction – alkali carbonation" process, chemical regeneration will have to be performed or the chemicals will have to be produced by a low cost, low energy consumption process. Recently, the well-known "chlor-alkali" electrochemical process has been revisited with regard to HCl and NaOH production from NaCl and/or "salt water" (Calera Inc., Skyonic Inc.). On the other hand, the possibility of producing the valuable products (for example high purity silica) will have to be integrated into CCSM process, but none of the suggested options described in the literature have yet resulted in a thorough techno-economic evaluation as well as large-scale production. A valuable end product would allow for much higher operational costs for a carbonation plant and possibly make it profitable.

11.4.1 Chemical Activation Conclusion and recommendations

The current mineral processing industry that utilizes various acids, alkalis and complexing agents for the extraction of valuable components from natural ores is well situated for large-scale silicate dissolution processing and does not require any specialized equipment.

No significant breakthrough approaches were developed during 2008 – 2010 in the area of chemical activation of silicate minerals for CCSM. It was confirmed that mineral dissolution rates increase with increasing acid concentration (up to 5M), decreasing particle size, and increasing temperatures (up to 150°C). Mechanical activation of minerals was shown to increase mineral dissolution rates at ambient conditions, but it requires additional energy input.

In acidic media, the dissolution of olivine can be generally described by the "particle shrinking" model (or congruent dissolution) with the chemical reaction at the particle surface as a rate-limiting step. The dissolution of serpentine follows the "core shrinking" model (or incongruent dissolution) with the layer diffusion as a rate-limiting step. The experiments with the dissolution of mechanically activated minerals showed that the dissolution mechanisms are governed by complex mechanisms. In particular, the directional dissolution path along specific crystallographic planes was discussed.

In order to improve the economics of a multi-step "acid dissolution – alkali carbonation" process the following options are suggested: (a) production and separation of silica during acid dissolution step; (b) utilization of "chlor-alkali" process for generation of HCl acid and NaOH alkali form salt and/or salt waters. The detailed techno-economic analysis of these options has not been documented in the literature and is recommended for a follow up study.

11.5 MECHANO-CHEMICAL ACTIVATION

The mechanical grinding of silicate material smaller than 10μm was previously shown to carry a significant cost penalty from energy consumption. Numerous chemical pre-treatment technologies reviewed by Hujien, 2005 and Zevenhoven, 2008 indicate that large amounts of acids (2-4 tonne per tonne CO_2) and alkalis for pH adjustment (2.4 tonne of NaOH per tonne CO_2) would be required for CCS MS. Optimistically, the overall process cost estimate is in the range of 220-350$/tonne CO_2 [Tier, 2007]. Therefore, alternative methodologies that minimize the chemical and energy consumption are desired. One approach known as mechano-chemistry may be very promising.

Mechano-chemistry can be described as the integration of chemical and mechanical engineering since chemical transformation results from the application of mechanical stresses onto solids. Mechano-chemistry utilizes force to do mechanical work on a molecule, thereby raising its energy and changing its structure and chemical reactivity. In the mechano-chemical process, the chemical reactions occur at the interface of the particles and these are continuously re-generated during milling or grinding.

In spite of mechano-chemical reactions being ancient phenomena, the fundamentals of this process are still very much an open subject. Meanwhile, its potential application in materials science as well as in the industrial fields of ceramics and metallurgy is well recognized as a solvent-free green engineering process.

Literature searches indicate that this approach has been investigated for CCSM. The so-called single step mechano-chemical carbonation process integrates the pre-treatment grinding process with the chemical carbonation process (direct gas-solid method) [Nelson, 2004]. The chemical reaction potentially proceeds faster as new surface areas are created during the grinding. Process costs are potentially lower due to a simplification of the process design. However, research performed using this approach has not yet succeeded in significant carbonation of various silicate minerals – only ~2% maximum conversion has been demonstrated

Another approach involving the mineral pre-treatment step only combines mechanical and "wet" chemical treatments. This increases the mineral surface area as well as accelerates the dissolution rates of silicates in presence of various acids, alkalis, complexing agents, or electrolytes (ionic strength modifiers). An initial study by Zhang, 1997 indicated that up to

90% Mg and 45% Si was dissolved after 120min of grinding in presence of acids. Mg is preferentially extracted after the short time grinding of ~20min since the Mg/Si ratio is approximately 8 in solution. The Mg/Si ratio levelled off to ~2 (same as for starting olivine sample) after ~250min of mechano-chemical treatment.

The effect of the mechanical (or physical) activation on the dissolution of serpentine was investigated more thoroughly by Park [2003, 2004]. It was found that the fluidization of the serpentine slurry with 2mm glass beads was most effective in refreshing the surface of the serpentine particles during the dissolution process. This method could involve significantly less energy when compared to the conventional external attrition grinding. The mechano-chemical combination of the internal grinding and Mg leaching resulted in a rapid serpentine dissolution.

An interesting study was described by Puclin, 1995 on an acid dissolution of a related silicate mineral (ZrSiO4) after mechano-chemical treatment with corundum. It was stated that ZrO_2 was "released" from silicate structure by the following mechano-chemical reaction:

$$ZrSiO_4 + Al_2O_3 = 3Al_2O_3 \times 2SiO_2 + ZrO_2$$

In a very recent study by Zhao, 2009 the mechano-chemical dissolution of another silicate mineral ($Zn_4(Si_2O_7)(OH)H_2O$, hemimorphite) was successfully performed in alkaline media due to amphoteric nature of zinc metal. It was shown that the dissolution of silica was considerably inhibited by adding CaO, but the zinc extraction was almost unchanged: under optimum conditions the metal extraction was increased up to 93.6% while Si extraction fell dramatically from 74% down to 6.7%. It was concluded that the following reaction takes place during mechano-chemical treatment:

$$Zn_4(Si_2O_7)(OH)H_2O + OH^- + CaO \rightarrow [Zn(OH)_4]^{2-} + Ca_2SiO_4$$

In addition, a very similar approach was described by McCormick, 2002 for the selective extraction of aluminium from alumosilicate mineral bauxite by mechano-chemical treatment with alkaline CaO:

$$Al_2O_3 \times \times SiO_2 \times Fe_2O_3 \times H_2O + OH^- + CaO \rightarrow [Al(OH)_4]^- + Ca_3AlFe(SiO_4)(OH)_8$$

It was stated that this reaction prevents the formation of aqueous silica gel that is very difficult to filter.

It was mentioned in previous chapter that a special effect was observed when milling olivine in a nutating mill in the presence of water. The less water applied, the higher values for the surface area were obtained. The effect from the addition of small amounts of a liquid to accelerate the solid-state reactions carried out by milling is called kneading in chemical engineering. Kneading is a well-known process in preparation of ceramic green bodies for the extrusion process and is related to the disintegration of solid materials by applying a sheer force instead of impact loading from grinding in planetary mill. The layered crystal structure of the material of interest (such as clays, talc, serpentine, etc.) plays an important role on the effectiveness of kneading. The possibility for a hydrothermal process under mechanical milling with water has also been discussed in the literature [Avvakumov, 1994; Boldyrev, 2002]. It is known that with ceramics, an induced shear stress enhances the chemical reaction between the stretched bonds and the adsorbed polar molecules such as water. The reaction lowers the surface energy of the bonds and so ceramics will typically break at lower applied loads [Watanabe, 1996]. On the other hand, kneading has also been described as a sort of catalysis, where adding a small amount of solvent provides a media for solid-state diffusion and formation of a transition state species during chemical transformation. A number of interesting studies were performed where small amounts of water as well as organic solvents were used for the mechano-chemical reactions of inorganic and organic solids [Brage, 2005; Shan 2002].

11.5.1 Mechano-Chemical Activation Conclusion and Recommendations

Mechano-chemical methods could provide an alternative, low cost approach to CCSM. However, these methods have not been fully explored and data on energy consumption and cost of these processes was not found in the literature. Some of the prospective methods include the following:

- Mechano-chemical mineral pre-treatment in presence of small amounts of liquid media under shear force load
- Mechano-chemical mineral pre-treatment in presence of special additives for selective Mg extraction
- Mechano-chemical mineral pre-treatment step followed by mechano-chemical carbonation step

12 Carbonation

CCSM technologies can be divided into several groups: (a) gas-solid vs. gas-aqueous media-solid, (b) direct (or single step) vs. indirect (or multi step), (c) additive enhanced or without chemical additives, (d) combination of them. The rate-limiting steps, mechanisms of the rate-limiting steps and controlling parameters of various CCSM groups are discussed in this chapter. Transport phenomena as well as chemical reaction fundamentals are mainly controlled by the solid particle size, temperature, pressure, activation energy and concentration of chemical species.

12.1 AQUEOUS CARBONATION CONTROL MECHANISMS AND PARAMETERS

The main barriers to the commercial deployment of CCSM are high-energy intensity, low reaction yields, slow reaction kinetics, and the competition with other technologies such as geologic storage and renewable energy (Santos et al, 2010). The direct (single step) gas-solid carbonation is similar to other heterogeneous gas-solid chemical reactions and is rather well understood. CO_2 gas diffusion through the solid product layer (carbonates and silica) is the rate-limiting step in this case (see also discussion in Appendix 10, p.318-320). Meanwhile, aqueous carbonation routes are much more complex. To reach the highest aqueous carbonation efficiency the controlling mechanisms and optimal parameters for aqueous carbonation routes need to be defined.

12.1.1 Aqueous Carbonation Rate-Limiting Steps and Mechanisms

CCSM routes that involve aqueous liquid media can be accomplished in a single step (also called “direct carbonation”) or in two and multiple steps (also called “indirect carbonation”). Direct carbonation routes involve mass transport and chemical reaction between CO_2 stream and mineral (or mineral aqueous slurry) in one-step process. In contrast, indirect carbonation is based on chemical reaction of CO_2 with aqueous solutions of Mg and Ca cations extracted from minerals in a separate step. Consequently, direct aqueous carbonation and indirect multistep carbonation present different controlling mechanisms.

Direct aqueous carbonation occurs via sequential diffusion steps (mass transport) and chemical reaction steps (dissolution and carbonation). Initially, CO_2 gas diffuses rapidly into aqueous media and is transported toward the thin aqueous films that coat the mineral particles. Then carbon dioxide diffuses through the aqueous film into the solid mineral matrix where the carbonation reaction takes place. In parallel, the mineral dissolution in aqueous media occurs. In aqueous media at neutral pH the **mineral dissolution** is the overall rate-limiting step of the direct aqueous mineral carbonation systems. This is due to the absence of highly reactive protons enabling ion exchange reaction between metal cations (Mg^{2+}, Ca^{2+}) in aqueous media and silicate mineral framework (O’Connor, 2001, Bonfils et al, 2010). As it was discussed in Chapter 11.4, mineral dissolution can follow two mechanisms: particle shrinking (typical for olivine) and core shrinking (typical for serpentine). In a later case, the ion diffusion through the silica layer is a controlling mechanism.

In order to optimize the total CCSM technology, two- and multi-steps processes have been investigated where the dissolution of the minerals is optimized in a separate stage prior to carbonation stage. In this case, the **CO_2 dissolution** of the carbonation stage becomes an overall rate-limiting step. Therefore, the diffusion and transport of carbon dioxide in aqueous media becomes a controlling mechanism (Levenspiel O, 1972; Daval et al, 2009). Meanwhile, chemical reaction of CO_2 and water as well as chemical reaction of extracted (dissolved) Mg, Ca cations with the dissolved CO_2/HCO_3^- is significantly faster.

The controlling mechanisms of carbonation using pure CO_2 and flue gas are expected to be similar, but the reaction rate of diluted CO_2 is slower due to the rate is proportional to CO_2 concentration or pressure (Stumm et al, 1996; Arickx et al, 2006).

12.1.2 Aqueous Carbonation Parameters

Particle size is an influential parameter for any heterogeneous chemical reaction involving solids (gas-solid, liquid-solid, etc.). With regard to carbonation, the reduction of size increases surface area of solid mineral, availability of Mg and Ca ions and improves the diffusion of CO_2 through the solid (starting mineral and carbonation products). As it was discussed in Chapter 11.4, mineral dissolution rate is a function of particle size distribution. Stirring, agitation or sonication (sound waves between 16 and 100kHz) improves mass transport in the heterogeneous system and, as an example, removes the carbonate product layer allowing further diffusion and dissolution of Mg and Ca out of the silicate framework as well as diffusion of CO_2 into the solid (Santos et al, 2010, Kodama, 2008). A so-called internal grinding (physical agitation without significant energy requirements) can remove the passive SiO_2 product layer during carbonation enhancing further dissolution of the inner Mg layer and carbonation reactions (Park et al, 2004).

A direct single-step carbonation process (such as the ARC process) is controlled by mineral dissolution rate and requires fine mineral grinding below 75µm, which consumes too much energy (1,000-2,000kWh/tonne CO_2 sequestered for the activation stage). Instead, a coarser particle size (100-300µm) is acceptable in the indirect multi-step processes that carbonate the extracted Mg and Ca (Zevenhoven et al, 2010).

Temperature influences both the dissolution rates (CO_2 dissolution and mineral dissolution) and carbonation rates. Low temperatures enhance the diffusion of CO_2 while high temperature increases the magnesium and calcium dissolution. These contradictory trends will have to be balanced. Interestingly, the best carbonation efficiency was obtained at low temperature in presence of 20% CO_2 and at higher temperature in presence of 100% CO_2. Therefore, the diffusion of gaseous CO_2 seems to be the controlling parameter when flue gas is used and low temperature should be favored. On the other hand, dissolution of reactive ions and carbonation at high temperature is preferred when concentrated CO_2 is used (Santos et al, 2010, Baciocchi et al, 2009). For example, 100% of magnesium was extracted from serpentine mineral at temperatures of 90-100°C (Wang and Maroto-Valer, 2010). In another example, direct single-step dissolution and carbonation of silicate rocks can be performed at 120°C and 20bar pressure of CO_2 (Bonfils et al, 2010). Direct carbonation of steel slag indicates that at temperatures between 25 and 150°C the dissolution of mineral (wollastonite) is probably the rate-determining reaction step while above 200°C a reaction step involving dissolution of CO_2 becomes rate limiting (Huijgen, 2007).

High pressure can be used to (a) enhance the dissolution of CO_2 in the aqueous media and improve processes where CO_2 dissolution is a rate-limiting step, (b) enhance the diffusion of the gaseous CO_2 into the solid matrix and improve processes where CO_2 diffusion into solids is a rate-limiting step, and (c) enhances the carbonation efficiency for all groups of CCSM (O`Connor et al, 2000; Huijgen, 2007).

Liquid/solid ratio is an important parameter for aqueous carbonation routes because it defines concentration of the reactive species in aqueous media, its ionic strength, and chemical reaction rates. In addition, a specific L/S ratio is required for adequate mass transport through mixing, stirring, agitation (Santos et al, 2010). It has been shown that at L/S-ratios lower than 2 the reaction mixture cannot be stirred sufficiently in an autoclave reactor and may result in poor CO_2 gas-liquid and solid-liquid mass transport.

A reduction of the L/S-ratio leads to a substantial improvement of the heat balance of the process and, thus, the overall CO_2 sequestration efficiency. However, if the L/S-ratio becomes too low, pumping and stirring problems might arise because of an increased viscosity, which would lead to a significant decrease of the conversion as well as increased power consumption by mixing machine. Therefore, L/S parameter should be optimized for various CCSM processes.

12.2 CONCLUSIONS

The main parameters of the direct (single-step) and indirect (multi-step) aqueous carbonation have been summarized in Table 15 to compare them under the different process conditions. The slow mineral dissolution and poor availability of reactive Mg or Ca cations is the main rate-limiting step in the direct single-step aqueous carbonation as can be clearly observed in the table where the dissolution of mineral is incomplete. In addition, high pressure and temperature is required for sufficient CO_2 diffusion. However, the efficiency of direct carbonation is still not satisfying so far and pre-treatment (fine grinding or thermal activation) are required to enhance the single-step processes efficiency by enhancing the dissolution of minerals. These pre-treatments are able to increase the process efficiency to 80-85% with temperature and pressure > 100°C and 100bar, respectively. The 2-step and multistep processes are the category of aqueous carbonation that is able to reach high carbonation efficiency (80-90%) using mild process conditions and short duration (faster reaction kinetic). However, this category still presents high complexity and the issue of recycling the chemicals. Overall, single-step with additives and multistep aqueous carbonation processes are able to reach 80% of efficiency and might be economically attractive.

Single step (direct)

						Heat activation	Leaching		
	Temp (°C)	Pressure (bar)	Time (hr)	Efficiency (% CO_2)	Particles (μm)	Temp (°C)	Temp (°C)	Pressure (bar)	Time (hr)
range	30-250	1-150	0.16*-21	8-69	5-300	/	/	/	/
optimum**	150-200	35 (1.2)	1 (20.16)	69 (25)	37	/	/	/	/

* leaching of 20 hrs; **wollastonite; ( ) CAT, olivine

** wollastonite

Single step (additives)

						Heat activation	Leaching^2		
	Temp (°C)	Pressure (bar)	Time (hr)	Efficiency (% CO_2)	Particles (μm)	Temp (°C)	Temp (°C)	Pressure (bar)	Time (hr)
range	25-185	1-185	1-24	60-84	5-300	630^1-650	22	1	96
optimum*	150	115	6**	80	75	650	/	/	/

* Brent; ** ARC, olivine and serpentine, 1 serpentine heated for 2hr at 650°C; 2 Calera process

Multistep

						Heat activation	Leaching		
	Temp (°C)	Pressure (bar)	Time (hr)	Efficiency (% CO_2)	Particles (μm)	Temp (°C)	Temp (°C)	Pressure (bar)	Time (hr)
range	20-100	1-40	0.16-2	50-90	5-300	950^1	15-100	1	1-14
optimum*	90	1	1	80	75-150	/	100^2	1	3

* UoN (flue gas), 1 Kodama (waste activation for 0.5 hr); 2 300°C are required to regenerate the ammonia

Table 15 Aqueous carbonation process conditions [Copyright University of Nottingham]

13 Post-Processing

The CCSM products might be used for a wide range of applications, both low value and high-value applications. However, global success of CCSM could flood markets and erode margins and also a higher value will require more sophisticated processing including drying leading to large cost penalties. Land reclamation may allow for transport and grinding synergies representing at this stage of the programme the only viable opportunity. Avoid sending material to landfill produces a cost saving for the process. This would be a similar model to the sale of gypsum from flue-gas desulphurisation. The exact CCSM technology chosen will play a very important role on the available post-processing routes and accessible markets due to the purity of the resultant materials. It is unclear if the quality of the CCSM products would be enough to access the high-value market where micro-silica and PCC have selling prices above 200-300£/tonne, which might render the process economical. Therefore, further investigation is required to establish the technical and economic feasibility of this pathway.

13.1 INTRODUCTION

One of the options suggested for improving the economics of CCSM is to explore post-processing options that produce products with a marketable value in the best case (Doucet, 2010; Teir et al., 2005). In the worst case, where no marketable products are possible, the ideal state would have the products classified as nonhazardous wastes so that disposal costs are minimal. This may well be the case. However, irrespective of purity levels, current volumes, and diversity of applications, the market value of calcium carbonate minerals significantly outweighs that of magnesium carbonates. Paradoxically, the level of calcium carbonate produced by mineralisation of industrial waste and by-products would be significantly lower than that arising from the mineralisation of serpentinite, producing magnesium carbonates (Styles et al, 2010). In addition, the significant quantities of silica produced by mineralisation would also offer significant opportunities for post-processing.

The main objectives of this section are to:

1. Determine a network of post-processing routes for CCSM products ranging from low level technologies requiring minimal additional processing through to high level and advanced materials
2. Select only the non-calcination routes for post-processing already available (or possible) for primary-sourced carbonate and silica powders. Besides (hydro-) carbonates and silica it can also be speculated that there may be several other minor products such as iron oxides, non reacted mineral, and even material contaminated with chemical additives that potentially can be marketable once extracted. However, this review only focuses in detail on the primary products
3. Critically compare the difference between desired physical properties and chemical composition of primary sourced carbonates and CCS carbonates for each selected post-processing route, and identify potential applications where magnesium carbonates could feasibly be used to replace those already known or established for calcium carbonates. Indicating the post-processing required to meet the quality of final products

13.2 SCENARIOS OF CCSM PRODUCTS QUALITY

The different CCSM technologies illustrated in Chapter 14 of this report produce a range of different products as shown in Table 16. These technologies can be divided into two groups, for simplicity where:

1. The CCSM technology produces a mixture of carbonates (magnesium or calcium carbonate), silica sand, iron oxides, and silicate rock residue (e.g. ARC process).
2. The CCSM process involves the separation of the three different streams with variable purity level: silica, carbonate, and iron oxide (e.g. Åbo A. and UoN processes).

These two different scenarios are used to describe and select the group of technologies needed to obtain final sellable products.

For example, in the 1st scenario the ARC technology produces a slurry containing about 55% of magnesium carbonate, 30% of silicon dioxide, 5% of iron oxide, 0.5% of Na_2O and 0.2% of Al_2O_3 plus other minor contaminants (O'Connor et al, 2000). Therefore, this slurry might be landfilled or only used for low-end applications (e.g. land reclamation) because complex post-processing is needed if silica and carbonates are to be produced as raw materials for high-end applications. This could render the post-processing too costly and require too much energy.

Differently, the second scenario illustrated a situation in which the post-processing to produce final products is less complicated and requiring fewer stages. For example, the Åbo A process produces 1.1 tonne/tonne CO_2 of silica sand with 82-88% purity, 0.5 tonne/tonne CO_2 of iron oxides and 2.7 tonne/tonne CO_2 of hydromagnesite 99% pure, with uniformly sized and spherical crystals with a lamellar structure (Teir S et al, 2009). Similarly, the UoN process could produce 3 products: silica (90% pure), magnesium carbonate (90-95% pure), and iron oxide (Wang X, 2010). In the last process, the silica sand might be directly used as flux sand for iron and steel making, considering the characteristics and requirements (Section 4.3.1).

		Composition, wt%								
		SiO_2	$MgCO_3$	Fe_2O_3	CaO	Al_2O_3	Na_2O	SO_4	Mg-silicate	$FeCO_3$
Single product (ARC)	Slurry	28	54	5	0.25	0.2	0.4			?
Multiproducts (Åbo A)	Silica	82-88		5-8 ?					7-14?	
	Iron oxide			?						
	$MgCO_3$		93-99*							?
Multiproducts (UoN)	Silica	90		4	< 0.1			< 0.5	6	
	Iron oxide			40**	< 0.5			< 0.5	50?	
	$MgCO_3$	< 0.5	90-95	1	< 0.1			1-1.5		2-4

* hydromagnesite, ** FeOOH

Table 16 Comparison of a single product vs. separated products technologies [Wang et al, 2010; Teir et al, 2009 and O'Connor et al, 2000]

The different products that can be produced by mineralisation and their current applications are discussed in the next sessions.

Mixed slurries can be used in low-end applications such as land reclamation or as soil amendment with minor post-processing such as dewatering and removal of environmental contaminants where present.

13.3 CONVENTIONAL SILICA APPLICATIONS SUITABLE FOR CCSM PURIFIED SILICA PRODUCT

Silica occurs commonly in nature as sandstone, silica sand, or quartzite. It can exist in an amorphous form (vitreous silica) or in a variety of crystalline forms. There are three crystalline forms of silica: quartz, tridymite, and cristobalite. A high purity grade of silica, fused silica (~ 99.4-99.9+% SiO_2) is produced by carbon arc, plasma arc; gas fired continual extrusion, or carbon electrode fusion. Fused silica is primarily used in the electronics industry (around 70% of the total market) where its good dielectric and insulating properties are exploited. Silica is a group IV metal oxide, which has good abrasion resistance, electrical insulation and high thermal stability and it is soluble only in hydrogen fluoride (HF) (AZO Materials, 2010). CCSM generally produces silica in the amorphous phase and small particle diameter that is highly desirable in the construction industry as a cement additive (Gronchi et al, 2004).

13.3.1 Applications

Silica is a widely used ceramic material both as a precursor to the fabrication of other ceramic products and as a material on its own. The most common applications are:

- Silicon production (ferrosilicon or silicon manganese) for steel making
- Fused silica for circuit boards
- Refractory materials such as of silica-refractory bricks
- Silica glass production
- Silica sand
- Silica pozzolans
- Filler material in paints, plastics, rubber, adhesives, putty, and sealants.
- Microsilica for ceramic matrix composite materials.

13.4 CONVENTIONAL MAGNESITE APPLICATIONS SUITABLE FOR CCSM PURIFIED PRODUCTS

About 98% of magnesite is converted to magnesia for conventional applications. Therefore, a limited number of applications are currently available for magnesite such as those for precipitated magnesium carbonate or agricultural applications. Magnesite is used to produce magnesium metal and basic refractory bricks. Magnesite is also used in flooring, fireproofing, fire-extinguishing compositions, cosmetics, dusting powder, and toothpaste. Other applications are as filler material, smoke suppressant in plastics, a reinforcing agent in neoprene rubber, drying agent, a laxative, and colour retention in foods. In addition, high purity magnesium carbonate is used as antacid and as an additive in table salt to keep it free flowing. Magnesium carbonate is also used in niche applications such as taxidermy for whitening skulls. It can be mixed with hydrogen peroxide to create a paste, which is then spread on the skull to give it a white finish or mixed with carbonate hydroxide is used as a clay in face masks. The main uses without calcination are:

- Magnesite or magnesium carbonate (precipitated)
  - Insulation, rubber
  - Paint pigments and Ink

  - Glass and ceramics
  - Chemistry
- Magnesite for agricultural application

13.4.1 Magnesite as a Building Material

A process for manufacturing a magnesium carbonate board that is useful as building material was patented in 1980. The method consists of forming an aqueous suspension with neutral magnesium carbonate, fibrous material, and active magnesia. This is followed by casting the resulting formed aqueous suspension onto a porous permeable carrier to form a layer of solids up to about 1,500g of solids per square meter and water content in the range 30-50% by weight per layer. Bulk materials are formed by laminating or building up a number of layers and pressing with heat curing at a temperature less than about 100° C in a relative humidity greater than 80%, forming magnesium carbonate board with a relatively high specific gravity of 0.78-1.15 (Nakajima and Miyata, 1980).

Recently, a spinoff company at Imperial College (London) namely Novacem claim to be making a carbon neutral cement material based on magnesium silicate materials. Novacem's cement composition contains 50-80% MgO with the rest comprising hydrated magnesium carbonates. The carbonates added modify the hydration of MgO and allow rapid development of strength even when no CO_2 is present. The material produced can be classified as a non-hydraulic binder, similar to lime putty or dry hydrate of lime ($CaOH_2$ powder) (Novacem, 2010).

13.5 CONVENTIONAL CALCITE APPLICATIONS

The focus of current analysis of CCSM process based on serpentines, therefore various conventional applications for calcite is discussed in the Appendix.

13.6 LOW-END APPLICATIONS

13.6.1 Agricultural Applications

Calcium and magnesium carbonates are used as a liming agent to buffer the acidity of manure-rich and/or clay-rich soils. A high amount of steel slag (graded from 4mm down) is now used for agricultural liming due to its high lime (CaO) content (40-45wt%).

13.6.2 Land reclamation

Creating new land from sea using both magnesium and calcium carbonates is another low tech-high volume application compared to use as filler. In addition, carbonates can be used to build dikes or dams with the aim to contain sweet water for agricultural use or to keep sea (saline) water out.

13.6.3 Precipitated Magnesium Carbonate (PMC)

PMC production processing includes calcination of carbonates (release of CO_2) followed by re-precipitation while PCC from CCSM can be produced directly by re-grinding minimising the CO_2 emissions. Chemical purity, particle size distribution, density and free flowing properties are fundamental to determine the performance in every application and the precipitated magnesium carbonate can be divided into two categories: pharmaceutical and technical grade (Solvay chemicals, 2010). Pharmaceutical magnesium carbonate possesses high purity, brightness and fineness of particles and is widely used in pharmaceutical, cosmetic and food applications:

- As laxative and gastric antacid or mineral supplement
- As mild abrasive ingredient in toothpastes
- As nutritional supplement and anti-caking agent
- As magnesium source in soft drinks
- In talcum powders giving moisture stability, fragrance retention and flow control
- As carrier in perfumes.

The carbonate for pharmaceutical applications should meet the following criteria (European Pharmacopoeia, 2005):

- CaO < 0.75%
- Assay (MgO) 40-45%
- Heavy metals < 20ppm
- Cl < 0.003%
- SO_4 < 0.001
- Iron < 400ppm
- Particle size ~ 0.45µm
- Specific surface $23m^2/g$

Alternatively, technical grade magnesium carbonate is used in the paper, plastic, rubber, and printing ink industries mainly as filler and it should have the following properties (Solvay chemicals, 2010):

- CaO < 1.1%
- Assay (MgO) 40-45%
- Cl < 0.07%
- SO_4 < 0.01
- Iron < 0.02%
- Particle size ~ 0.70µm
- Specific surface $22m^2/g$

13.6.4 Filtration and reclassification of hazardous wastes by decreasing the leaching of heavy metals

Considering the Hazardous Waste Regulations, Municipal solid waste and cement kiln dust are considered hazardous mainly because of their high levels of copper, zinc, or lead (>1,000mg/kg). In addition, cement kiln dust presents a significant Lead concentration and concentrations of antimony, arsenic, molybdenum, nickel, and selenium below 100mg/kg. Significantly, carbonation of the anhydrous powder results in the partial neutralisation of the pH of the leachates from about 12-13 to below 11.5, which is the limit to avoid their classification as a 'hazardous waste'. The regulatory limits for inert, stable non-reactive and hazardous landfills are reported in Table 17 (Gunning et al, 2010).

Overall, CCSM reactions appear to have a positive effect on the leaching of Pb, Zn, Cu and As whilst it has a negative effect on the leaching of Cd and Sb. Lead levels in the cement kiln dust after carbonation were reduced from hazardous to within stable non-reactive landfill limits. In addition, leaching of lead in MSW dramatically decreases after carbonation (Li et al, 2007). CCS by mineralisation reduced barium leaching to below inert levels for paper sludge incineration waste. Hazardous levels of chromium were leached from MSW and biomass waste but were effectively reduced to 'stable non-reactive' status by carbonation.

In addition, hazardous levels of sulphate were found in the biomass ash and cement kiln dust. When the overall leaching behaviour is considered, carbonation treatment facilitated the reclassification of several wastes. MSW, biomass, and wood waste were reclassified from hazardous to stable non-reactive hazardous wastes (Gunning at al, 2010).

Wastes such as foundry sludge and petroleum drill cuttings containing a mixture of organic compounds, heavy metals and water-soluble salts that were immobilized using carbonation technique based on Portland cement, lime and pozzolanic binders, in addition to a wide range of additives (Coz et al, 2004; Al-Ansary and Al-Tabbaa, 2007).

	Ba	Cl^- ($x10^3$)	Cr	Pb	Se	$SO4^{2-}$ ($x10^3$)
Inert limit	20	0.8	0.5	0.5	0.1	1
Stable non-reactive limit	100	15	10	10	0.5	20
Hazardous limit	300	25	70	50	7	50

Table 17: Leachate concentration limits in the UK landfills of some elements [Gunning et al, 2010]

13.7 POST-PROCESSING REQUIRED TO CONVERT THE CCSM PRODUCTS INTO POTENTIAL FINAL PRODUCTS

The previous sections of the report illustrate all the wide range of post-processing application that might be suitable for the mineralisation products. Among them, silica sand and high quality precipitates magnesium and calcium carbonate and grounded calcium carbonate are the most promising. The recovery of precious metals such as platinum and iron oxides can generate profit but only iron oxide will be treated here.

However, the quality of the CCSM products (Table 20) does not directly match that of commercial products and a set of processes need to be employed to meet the quality required. A series of different CCSM scenarios, from the simple option to landfilling the slurry to the recovery and purification of the totality of the products are illustrated below and will be considered to describe the post-processing technologies. The 4 cases are:

1. Mixed slurry from dry/wet CCSM processes that goes to landfill. It might be dewatered (wet slurry) and dumped wet or sent directly in sea wet for land reclamation after removing potential pollutants. Not much post-processing is required. Cheaper solution, no revenue
2. Mixed slurry is treated to recover iron oxide and/or precious metals and/or silica while the carbonates are sent to landfill because their purification is costly. Small revenue

3. All the products are recovered from mixed slurry, carbonates included, high costs, complex process, very expensive, revenue, might be not practicable
4. Multistep carbonation allows precipitating three different products: silica, carbonates, and iron oxide/precious metals. These three products can be separated by decantation. These products need to be industrially purified to meet the strict regulation for precipitated silica, PCC, PMC or to be used in the construction industry. Moderately expensive, high revenue. Flexibility, post-processing the marketable fraction of the CCSM product and landfilling the other fractions

For simplicity, the above scenarios can be separately analysed considering the processing of silica, carbonates and iron oxide as follow.

13.7.1 Silica Processing

Silica sand processing is the set of process involved in the production of silica where the main contaminants to be removed are iron oxide, alumina, and titania. In addition, Na_2O, CaO, and K_2O might need to be separated for the silica sand. Iron oxide with a consistent content is allowed in silica used for the production of amber glass containers. The value per tonne of silica is low and to be competitive the production site cannot be located more than 30-40 miles from the final use site. However, a slightly complex and costly refining process of poor quality sand is often preferred than long distance transportation of good quality sand. The process starts with a washing stage to remove the silt followed by attrition scrubbing if the silt is more difficult to remove because strongly bonded to the silica grains. This step has typical capital costs of 1,000-2,000$/tonne per hour. The next step, namely de-sliming removes the particles lower than 100µm using cyclones (where 3wt% < 10µm) or hydrosizers that are hindered setting devices. De-sliming capital costs are about $1,000/tonne/h for high feed rates. Hydrosizers or screens are typically used to size high quality sand at the wanted particle size range between 100 and 500µm.

Gravity separation is carried out to concentrate the heavy metals in a concentrate (90% heavy metals) and it consists in a multistage process (rougher, scavenger, cleaner, recleaner, finisher). It requires between 0.2 and 8 kWh/tonne and a capital costs of $1000/tonne/h.

Flotation is also used to remove iron oxides in glass sand. This process last for only 5 minutes and is carried out in multi flotation cells of 3 x $8m^3$ each. Capital costs, operational costs, and power consumption of flotation in sand processing are 6,000-8,000$/tonne/h, 1-1.25$/tonne, and 10 kW/tonne, respectively.

Silica drying is carried out using fluidised bed dryers (FBD) and represents the most expensive unit operation in the silica processing. Rotary dryers were used in the past but abandoned due to low fuel efficiency (9L of fuel oil consumed per tonne) compared to FBD that consumes only about 5L/tonne.

The earth roll magnetic (ERM) separators are currently used to separate the iron bearing minerals in the silica industry. ERM separators can treat between 3 and 7 tph/meter depending on the purity of feed and characteristics wanted of product, with capital costs of 6,000-10,000$/tonne/h. CCSM might be able to produce a different range of silica products tuning the particle size of starting serpentine and this step would not be required in the post-processing. For example, all silica sand for glass, textile, and amorphous microsilica (< 2µm) could be produced if the serpentine is ground to <300µm. Costs and energy required for grinding is extensively treated in the pre-processing section of this report. All the processing units above described can be combined in different way to achieve the desired end material (Outotec, 2010).

When the starting material is slurry with mixed carbonates, iron oxide and silica, the process to obtain final pure products (silica sand) is much complex and costly and to be competitive would require a local use of the premium products to minimise the transport costs. Carbonates represent about 50-60wt% of the slurry and multi gravity separations and flotation need to be employed to separate the three products as can be seen in Figure 40.

The production of high-grade silica sand from a CCSM slurry would be costly and after the vary concentration passages, several magnetic separation are required to produce a product with iron content less than 0.05%. Dry magnetic separation with low intensity can be used to separate magnetite (Fe_3O_4). High intensity magnetic separation can be used for ilmenite (TiO_2FeO). The finishing can be carried out with rare earth magnetic drums followed by rare earth magnetic rolls (from clearing the circuit) or electrostatic separation (Wills, 2006).

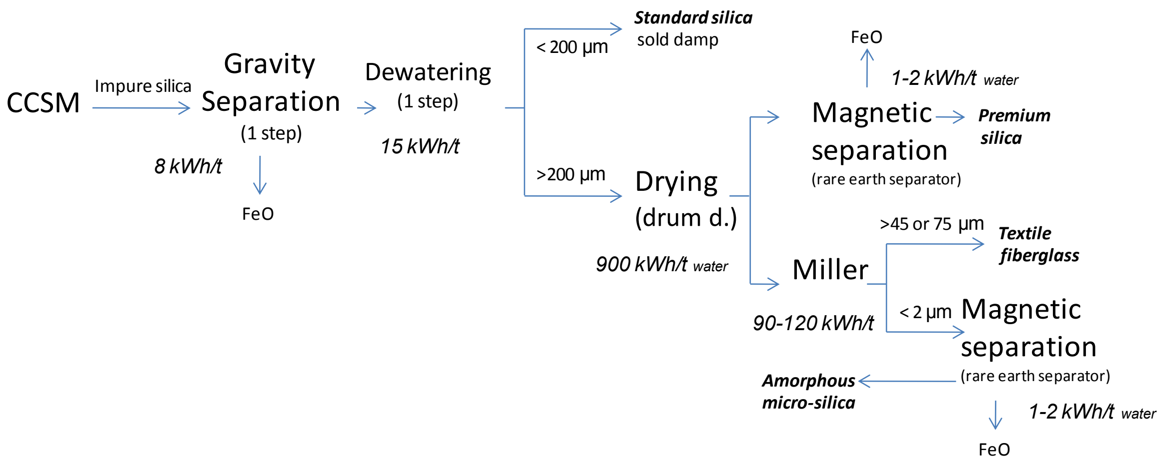


Figure 39 Processing of silica produced in a multiphase mineralisation process [Outotec, 2010]

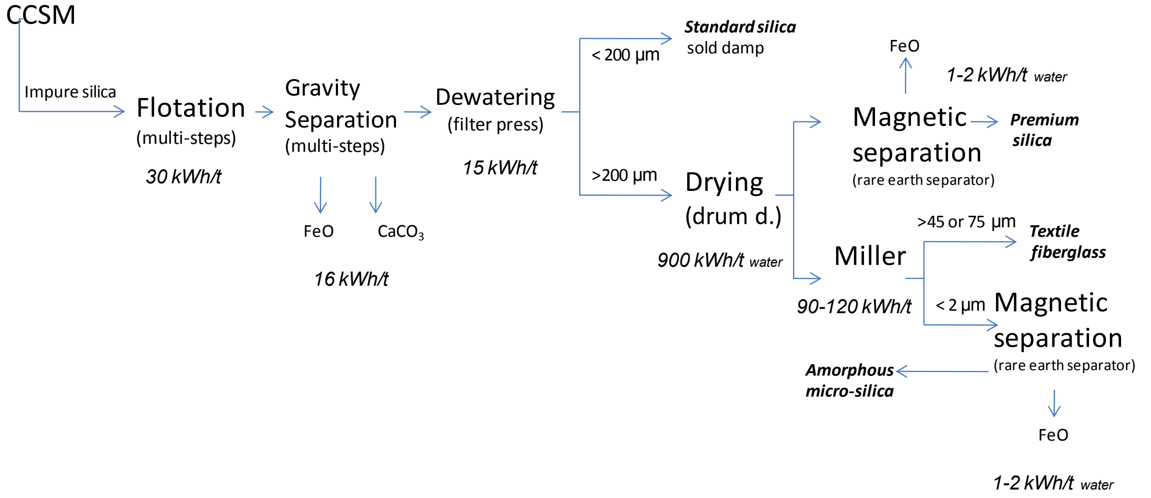


Figure 40 Slurry product processing for the production of silica sand [Outotec, 2010]

13.7.2 Ground and Precipitated Carbonates processing

Separation of carbonates from silicates can be achieved by using flotation or/and hydrocyclones in relation with the size particle difference between silica and calcite/magnesite. The liberation of quartz from calcite occurs at very fine size and CCSM technologies that work at particle size lower than 200µm can favour this separation process (Viswanathan et al, 1980). Flotation is also used to purify low grade magnesite coexisting with dolomite where reverse flotation is used to remove silicate minerals and positive flotation to concentrate magnesite. In this process, silica content was decreased from about 18% to 0.2% (Li et al, 2010). This technology might be used in CCSM post-processing.

CCSM with production of separate product streams (silica, carbonates and iron oxide) results very similar to the downward part of a typical industrial processing and a purification plant mainly to separate iron oxide (magnetic separation) can be configured following the strong experiences of companies such as Westfalia (Westfalia, 2010). In addition, the most expensive operations such as crushing and calcination would not be required and none CO_2 would be released during the process. New advanced decanters are available to separate solid for liquids by different particle size and liquid densities to meet the stringent requirements for high-quality PCC. Additional multi-treatments (flotation, gravity separation, magnetic separation) are needed if the CCSM produces single slurry (Westfalia, 2010).

Figure 41 and Figure 42 illustrate the post-processing that might be required to produce high-end products from a multiphase (producing 3 separated products) and a single phase (producing a mixed slurry) CCSM, respectively.

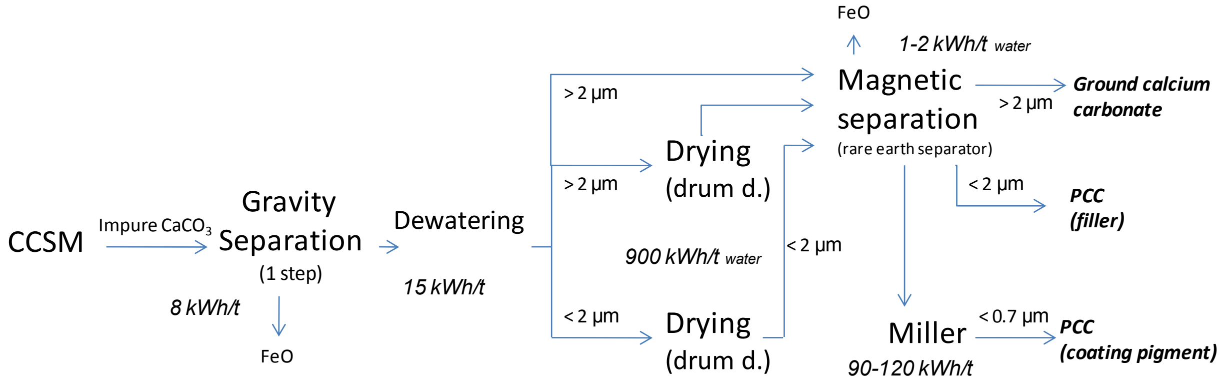


Figure 41 Processing of carbonates produced in a multiphase mineralisation process [Outotec, 2010]

A method for producing a PCC with about 5-75% particle size < 2µm by further grinding a ground calcium carbonate feed with top particle size of 50 µm has been proposed in a recent patent (Kostuch et al, 2010). This method can be used to estimate the energy required to grind carbonates generated by CCSM technology due to the similar starting particle size. Ground calcium carbonate slurry can mixed with additional water to lower the solid content to 20-35wt% solids and grinded using low solids grinding (Kostuch et al, 2010). During the past decade, due to the development of paper-making industry, the annual output of GCC has been increased by at least 10%, causing the rapid development of the corresponding technology for grinding calcium carbonate into ultra-fine products, in particular, large stirred bead mills for wet ultra-fine grinding with mill capacity of 0.3t/h and specific energy input of 250kWh/tonne in 1995, 0.5t/h and 180 kWh/tonne in 2003, to reach 2.0t/h and 90kWh/tonne in 2005 (Zheng, 2007).

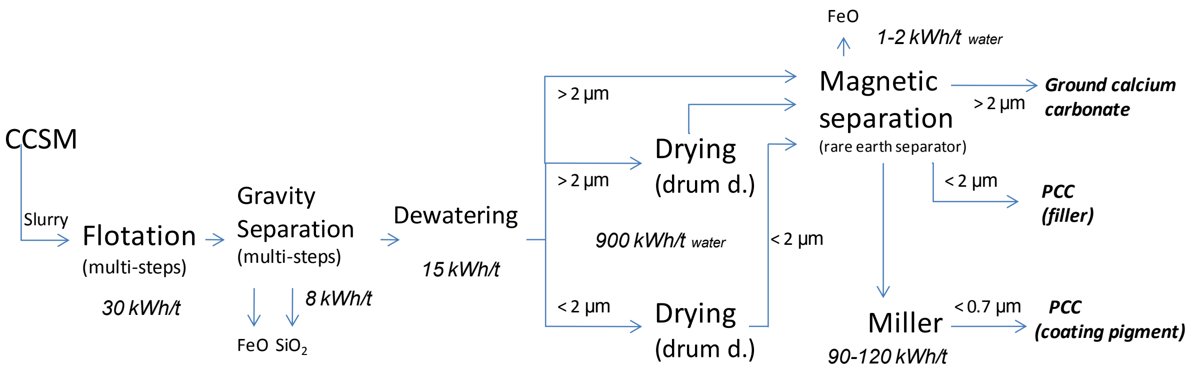


Figure 42 Processing of slurry for high-grade carbonates production [Outotec, 2010]

13.7.3 Iron Oxide processing

CCSM technology can produce mixed slurries with about 5% iron oxides or a separated product stream with about 40% iron oxides. Typically, the mineral industry requires a mineral content higher than 4-5% to justify the mineral ore processing (Zemskova S.M, 2010). Therefore, CCSM products can be consider attractive for the recovery of iron oxides. Currently, the waste from steel and iron industries is mainly recycled as blast furnace and basic oxygen furnaces feedstock, in red and glass ceramics and in minor grade as iron oxide for pigments (Shen et al, 2010). A typical iron ore pellet has iron, silica, and lime content of 65%, 4.5%, and 0.7%, respectively while 2-6% iron is the content of slurry produced by CCSM. A much closer iron content of 40-50% can be obtained in a multistage mineralisation process such as the Åbo A. and UoN processes.

Therefore, a single stage process that produces slurry required a gravity separation stage (e.g. carried out by multistep by spirals (rougher, scavenger, cleaner, recleaner, and finisher) where the heavy metal is separated from the silicate residue into a concentrated iron slag. This process consumes between 0.2 and 8kWh/tonne.

CCSM technology can precipitate iron oxides as well as pigments (Shen et al, 2010). However, the purification of the iron oxide to meet the market specifications require a post-processing much more complex than that needed to feed a blast furnace or a steel work. Figure 43 illustrates the post-processing required to produce feedstock for iron and steel production and pigments from CCSM products.

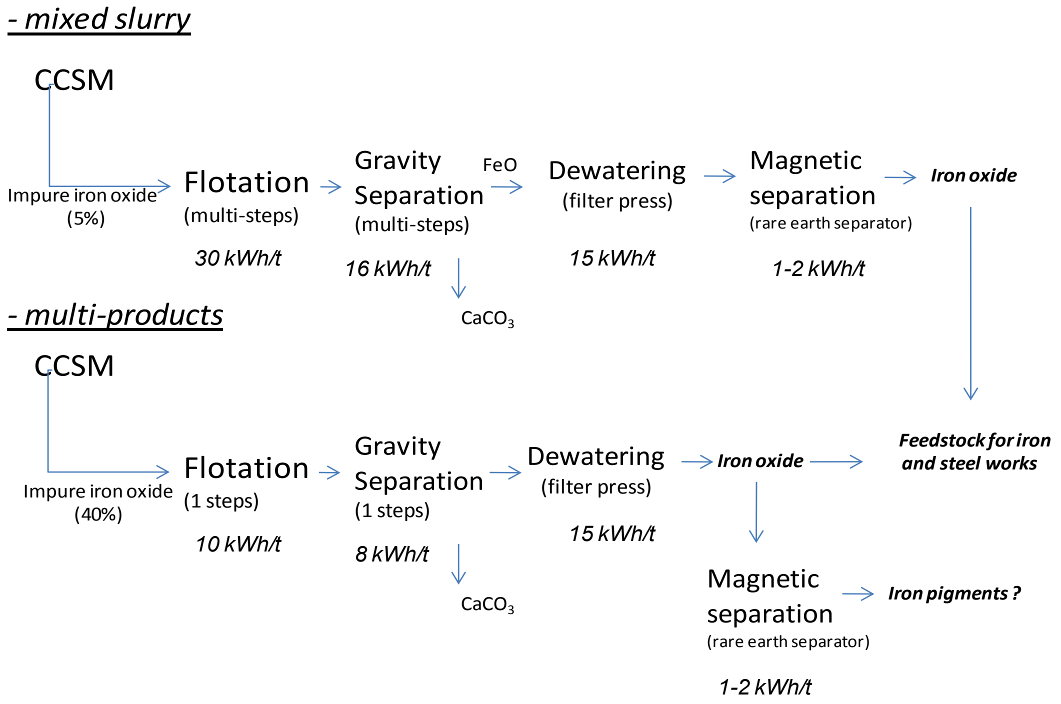


Figure 43 Processing of CCSM products for iron oxide production [Outotec, 2010]

13.8 ENERGY AND ECONOMICAL ROUGH ESTIMATION

The technologies typically used in mineral processing (e.g. silica sand and GMC/PMC) can be applied to post-process the CCSM products. A complex set of technologies would be required to treat a mixed slurry minimising or removing the advantages of a partial separation/purification treatment that occur in a multiphase mineralisation process able to separate silica form carbonates and iron oxides. Differently, the 'multi-products' mineralisation technologies can be able to provide products with properties much similar to those of final commercial products and would require less complex post-processing that can be competitive with raw materials processing.

Dry products do not require a drying process but the majority of separation/concentration processes are carried out in wet conditions. Therefore, dry multi-products might be economical versus wet ones if final drying is required and none if not (e.g. PCC as filler is sold damp), while dry slurries would require similar treatment of wet slurries. The energy required per tonne of material treated, the costs per tonne of CO_2 sequestered and the CO_2 emission during the post-processing (transport were not included in both costs and emissions) are summarised in Tables 24, 25 and 26 for silica, iron oxide and ground/precipitated calcium carbonate, respectively.

The energy required to process all the slurry single-step CCSM products varies from 140kWh/tonne to 470kWh/tonne of material treated, while only between 63kWh/tonne and 377kWh/tonne of material treated are necessary for a multistage process. The low value is related to the production of low-end products (standard silica sand, feedstock for iron and steel works and ground calcium carbonate) while the high values are related to the production of high-end products (micro-silica, iron pigments and PMC). However, the values decrease to 93-262kWh/tonne and 37-192kWh/tonne if the calcium carbonate stream is landfilled. The production of low-end products using multistep processes seems particularly attractive under the energy point of view. About 10kWh/tonne are needed if only silica is produced by multistage processes and 30kWh/tonne when iron oxide for steel works is produced by the same technology.

The costs were estimated considering the following mass balance:

$$3.4\text{t serpentine} + 1\text{t } CO_2 \rightarrow 2.6\text{t } MgCO_3 + 1.5\text{t } SiO_2 + 0.5\text{t } Fe_2O_3$$

It was also assumed that PMC could be sold as PCC for fillers and pigments. The cost to landfill the totality of the products (excluding the chemicals not recyclable) was estimated in £9-10 while the cost of post-processing all the materials to low-end products (standard silica sand, feedstock for iron and steel works and ground calcium carbonate) was estimated in £17 and £7 per tonne of CO_2 sequestered for slurry single-step and multistep technologies, respectively. The estimated cost rose to £70/tonne CO_2 and £60/tonne CO_2 if micro-silica, iron pigments and PCC are produced by slurry and multistep technology, respectively. The production of low-end products seems particularly competitive with landfilling and iron oxide for steel production and pigments might be economical. The high-end products such as micro-silica and PCC (it is assumed that PMC can be sold for the same propose) require high costs even if their selling price above 200-300£/tonne might render economical the CCSM products. Between 4 and 140kg of CO_2 are emitted during the post-processing operations where the high value is emitted if microsilica and PMC is produced. The production of PMC from silicate rocks can decrease the emission of carbon dioxide of its processing. The traditional production method include calcination of lime in kilns at high temperatures (900°C) carrying the release of 0.5 tonne CO_2 every tonne of PCC produced plus the fuel consumed during the heating process, rending the overall process carbon positive. The release of 0.5 tonne CO_2 would be avoided if the PMC were produced from silicate rocks like in the CCSM process converting the PMC production into a carbon negative technology (Teir et al, 2005).

			Slurry single stage mineralisation			Multi-phase mineralisation		
Post-processing		**Landfill**	**Standard silica**	**Premium silica**	**Micro-silica**	**Standard silica**	**Premium silica**	**Micro-silica**
	kWh/t	kWh/t	kWh/t	kWh/t	kWh/t	kWh/t	kWh/t	kWh/t
[1] Load & Haul	1	0	1	1	1	1	1	1
[1,2] Flotation	7-10	0	20	20	30	0	0	0
[3] Gravity separation	0.2-8	0	16	16	16	8	8	8
[4] Magnetic separation	0.4-1	0	0	1	4	0	1	2
[5] Water pumping	3	0	1	1	1	1	1	1
[6] Dewatering	15-350*	0	0	15	53	0	15	53
[7] Drying	800-1300**	0	0	0	0	0	0	0
[8] Milling	75-90***	0	0	0	90	0	0	90
[9] Agglomeration	25-35**	0	0	0	0	0	0	0
Total			38	54	195	10	26	155
[10] Cost (£)	(£/kwh)^ 0.08		3	4	16	1	2	12
[10] Cost (£/t CO)	(t SiO_2) 1.5	3	5	6	23	1	3	19
[11] kg CO_2/t product	^^ 0.263		15	21	77	4	10	61

* 350 kWh/t for a complete drying; ** required only in particular cases; *** required only for PCC and micro-silica; ^ using LPG;

^^ CO2 emitted by a diesel source (kg x kWh)

Table 18 Estimation of energy, cost, and CO_2 emission for silica production [1 CRCORE, 2010; 2 Stassen, 1991; 3 Bilitewski et al, 1996; 4 Hardy-Smith, 1983; 5 Fuerstenau M.C et al, 2003; 6 EIMCO, 2010; 7 Mujunder A.S, 2007; 8 Zheng, 2007; 9 Outotec, 2010; 10 Biomass Energy Centre, 2010; 11 DEFRA. 2009]

			Slurry single stage mineralisation		Multi-phase mineralisation	
Post-processing		**Landfill**	**iron oxides** for steel works	**Iron oxides** for pigments	**iron oxides** for steel works	**Iron oxides** for pigments
	kWh/t	kWh/t	kWh/t	kWh/t	kWh/t	kWh/t
[1] Load & Haul	1	0	1	1	1	1
[1,2] Flotation	7-10	0	20	30	0	10
[3] Gravity separation	0.2-8	0	16	16	8	8
[4] Magnetic separation	0.4-1	0	2	4	1	2
[5] Water pumping	3	0	1	1	1	1
[6] Dewatering	15-350*	0	15	15	15	15
[7] Drying	800-1300**	0	0	0	0	0
[8] Milling	75-90***	0	0	0	0	0
[9] Agglomeration	25-35**	0	0	0	0	0
Total			55	67	26	37
[10] Cost (£)	(£/kwh)^ 0.08		4	5	2	3
[10] Cost (£/t CO)	(t Fe_2O_3) 0.5	1	2	3	1	1
[11] kg CO_2/t product	^^ 0.263		7	9	3	5

* 350 kWh/t for a complete drying; ** required only in particular cases; *** required only for PCC and micro-silica; ^ using LPG;

^^ CO2 emitted by a diesel source (kg x kWh)

Table 19 Estimation of energy, cost, and CO_2 emission for iron oxide production [1 CRCORE, 2010; 2 Stassen, 1991; 3 Bilitewski et al, 1996; 4 Hardy-Smith, 1983; 5 Fuerstenau M.C et al, 2003; 6 EIMCO, 2010; 7 Mujunder A.S, 2007; 8 Zheng, 2007; 9 Outotec, 2010; 10 Biomass Energy Centre, 2010; 11 DEFRA. 2009]

			Slurry single stage mineralisation			Multi-phase mineralisation		
Post-processing		**Landfill**	**GMC**	**PMC (filler)**	**PMC (pigment)**	**GCC**	**PMC (filler)**	**PMC (pigment)**
	kWh/t	kWh/t	kWh/t	kWh/t	kWh/t	kWh/t	kWh/t	kWh/t
[1] Load & Haul	1	0	1	1	1	1	1	1
[1,2] Flotation	7-10	0	20	20	20	0	0	0
[3] Gravity separation	0.2-8	0	8	8	8	8	8	8
[4] Magnetic separation	0.4-1	0	2	4	4	1	2	2
[5] Water pumping	3	0	1	1	1	1	1	1
[6] Dewatering	15-350*	0	15	53	53	15	53	53
[7] Drying	800-1300**	0	0	0	0	0	0	0
[8] Milling	75-90***	0	0	90	120	0	90	120
[9] Agglomeration	25-35**	0	0	0	0	0	0	0
Total			47	177	207	26	155	185
[10] Cost (£)	(£/kwh)^ 0.08		4	14	17	2	12	15
[10] Cost (£/t CO)	(t $MgCO_3$) 2.6	5.2	10	37	43	5	32	38
[11] kg CO_2/t product	^^ 0.263		32	121	142	18	106	127

* 350 kWh/t for a complete drying; ** required only in particular cases; *** required only for PCC and micro-silica; ^ using LPG;

^^ CO2 emitted by a diesel source (kg x kWh)

Table 20 Estimation of energy, cost, and CO_2 emission for GMC and PMC production [1 CRCORE, 2010; 2 Stassen, 1991; 3 Bilitewski et al, 1996; 4 Hardy-Smith, 1983; 5 Fuerstenau M.C et al, 2003; 6 EIMCO, 2010; 7 Mujunder A.S, 2007; 8 Zheng, 2007; 9 Outotec, 2010; 10 Biomass Energy Centre, 2010; 11 DEFRA. 2009]

The above rough energy assessment indicates that CCSM towards sellable products might be economical viable and that the post-processing to produce silica sand and impure iron oxide as feedstock for steel and iron works will not be high energy intensive and costly. Differently, high-end products such as micro-silica and PCC require much more energy in particular for the particles size reduction step (160-210kWh/tonne material). Further investigations are needed to establish a more accurate energy and economic assessment and to compare these post-processing to the traditional production processes.

Micro-silica and PCC might be produced directly by screening the large volumes of CCSM products avoiding the energy intensive milling step. In this case, only 60-100kWh/tonne and 60-90kWh/tonne would be required to produce micro-silica and PCC, respectively, where the low values can be achieved using a multistep process. For example, micro amorphous silica (1-100nm) was produced by carbonation of calcium silicates under mild conditions (20bar, 20°C, 1:16 S/W ratio; 1hr dissolution; 2hrs treatment with sodium aluminate solution (1M NaOH, 0.01M Al); centrifugation and drying for 4 hrs (110°C)) without any milling stage. The product had 97% Silica, 0.6% alumina, 1.4% lime, 1.3% NaOH, and 0.01% iron oxide (Gronchi et al, 2004). Therefore, the carbonation of large rocks volumes might be able to produce enough silica and calcium carbonate with properties similar to those of microsilica and PCC.

13.9 MINERALISATION PRODUCTS MARKET

An approximation of the current and recent market size and market value for the basic material commodities that could be produced from CCS mineralisation products is presented in the following section. *The international non-EU, EU and UK market sizes are summarised, and approximate commodity market values are given (or converted to) in Pounds Sterling per tonne at current exchange rates which, at the time of writing, were taken as* ***\$1 US = £0.64****, *and* ***Euro 1 = £0.85***** *on 21st September, 2010.* Assuming that each mineral phase can be extracted from the CCSM product with a purity not less than 90%, it may be possible to enter the market for supplying these basic material commodities (e.g. silica, carbonates) which could be used in one or more of the post-processing routes identified in the previous sections. The added value of materials post-processing is unclear at this stage. It could require a capital investment for on-site manufacturing or additional purification or refinement.

13.9.1 Global Silica Market (112 Mt global production, ~£2.5bn* market value)

Industrial sand and gravel, often called "silica sand" or "quartz sand," includes sands and gravels with above 90% silicon dioxide (SiO_2) content. About 120Mt of quartz and silica were produced worldwide in 2008 while the production dropped to 112Mt in 2009. The silica sand output in the UK (5.6Mt in 2009) is small compared to the total production of construction sand (42Mt in 2007) but enough to guarantee self-sufficiency in the UK. Silica sand is, however, a scarce resource in the UK with a total 31Mt of reserves estimated in 2007. The average value of U.S. industrial sand and gravel was £20/tonne* in 2008. The average price for sand ranged from £6/tonne* for other whole grain silica to £84/*t for ground foundry sand. The silica sand market in US was valued at £0.6B* in 2007 (for 30Mt consumed), while the value in the UK was estimated at £67M in the same year. Globally, a £2.2B* market can be estimated from the US market, considering that 30Mt were valued £0.6B*. Furthermore, the glass industry, which is the main consumer of silica sand, generated about 2Mt of glass containers valued at £524M* (US Geological Survey, 2010; British Geological Survey, 2009).

World Markets for precipitated silica and sodium aluminium silicates was worth about £1.3B* in 2008. These materials were mainly used as fillers and performance additives across a wide range of products, including fuel-efficient tyres, rubber goods, footwear, dentifrice, food/feed, paper, plastics, and paint. World demand for speciality silica including precipitated silica, fumed silica, silica gel and silica sol, is predicted to rise at a rate of 6.3%/year to 2.7Mt in 2014. This growth will be driven by a rise in world manufacturing activity, particularly in key silica markets such as tires, rubber, chemicals, and agricultural products. The market forecast for precipitated silica alone is 1.5Mt/yr for 2010, with the European Union representing 31% of world demand in 2003. A value of £640/tonne* is estimated for a potential global market value of £0.9M*. The world demand for precipitated silica as a reinforcing filler in the rubber industry accounts for 70% of total precipitated silica demand in 2009 and will most likely remain the leading product type (Notch Consulting Group, 2010; Reportlinker Adds, 2010).

13.9.2 Magnesium Carbonate (8.5Mt global production)

Magnesite is fully converted in magnesium oxide by calcination and precipitated magnesium carbonate (PMG) does not appear among the main traded minerals. The global extraction of $MgCO_3$ is of 8.5Mt of which (Industrial Minerals, c, 2010):

- 6.5Mt are 'dead burned' (heated to 1450°C) to produce refractory materials,
- 1.5Mt are calcined (heated at 800-1000°C) and used to produce refractory materials, although around 70% is used in iron and steel making.
- 0.64Mt are fused (heated to 3000°C) and used for refractory and electrical applications.

About 50% of the global production of $MgCO_3$ is in China with a further 12% produced in Russia. In Europe, $MgCO_3$ is mainly extracted in Slovakia (130Mt of reserves), Greece, Austria, and Spain producing 15% of the global demand (Kramer D.A, 2009). About 85% of the global resource is currently extracted from carbonate rock quarries and in the form of coarse particles, whilst the remaining 15% is extracted from ultramafic rocks (Industrial Minerals, c, 2010). In 2002, more than half of U.S. magnesium compounds were used in refractory materials, as for example in the linings of Iron and steel furnaces; thus, the magnesite-mining segment of the industry is strongly affected by economic trends in the Iron and steel industry. Magnesium compounds are also used in agricultural, chemical, environmental, and industrial capacities. (Reference for business, 2010; Mineral Zone, 2010)

13.9.3 Iron oxide (1.4Mt global production, £0.7bn* market value)

Natural iron oxides include a combination of one or more ferrous or ferric oxides, and impurities, such as manganese and clay. Synthetic iron oxides can be produced in various ways, including thermal decomposition of iron salts, such as precipitation to produce yellows, reds, browns, and blacks. World production of iron oxide pigments (natural and synthetic) was estimated to be 1.4Mt and valued at £0.7B* in 2006. China was the world's leading producer of natural and synthetic iron oxide pigments in 2006 with 49% of the total, whilst Europe produced 25% with Germany accounting for 69% of European production. The average annual production cost in the USA ranged from £137/tonne* to £147/tonne* in 2008 (Virta R.L et al, 2010; Raymond W, 2008).

13.10 SUMMARY OF THE POTENTIAL USES OF CARBONATED ROCKS AND WASTE MATERIALS

A wide number of applications have been identified in this review where the non-calcination routes for primary-sourced carbonate and silica powders were described. Table 21 shows the overall application available subdivided between low-end and high-end carbonates applications and silica applications. Low-end applications include land reclamation and waste reclassification while among high value application micro-silica has been identified as the most promising. Chemical purity, particle size and distribution, density and free flowing properties are fundamental to determine the performance in the high-end applications. These properties change in bases at the application considered as can be seen in Table 22 and Table 23. Therefore, products with high value will require more sophisticated processing including drying and will lead to large cost penalties. Land reclamation may allow for transport and grinding synergies representing at this stage of the programme the most viable opportunity.

The exact CCSM technology chosen will play a very important role on the available post-processing routes and accessible markets due to the purity of the resultant materials. Also, the flexibility of the CCSM processes that guarantee both the production of high volume/low value or low volume/high value products in function of the market is critical for the development and commercialisation of the accelerated carbonation technology under the post processing point of view.

The post-processing that the production of silica, PMC, and feedstock for iron and steel works would require was investigated. A separated impure silica stream from a multistep CCSM process would require similar treatment used in traditional silica sand processing that involves removal of contaminants such as iron oxide, alumina and titania. This might be economic even considering that a slightly complex and costly refining process of poor quality sand is often preferred than long distance transportation (> 30-40 miles) of good quality sand. Differently, a single-step CCSM technology would need a much complex and costly processing (flotation, gravity separation magnetic separation in multistage) to separate carbonates and other contaminants from the silica stream. Multistage CCSM post-processing results very similar to the downward part of a typical industrial processing (the energy intensive crushing and calcination stage will not be required) and a purification plant to separate iron oxide are currently available. Additional multi-treatments (flotation, gravity separation, magnetic separation) are needed if the CCSM produces single slurries. An iron content of 40-50% can be obtained in a multistage mineralisation process such as the Åbo A. and UoN processes while 2-6% iron is the content of slurry produced by CCSM. A typical iron ore pellet has iron, silica, and lime content of 65%, 4.5%, and 0.7%, respectively and it could be easily produced from a multistage CCSM iron oxide stream.

The current global market for the raw commodities that could be produced by rock and/or industrial waste/by-product mineralisation is valued at about £2.9B. Therefore, it appears that if the CCSM process were able to produce significant quantities of silica with ‘sufficient’ purity (e.g. precipitated silica), in addition to a small amount of iron oxides and PCC, the post-processing route would be able to generate revenue/profit whilst negating the costs associated with transportation and landfill taxation. In particular, silica sand is considered a scarce resource in the UK whilst the global calcium carbonate market is growing rapidly. However, the global deployment of CCSM technology will produce large volumes of products that can easily flood the market and erode the operation margins.

The rough estimation of the post-processing costs shown in Table 24 indicates that the post-processing of multistage CCSM processes to low-end products seems competitive with landfilling while post-processing towards high-end products might present a high cost between 60 and 70 £/tonne CO_2 (±20£/tonne CO_2). However, micro-silica and PCC have selling price above 200-300£/tonne that might render economical the CCSM products. Therefore, further investigations are needed to establish the technical and economic feasibility of this pathway.

Carbonates low-end applications	Carbonates high-end applications	Silica applications
Construction industry	***Hazardous waste reclassification***	***Silicate glasses***
aggregate	***Contaminated land remediation***	***Ceramics***
cement voids filler	***Chemical applications***	***Silicon for semiconductors***
feedstock for PC	***Gastric antiacid***	***Circuit boards (filler)***
cement additive	***CO_2 sorbents***	***Refractory materials***
$MgCO_3$ boards for construction	***Fillers (PCC, PMC)***	***Sand***
Agricultural applications	***High velocity sprayed coatings***	*ceramic grade*
liming agent	***Porous filtration coatings***	*foundry grade*
soil amendment in farms		*refractory grade*
Land reclamation		*flux sand*
Stabilisers		***Filler material (paint, plastic, rubber, etc.)***
		Microsilica (high quality pozzolan for use with cements and concrete)

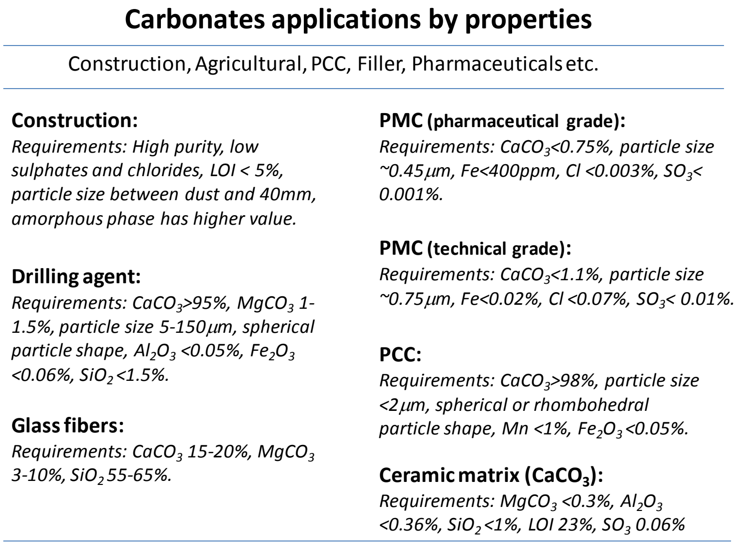
Table 21 Summary of the possible CCSM products applications. [Copyright University of Nottingham]

Conventional Silica Applications by properties

Building material, Refractory material, Circuit boards, Filler, Semiconductors

Silicon production:	Sand:
Most silicon is produced as a ferroalloy either ferrosilicon or silicon manganese, which is used exclusively in steel making. Silicon, as ferroalloy, is the most important deoxidiser in steel making. *Feedstock for silicon production has SiO_2 >98.5-99%, Fe_2O_3 <0.1% and Al_2O_3 <0.15%.*	• Ceramic grade sand *is less than 75μm and has a silica content above 97.5%, impurities include <0.55% Al_2O_3 and <0.2 Fe_2O_3.* • Foundry sand is *produced at particle size of less than 75μm. It has a silica content of 98% with limits placed upon on the amounts of magnesia (MgO) and lime (CaO) present.* • Refractory grade is produced for the manufacture of refractory materials which can be slightly *lower in purity (>95%SiO_2).* • Flux sand for iron and steel making *SiO_2 >90%.*

Table 22 Summary of the properties required for the different silica applications [Azo Materials, 2010]



Carbonates applications by properties

Construction, Agricultural, PCC, Filler, Pharmaceuticals etc.

Construction:
Requirements: High purity, low sulphates and chlorides, LOI < 5%, particle size between dust and 40mm, amorphous phase has higher value.

Drilling agent:
Requirements: $CaCO_3$*>95%,* $MgCO_3$ *1-1.5%, particle size 5-150μm, spherical particle shape,* Al_2O_3 *<0.05%,* Fe_2O_3 *<0.06%,* SiO_2 *<1.5%.*

Glass fibers:
Requirements: $CaCO_3$ *15-20%,* $MgCO_3$ *3-10%,* SiO_2 *55-65%.*

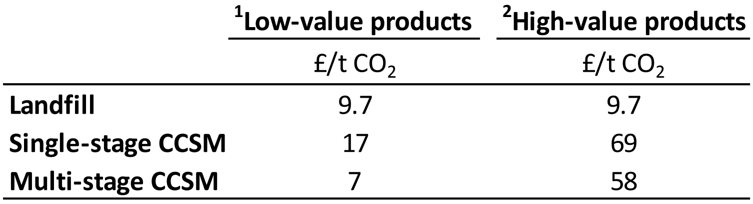
PMC (pharmaceutical grade):
Requirements: $CaCO_3$*<0.75%, particle size ~0.45μm, Fe<400ppm, Cl <0.003%,* SO_3*< 0.001%.*

PMC (technical grade):
Requirements: $CaCO_3$*<1.1%, particle size ~0.75μm, Fe<0.02%, Cl <0.07%,* SO_3*< 0.01%.*

PCC:
Requirements: $CaCO_3$*>98%, particle size <2μm, spherical or rhombohedral particle shape, Mn <1%,* Fe_2O_3 *<0.05%.*

Ceramic matrix ($CaCO_3$):
Requirements: $MgCO_3$ *<0.3%,* Al_2O_3 *<0.36%,* SiO_2 *<1%, LOI 23%,* SO_3 *0.06%*

Table 23 Summary of the properties required for the conventional carbonates applications [Solvay chemicals, 2010; Aristocrat holding, 2010; European Pharmacopoeia, 2005]



	[1]Low-value products	[2]High-value products
	£/t CO_2	£/t CO_2
Landfill	9.7	9.7
Single-stage CCSM	17	69
Multi-stage CCSM	7	58

Table 24 Rough estimated CCSM post-processing costs (transport and chemicals excluded) [Industrial Mineral prices, b, 2010; USGS, 2010; Cardero, 2004; Virta et al, 2010]. [1] standard silica sand, feedstock for iron and steel works and ground calcium carbonate; [2] micro-silica, iron pigments and PCC.

14 Identified CCSM System Technologies

This section of the report gives a description and comparative assessment of CO_2 mineralization processes. Until few years ago, the challenges of CCSM resulted in a limited interest for the technology outside academia and laboratory environments.

An important recognized feature that gives CCSM an advantage is that in principle the method can operate on flue gases (or CO_2 containing process gases in general) directly, without a pre-separation of CO_2. A survey of the published literature identified 25 CCSM technologies. These were evaluated against the criteria identified earlier including TRL status. Note that not all cases deal with complete processes; sometimes only one process step is described, or only a partial assessment was made. The data shows that CCSM processes have net CO_2 reduction as long as energy requirements stay significantly below 1.5kWh/kg or 1,500kWh/tonne, and the assessment shows that at least several processes have the potential to fix CO_2 at a similar overall energy requirement. The CO_2 fixation efficiency is of the order of 60-80% for the most processes for which experimental tests have been done. Since a number of processes are new and lack evidence of what is feasible, further experiments to generate complete data sets should be made to ascertain claims. It is clear that further applied research is required to develop the promising processes identified here into commercially executable mineral carbonation process that works at industrial scales and is complete and permanent.

14.1 OVERVIEW

Twenty years of R&D work since 1990 has produced many promising CCSM systems although none are commercially viable for global application yet. Even so, mineral resources and several other well-documented advantages such as scalability, applicability to regions without geologic storage capacity, and the inherent stability of the products of reaction support the ongoing work.

The main challenges initially encountered were:

- Process energy economics,
- Chemical reaction rates
- Handling rather large amounts of solid material

These challenges resulted in limited interest for the method outside academia and laboratory environments – until about six years ago.[2] As illustrated by Figure 44, several patents are currently granted each year. These add valuable information to the existing scientific literature while indicating that several features or complete processes may result to large-scale application of CCSM within, say, a decade. This presents the possibility of offering CCS at a reasonable cost or in some fortunate cases with economic benefit.

The options with potential for "quick success" (offering offer a financial profit rather than minimised costs) have been amongst the first to be explored as is demonstrated by the

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[2] Much of the current attention for CCSM is certainly the result of the fact that the deployment of CCS that involves underground sequestration has lost much of its momentum, with a total storage rate of around 7 Mt CO_2/a in a handful demonstration-scale projects for quite a few years already.

technologies described later in this section. Note, however, that much of what is patented appears to challenge the laws of physics, chemistry, or sound reasoning in general. Instead, this submits much of what is patented to the forces of market economies and risk capital investment. In those few cases where a process unit of significant size has been built and put into use, many useful data has been generated.

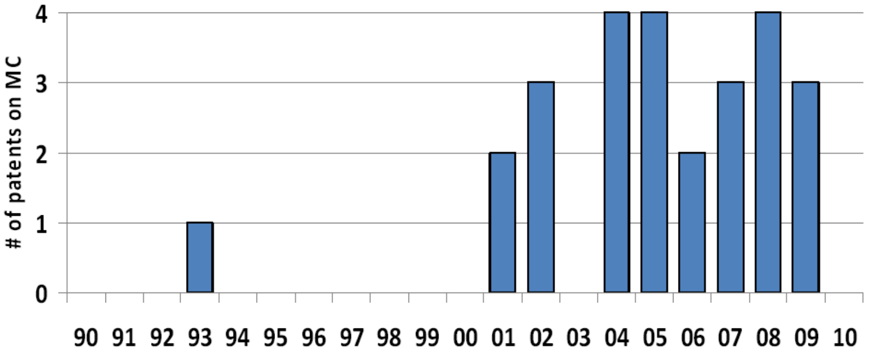


Figure 44 Patents awarded during recent years, dealing with CO_2 mineralisation [Delgado, 2010]

CO_2 mineralisation can make use of either calcium- or magnesium- based material. For calcium, these are typically by-products or wastes from industrial processing (with increasing interest mainly outside the “energy and fuel” sector since year 2000) while for magnesium it involves rock material that contains magnesium silicates like olivines/forsterites or serpentines.

A more recently recognised feature that gives CCSM an advantage is that in principle the method can operate on flue gases (or CO_2 containing process gases in general) directly, without a pre-separation of CO_2. The separation of CO_2 typically stands for 70% of the costs of the CCS chain. At the same time, it has become clear that conventional CO_2 removal from natural gas and similar petro-chemical gases, using alkanolamines like MEA and DEA becomes problematic when applied to flue gases that contain oxygen, oxides of sulphur and nitrogen and several other species besides CO_2, water and nitrogen. This explains why successful CCS demonstration projects (using underground CO_2 sequestration) are so far limited to natural gas processing and one gasification project.

For CCSM, however, it would not be a problem to process oxygen-containing gases (sulphur oxides would presumably be fixed as well) although it might involve transport of mineral to the CO_2 producing site (assuming that transporting the complete flue gas to a mineral deposit is not feasible). In such cases, pre-processing rock material at a mining site and transporting only an active component (e.g. magnesium hydroxide) to the CO_2 production site would be an option. The selection of sites for yet to-be-built, power plant or other process units that must be “capture-ready” for CCS could benefit from using locally available mineral resources and on-site carbonation with the flue gases (or process gases).

Besides this, the option of *in situ* CCSM is investigated at several locations where mineral resources are found near CO_2 production sites, (e.g. geothermal energy plants on Iceland) or where the rate of natural CO_2 mineral sequestration process may be increased by relatively simple means (such as in Oman). The current study will focus mainly on *ex situ* mineral carbonation, where rock material is taken into a process unit and reacts with CO_2 there.

The trends and pathways under investigation with respect to CCSM can be illustrated as in Figure 45 (Huijgen & Comans, 2005). A lot of attention still goes to single-step routes using aqueous solutions although water management is an issue of concern there (unless it is a once through process using seawater). Two-step (double-step) and multi-step processes are the other focus of research.

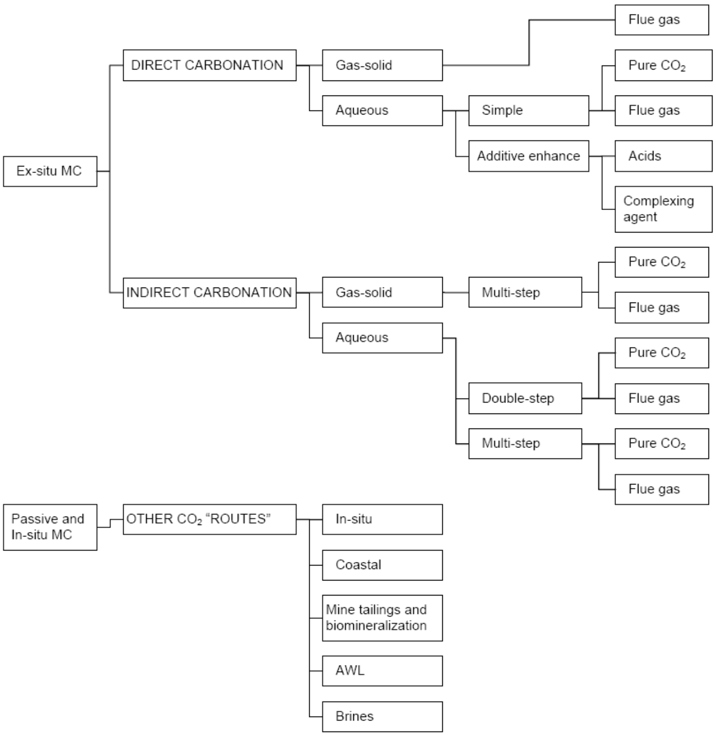


Figure 45 Pathways and process routes for CO_2 mineralisation currently under investigation (2008-2010) [Delgado, 2010]

Some more detail on minerals and alkaline (industrial residue) materials and chemical additives used for CCSM are given as Tables in the Appendix, taken from (Delgado, 2010).

The suitable minerals and wastes that can be used as reactants in the process are discussed in detail in the section of the report dealing with Work Package 1. This section of the report gives a description and comparative assessment of CO_2 mineralization processes that appear to offer a feasible CCS route in the near future. The decade 2010-2020 will be crucial for developing the technology and scaling it up to 1Mt CO_2/yr unit size. Apart from the processes under development by the consortium partners, the focus of the analysis has been processes for which patents have been filed since at least to the patentee these appear to be closer to application and business opportunity than what is reported by academia in journals and at conferences.

14.2 IDENTIFIED PROCESSES

14.2.1 Overview

After a literature and patent survey, approximately twenty-five processes were identified. In addition to these, several of the processes were described and presented in (Delgado, 2010). A list of patents identified by Delgado is shown in Appendix 6 of this report. Several of these were already described in the technology reviews (Newall *et al*, 2000; Huigen and Comans, 2003 & 2005; Sipilä *et al.*, 2008) or in 2 recent book chapters (Zevenhoven & Fagerlund, 2010a, b). Besides this, a process with involvement from ETI project partner Caterpillar was also identified (Kwon *et al*, 2009).

Most of the analysis of the processes was done at Åbo Akademi together with the team at ETH Zürich during Spring 2010. An MS-Excel table that was produced in parallel with this report shows and defines all assessment characteristics used and gives the available data for the processes analysed. The list below gives the names and identifiers for these processes - full references are given at the end of the chapter. Note that not all cases deal with complete processes; sometimes only one process step is described, or only a partial assessment was made.

1. Wet process Albany Research Centre (ARC) in the US: several cases serpentine 2004/2005 (O'Connor *et al*, 2005)
2. Wet process Albany Research Centre (ARC) in the US: several cases olivine 2004/2005 (O'Connor *et al*, 2005)
3. Shell flue gas (Verduyn *et al*, 2010, 2009)
4. Rau (and Caldeira) US patent
5. Nottingham process. (Wang & Maroto-Valer, 2010)
6. Hunwick WO patent (2008)
7. Brent PCT/AU patent (2007, 2010)
8. Åbo Akademi staged process, (Fagerlund *et al*, 2007)
9. Huijgen PhD thesis (2007)
10. Baldyga *et al.* (2010)
11. Munz *et al.* (2009)
12. Lin *et al.* (2008)
13. APC residue wet and dry processes (Baciocchi *et al.*, 2009)
14. Reddy US patent (2009)
15. Kodama *et al.* (2006)
16. Krevor *et al.* (2009)
17. Kwak *et al.* (2010)
18. Schiller (2006)
19. Maroto-Valer *et al.* (2005)
20. Calera process (Constantz, 2009; Constantz *et al.*, 2009; Constantz *et al.*, 2010a, b)
21. Vandor US (2010)
22. Caterpillar mineralisation process (2009)
23. Park (Park & Fan, 2004; Park *et al.*, 2003)
24. Jones (Jones, 2009; Layton, 2010)
25. DaCosta (DaCosta *et al.*, 2010)

14.2.2 Selected process data

For each process route, key parameters of a process are presented in a small table as to give quick insight into the main features. These parameters are:

i. Feedstock material (mineral)- following denotation are used: S-serpentine (serpentinite); O- olivine; W- wollastonite; IW- industrial waste;
ii. Mineral to CO_2 ratio (R_{real}) as kg of feedstock material needed/kg of CO_2 sequestered
iii. Mineral pre-treatment- denotation used are: M- mechanical, C – chemical, T- thermal. In parenthesis, particle size in µm and thermal treatment temperature in °C.
iv. Maximum temperature level in the process T_{max} in °C, T_{max}
v. Maximum pressure level in the process P_{max} in bar, P_{max}
vi. Chemical additives used.
vii. Percentage mineral cation (Mg, Ca, ….) reacted with CO_2 (degree of conversion)
viii. CO_2 fixing efficiency, including a penalty for CO_2 production due to energy input requirements (CO_2 F.E.)
ix. Reaction time (hours), multiple values for staged processes

Denotation n.d. = "no data" and dna = "does not apply" are used.

In addition to the table, a short description of each process is given. Finally, in order to carry out a comparison analysis, the assessment criteria described in previously were considered essential for evaluating the process routes and consequently ranking them. The process descriptions are kept short to a minimum since the objective was *not* to give a literature review but merely give supporting information for the assessments.

One other key factor though not included here is public acceptance *i.e.* is the process likely to be accepted to the communities near the CCSM plant site?

NOTE: The final assessment's small tables will also be given as combined in one Table in the Conclusions section for a quick overview.

14.3 PROCESS EVALUATIONS

14.3.1 ARC Process: serpentine [O'Connor *et al*, 2005]

Feedstock	**R_{real}**	**Pre-treatment**	**T_{max}**	**P_{max}**	**Additives**	**conversion**	**CO_2 F.E.**	**Reaction time**
S	3.39	M, T (75µm, 630°C)	155°C	120bar	0.64M $NaHCO_3$, 1M NaCl	62 %	77%	2 hours*

*1 hour heat up time included

14.3.2 ARC Process: olivine [O'Connor *et al*, 2005]

Feedstock	**R_{real}**	**Pre-treatment**	**T_{max}**	**P_{max}**	**Additives**	**Conversion**	**CO_2 F.E.**	**Reaction time**
O	2.22	M (38µm)	185$^{°C}$	150bar	0.64M $NaHCO_3$, 1M NaCl	61 %	- 100%	1 hour

This process is used here as a reference case as it is considered by most to be the state-of-the-art (although developed more than five years ago). The process involves the direct carbonation (after grinding and in some case thermal treatment) of magnesium (or calcium) silicate at 150-200°C, 100-150bar, in an aqueous solution with added salts (NaCl, $NaHCO_3$). Nonetheless, process flow diagram is given in Figure 46, tests done and the results are given in the two tables below, directly taken from (O'Connor *et al*, 2005)**.**

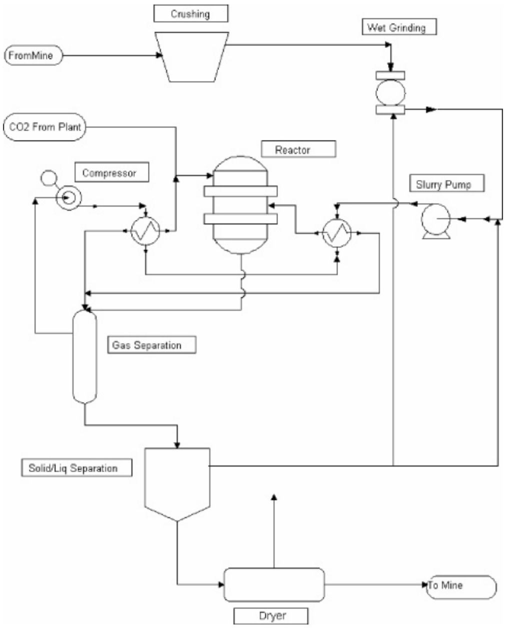


Figure 46 Process scheme of the single-step mineral carbonation of olivine in aqueous solution (ARC). [O'Connor *et al*, 2005] 'Single-step' indicates that mineral dissolution and carbonate precipitation take place simultaneously in the same carbonation reactor, whereas more steps are required for the whole process (preparation of the reactants, separation of the products).

Here, the assessment focuses serpentine types antigorite and lizardite (cases 6B, 2-4B and 6C as listed in the table below) as well as for olivine (case 1B). The results given in the MS-Excel$^{\circledR}$ table also show "corrected" values, where a distinction is made between heat and power requirements (and costs as a result of that) for the process as further explained in (Sipilä *et al*., 2008) and (Zevenhoven & Fagerlund, 2010).

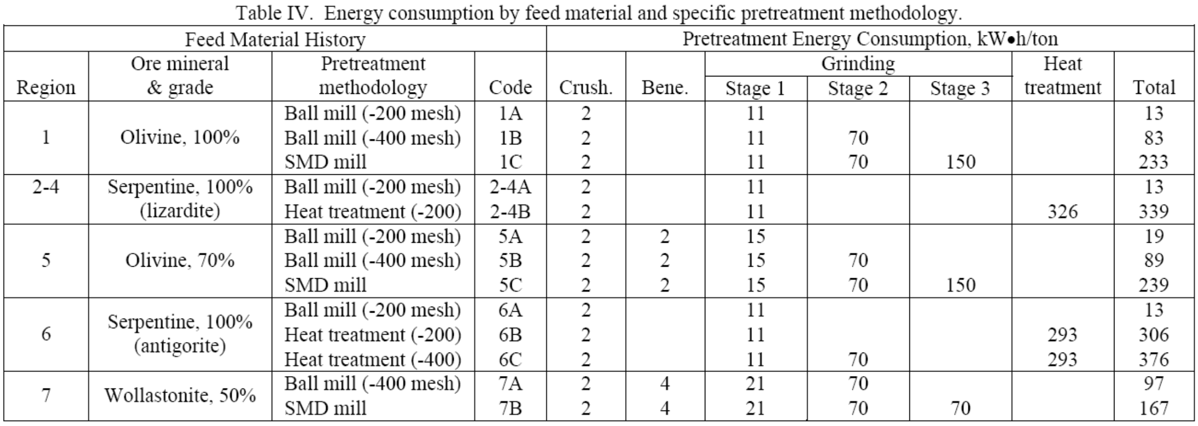


Table IV. Energy consumption by feed material and specific pretreatment methodology.

Feed Material History				Pretreatment Energy Consumption, kW•h/ton						
						Grinding				
Region	Ore mineral & grade	Pretreatment methodology	Code	Crush.	Bene.	Stage 1	Stage 2	Stage 3	Heat treatment	Total
1	Olivine, 100%	Ball mill (-200 mesh)	1A	2		11				13
		Ball mill (-400 mesh)	1B	2		11	70			83
		SMD mill	1C	2		11	70	150		233
2-4	Serpentine, 100% (lizardite)	Ball mill (-200 mesh)	2-4A	2		11				13
		Heat treatment (-200)	2-4B	2		11			326	339
5	Olivine, 70%	Ball mill (-200 mesh)	5A	2	2	15				19
		Ball mill (-400 mesh)	5B	2	2	15	70			89
		SMD mill	5C	2	2	15	70	150		239
6	Serpentine, 100% (antigorite)	Ball mill (-200 mesh)	6A	2		11				13
		Heat treatment (-200)	6B	2		11			293	306
		Heat treatment (-400)	6C	2		11	70		293	376
7	Wollastonite, 50%	Ball mill (-400 mesh)	7A	2	4	21	70			97
		SMD mill	7B	2	4	21	70	70		167

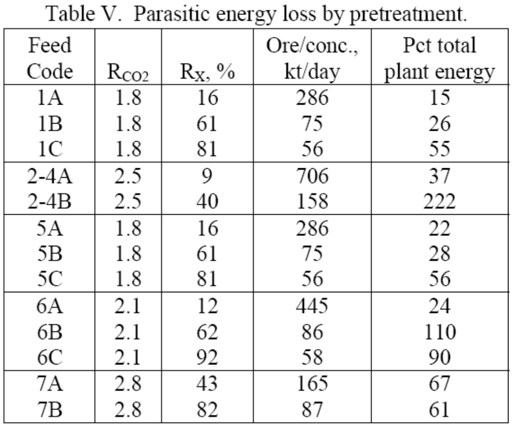


Table V. Parasitic energy loss by pretreatment.

Feed Code	R_{CO2}	R_X, %	Ore/conc., kt/day	Pct total plant energy
1A	1.8	16	286	15
1B	1.8	61	75	26
1C	1.8	81	56	55
2-4A	2.5	9	706	37
2-4B	2.5	40	158	222
5A	1.8	16	286	22
5B	1.8	61	75	28
5C	1.8	81	56	56
6A	2.1	12	445	24
6B	2.1	62	86	110
6C	2.1	92	58	90
7A	2.8	43	165	67
7B	2.8	82	87	61

Table 25 Process parameters for the ARC process experimental work (two tables) [O'Connor *et al*, 2005]

Final assessment:

Serpentine

Criterion	**Energy and efficiency**	**Material amounts**	**Products & additives**	**Simplicity & generality**	**Reliability, proven?**
Rating	B	C	D	A	A

Olivine

Criterion	**Energy and efficiency**	**Material amounts**	**Products & additives**	**Simplicity & generality**	**Reliability, proven?**
Rating	E	B	D	A	A

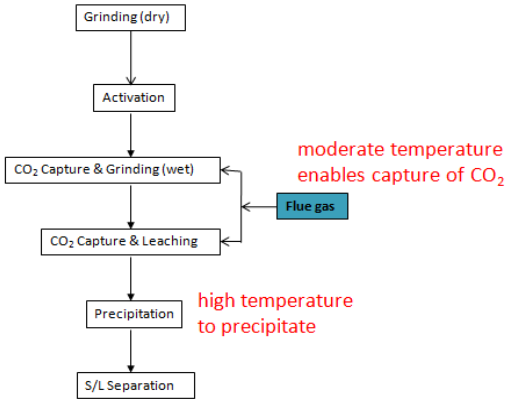
14.3.3 Shell Flue gases (Verduyn et al, 2010, 2009)

Feedstock	R_{real}	Pre-treatment	T_{max}	P_{max}	Additives	Conversion	CO_2 F.E	Reaction time
S (+O)	n.d.	M,T (650°C)	650°C	30 bar	$NaHCO_3$	n.d	n.d	n.d

Shell's mineralisation technology is an aqueous slurry-based process suitable for both serpentine and olivine mineral rocks. The process comprises pre-treatment, leaching and precipitation steps. Activation of serpentine is achieved by both mechanical and thermal means. Initial grinding (dry) reduces the mineral particle size. Thermal activation of serpentine turns it to amorphous material that is brittle, which lowers the requirements for subsequent grinding. Leaching is performed by contacting flue gas with the mineral slurry in a slurry mill as grinding proceeds (down to particle size 5-10 µm) as well as in a leaching basin at ambient temperature.

The slurry from the leaching step is pressurised (30-40bar) and heated up to 140°C in the precipitation step. Here, precipitation of dissolved $Mg(HCO_3)_2$ takes place as well as transformation of hydromagnesite into magnesite.

The Figure 47 below shows a block diagram of the process. Shell has carried out continuous tests ('Minerva' unit), the results showed that seawater can be used as aqueous phase and further, that seawater and dilute $NaHCO_3$ in water have comparable results. The use of seawater increases rate of leaching and precipitation.



1. Thermal activation step

$Mg_3Si_2O_5(OH)_4 = (MgO)_3(SiO_2)_2 + 2H_2O$

Dissolution of CO2 and dissociation of carbonic acid

$CO_2 + H_2O = H_2CO_3 = H^+ + HCO_3^-$

2. Leaching of Mg^{2+}

$(MgO)_3(SiO_2)_2 + 6H^+ \rightarrow 3Mg^{2+} + 2SiO_2 + 3H_2O$

3. Precipitation of $MgCO_3$

$Mg^{2+} + 2HCO_3^- \rightarrow MgCO_3 + CO_2 + H_2O$

Figure 47 Shell's direct flue gas mineralisation process concept (see also Appendix 4) [©Shell Global Solutions]

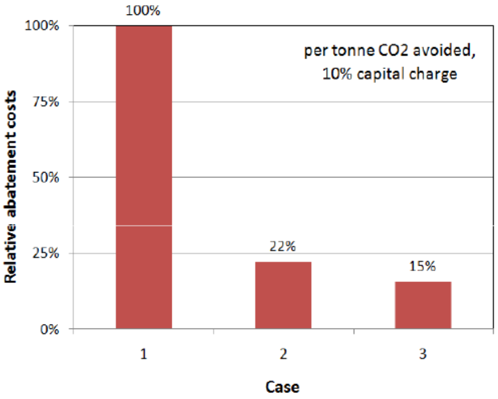


Figure 48 Shell flue gas process - cost reduction graph by change of mineralisation product [©Shell Global Solutions]

Simplifications proposed to reduce process costs include eliminating the S/L separation (drying) and precipitation steps. This makes it possible to omit the thermal unit associated with drying of the product and saves the energy required for precipitation, yielding magnesium bicarbonate that has a stoichiometric CO_2 storage advantage over magnesium carbonate. The product slurry of SiO_2 with dissolved $Mg(HCO_3)_2$ could still be used for land reclamation. Figure 48 shows a staircase graph of cost reduction for 3 cases:

1. With drying and precipitation (base case),
2. No drying and
3. No precipitation.

Comments

- ✓ No information on real amounts used, CO_2 fixation efficiency and energy input requirements, additives recovery or degree of carbonation conversion. Difficult to assess quantitatively, however, using the additional information given in Appendix 4 a qualitative assessment is done.
- ✓ This process would also operate well with serpentine/olivine mineral mixtures.

For a single pass of a 10%vol CO_2 stream through the wet grinding step, a CO_2 depletion percentage of 20-30% was achieved.

Final assessment:

SERPENTINE (+OLIVINE)

Criterion	**Energy and efficiency**	**Material amounts**	**Products & additives**	**Simplicity & generality**	**Reliability, proven?**
Rating	-	-	C	A	A

When using olivine as feed material, the thermal treatment is not required. In this process, finely ground olivine is reacted with pure CO_2 in a pressurised vessel at pressure 30bar and temperature of 140°C.

Shell's olivine process strongly resembles the ARC olivine process.

OLIVINE

Feedstock	R_{real}	Pre-treatment	T_{max}	P_{max}	Additives	Conversion	CO_2 F.E	Reaction time
O	1.82	M	140°C	30bar	$NaHCO_3$	80-90%	n.d	1-2 hours

Criterion	Energy and efficiency	Material amounts	Products & additives	Simplicity & generality	Reliability, proven?
Rating	-	A	C	B	B

14.3.4 Rau and Caldeira (2001)

Feedstock	R_{real}	Pre-treatment	T_{max}	P_{max}	Additives	Conversion	CO_2 F.E.	Reaction time
$CaCO_3$	2.8	n.d	n.d	n.d	Glycogen*	n.d	n.d	n.d

*a list of additives given among them: aromatic acids, citrate, galactose, acetate, EDTA, dextrose, succinate, taurine

Rau and Caldera describe a process referred to as advanced weathering of limestone (AWL) for sequestering CO_2 comprising of two steps. In step 1, CO_2 gas is hydrated to form carbonic acid and in the 2nd step the hydrated CO_2 is reacted with a metal (typically calcium, from limestone wastes) carbonate to form metal cations and bicarbonate in solution.

Considering a process realisation where the hydration and carbonation takes place the same vessel, water is sprayed or atomised from the top of the vessel (vent 104 as shown in the Figure 49 below). CO_2 gas enters the reactor vessel at three positions: upper side, lower side or the below of the vessel (112 a, b, c). The reaction takes place in the upper side reactor forms carbonic acid ($CO_2(aq)$ or H_2CO_3), which drops to the base or lower side of the bed where ground carbonates are lumped (152). The carbonic acid reacts with carbonate to form metal ion/bicarbonate solution 146. The mixture is bled from the reactor and disposed as waste solution.

Comments

- ✓ A more stable form of carbonate ($CaCO_3$) is transformed to aqueous solution (bicarbonate)
- ✓ Processed calcium source based process, hence limited potential
- ✓ To be operated near a coastline for disposal of products in the seawater or ocean.

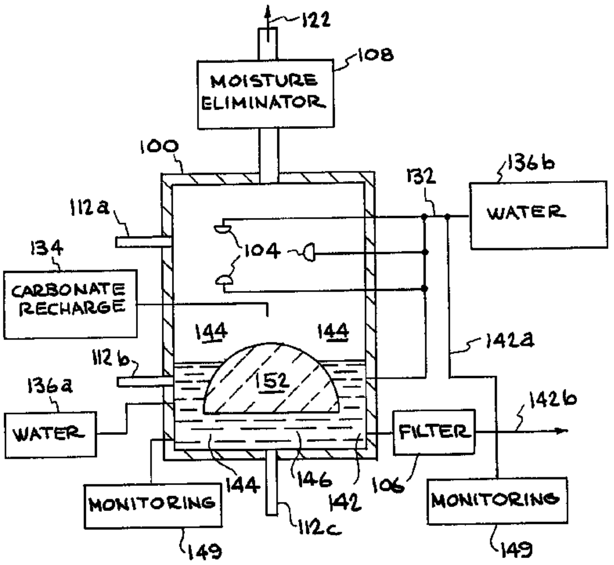


Figure 49 AWL process comprising an integrated configuration that extracts and sequesters CO_2 from a gas stream in which CO_2 is hydrated and reacted with carbonate in a reactor vessel. Stream 112a, b, & c are alternative gas inlet streams [Rau & Caldeira, 2001]

Final assessment:

Criterion	Energy and efficiency	Material amounts	Products & additives	Simplicity & generality	Reliability, proven?
Rating	-	-	-	-	-

14.3.5 Nottingham University Process (Wang & Maroto-Valer, 2010)

Feedstock	R_{real}	Pre-treatment	T_{max}	P_{max}	Additives	Conversion	CO_2 F.E.	Reaction time
S	3.0	M (75µm)	300°C	1 bar	1.4M NH_4HSO_4	70**	n.d	3 hours*

*mineral dissolution time is reported it excludes carbonation and regeneration steps (extraction only) **communication with the author

With the aim to improve the efficiency of mineral dissolution and be able to recover and re-use additives, Maroto-Valer and co-workers have proposed a pH-swing CO_2 mineralisation process using ammonium salts to overcome these barriers. At 100°C, 1.4M aqueous solution NH_4HSO_4 was found to extract 100% Mg from serpentine in 3 hours. In addition, it extracts 98% of Fe and 17.6% of Si under the same conditions. The work shows similarities with a US patent from 1967 (Pundsack, 1967)

The process proposed consists of five steps for which the main reactions are presented in Figure 50 and Table 26 below. In the first step, NH_3 is used to capture CO_2 from flue gas to produce NH_4HCO_3. In the mineral dissolution step, 1.4M NH_4HSO_4 is used to extract Mg from serpentine ground to a particle size range 75-125µm. The Mg-rich solution is neutralised by adding NH_4OH, after which impurities in the leaching solution are removed by adding NH_4OH. In a carbonation step, Mg-rich solution reacts with the product from the capture step NH_4HCO_3 to precipitate carbonates. Since formation and stability of hydrocarbonates is temperature dependent, $MgCO_3 \cdot 3H_2O$ (nesquehonite) can convert to $4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$ (hydromagnesite) at temperatures above 70°C. Precipitation of hydromagnesite results in a solution that mainly containing $(NH_4)_2SO_4$. The final step is regeneration of additives; decomposition of $(NH_4)_2SO_4$ starts from 250°C and ends at 330°C producing NH_3 for the capture process and NH_4HSO_4 to be reused in mineral dissolution.

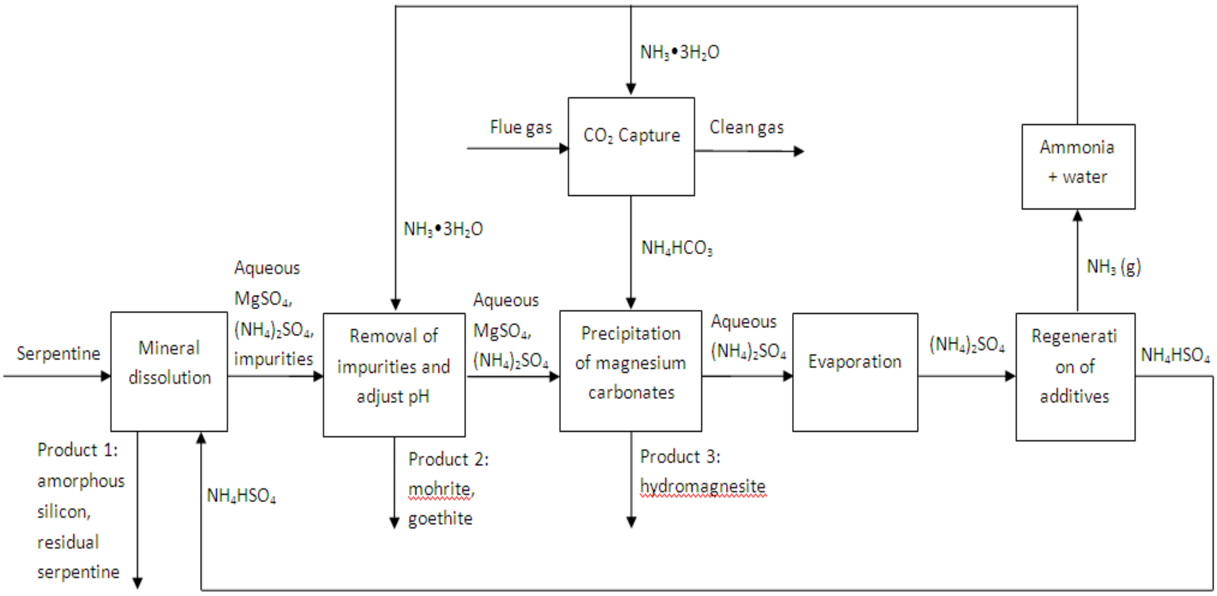


Figure 50 pH-swing CO_2 mineral carbonation process with recyclable ammonium salts [Wang & Maroto-Valer, 2010]

	Reaction equations	T(°C)	ΔH (kJ)	ΔG(kJ)
CO_2 capture	$NH_3 + CO_2 + H_2O \rightarrow NH_4HCO_3$	10	-127.0	-26.3
Mineral dissolution	$Mg_3Si_2O_5 \bullet (OH)_4 + 6NH_4HSO_4 \rightarrow 3MgSO_4 + 2SiO_2 + 5H_2O + 3(NH_4)_2SO_4$	90	-141.1	-431.8
pH adjustment	$NH_4HSO_4 + NH_4OH \rightarrow (NH_4)_2SO_4 + H_2O$	25	-116.0	-134.4
Removal of impurities	$(Fe, Al, Cr)_2(SO_4)_3 + 6NH_4OH \rightarrow 2(Fe, Al, Cr)(OH)_3 \downarrow + 3(NH_4)_2SO_4$	25	-673.0	-545.1
	$(Zn, Cu, Mn)SO_4 + 2NH_4OH \rightarrow (Zn, Cu, Mn)(OH)_2 \downarrow + (NH_4)_2SO_4$	25	-191.4	-144.4
Carbonation	$MgSO_4 + 2NH_4HCO_3 \rightarrow Mg(HCO_3)_2 + (NH_4)_2SO_4$			
	$Mg(HCO_3)_2 + 2H_2O \rightarrow MgCO_3 \bullet 3H_2O \downarrow + CO_2 \uparrow$			
	Overall reaction			
	$MgSO_4 + 2NH_4HCO_3 + 2H_2O \rightarrow MgCO_3 \bullet 3H_2O \downarrow + (NH_4)_2SO_4 + CO_2 \uparrow$	80	-6.6	-37.4
	Carbonate formation change			
	$5MgCO_3 \bullet 3H_2O \rightarrow 4MgCO_3 \bullet Mg(OH)_2 \bullet 4H_2O + CO_2 \uparrow + 10H_2O$	80	69.5	-18.2
Regeneration of additives	$(NH_4)_2SO_4 \rightarrow NH_4HSO_4 + NH_3 \uparrow$	300	111.6	90.4

Table 26 The table below shows chemical reaction and thermodynamic data of the process steps [Wang & Maroto-Valer, 2010]

Comment

- ✓ From the reaction equations, CO_2 is released during “carbonation” and “carbonate forming” steps. However, this emission can be eliminated with process/reactions optimisation. Experimental CO_2 sequestration efficiency of 80% has been shown.

- ✓ The last step may require a higher temperature than stated (above ~350$^{\circ C}$, release of NH_3 would start at temperature above 350°C, using HSC and as given as example 1 in patent (Pundsack, 1967).

Final assessment:

Criterion	**Energy and efficiency**	**Material amounts**	**Products & additives**	**Simplicity & generality**	**Reliability, proven?**
Rating	-	B	C	B	B

14.3.6 **R Hunwick** (Hunwick, 2008)

Feedstock	**R_{real}**	**Pre-treatment**	**T_{max}**	**P_{max}**	**Additives**	**Conversion**	**CO_2 F.E.**	**Reaction time**
S	3.33	M (37μm)	300°C	120bar	NH_3	70%	74%	1 hour

Hunwick (2008) came up with a method for capture and sequestration of CO_2 from power station flue gases.

Carbon dioxide sequestration is carried out in the following steps: The first step involves mixing aqueous slurry of metal silicate-containing rock (30% solids) with ammonia to form ammonia/water/metal silicate slurry. Serpentine is the preferred silicate rock, finely ground to 90% finer than 40 microns. Secondly, a flue gas stream is exposed to the solution from stage (1) hence absorbing the CO_2 into the reactive slurry. Finally, the reactive slurry is pumped to a reactor at an elevated pressure of 100bar and at a temperature of 225°C to enhance the rate of a reaction between CO_2 and serpentine reaction to produce magnesium carbonate and ammonia that is thus regenerated.

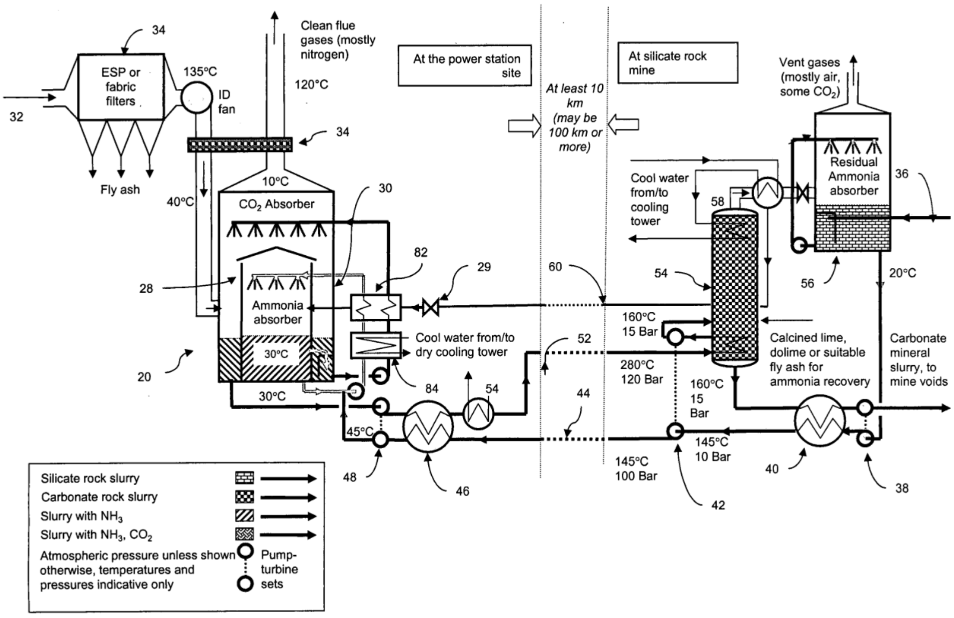


Figure 51 A schematic of a CO_2 sequestration system using a pipeline as a reactor [Hunwick, 2008]

The reactor types proposed by the inventor are: a pipeline reactor preferably with multiple flow paths and an underground chamber reactor. In the pipeline reactor, one flow path supplies ammonia/water/silicate slurry from the mining area for CO_2 absorption at the power plant. Another pipeline acting as a reactor connects the power plant to the serpentine mine site where the reaction product would be stored.

The second type of reactor set up as proposed by Hunwick is an underground chamber reactor. The reactor is a form of a chamber that may be excavated from bedrock at a depth of 100m sufficient to allow the carbonation reactions to occur quickly enough (a depth that provides sufficient pressure to enhance the reaction). Figure 51 shows a schematic diagram of the process utilising a pipeline as a reactor while Figure 52 shows a caved-in chamber located at such a depth that it provides sufficient pressure to enhance the reaction between the CO_2 and the metal silicate.

Comment

- ✓ Intensive energy is required to pump material from one end to the other, large transport distances for chemicals (including those that fixed the CO_2).
- ✓ Corrosion in the pipe can't be ruled out since ammonia is corrosive; moreover, the slurry may be abrasive.
- ✓ Looks very promising and deserve further assessment and testing. No further reporting was found.

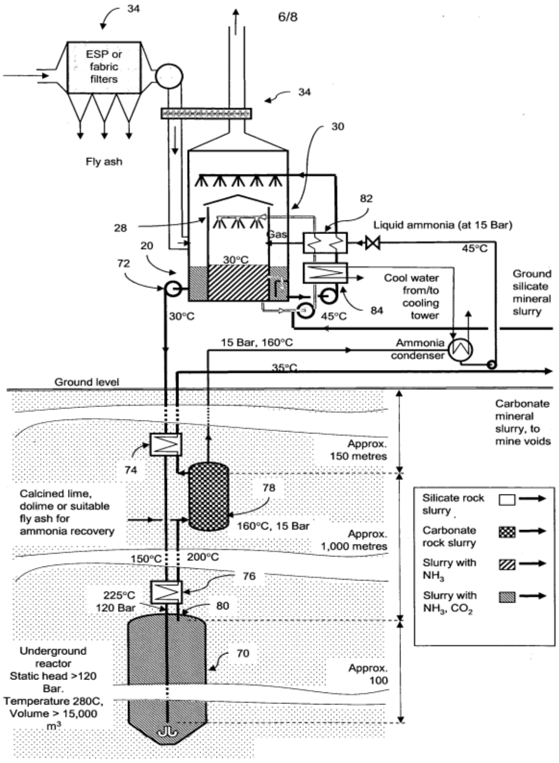


Figure 52 A schematic of a CO_2 sequestration system using underground chamber as a reactor [Hunwick, 2008]

Final assessment:

Criterion	**Energy and efficiency**	**Material amounts**	**Products & additives**	**Simplicity & generality**	**Reliability, proven?**
Rating	B	C	B	B	C

14.3.7 G F Brent (Brent, 2007; 2010; Brent & Petrie, 2010)

Feedstock	**R_{real}**	**Pre-treatment**	**T_{max}**	**P_{max}**	**Additives**	**Conversion**	**CO_2 F.E.**	**Reaction time**
S	5.25	M,T (75μm:630°C)	155°C	115 bar	0.64M$NaHCO_3$, 1M NaCl	80%	75%	1 hour

In this work, Brent negates the conclusions made by the Albany Research Centre (ARC) in their report (O'Connor *et al.*, 2005). That dismissed serpentine mineral as a preferred feedstock due to its high energy intensive for activation process. According to the invention, the finely ground feedstock preferably serpentine (75μm) is thermally active by energy supplied from burning natural gas, alkanes or renewable biomass fuel.

This is done after preheating the mineral feedstock in a combined series of heat exchangers utilising the exothermic heat from the carbonation reactor at a temperature of 120-150°C and low grade heat associated to the combustion of fuel in this case further raising the temperature of serpentine ore to around 300°C. The final and essential heat exchanger is provided by direct thermal activation in a furnace.

Separation of metal oxides other than MgO and Mg silicates from the ore is done to produce activated residual feedstock rich in MgO and Mg silicate. This removal of other metal oxides substantially reduces downstream process requirement and valuable oxides such as: Fe, Ni can be used for other purposes. The activated ore is mixed with a solvent prior to feeding it into a carbonation chamber operating at 115 bar and a temperature of 155°C. Figure 53 below summarises the process. The solid carbonate and silica residues are withdrawn for final disposal back at the quarry. The recovered solvent is re-used in the process.

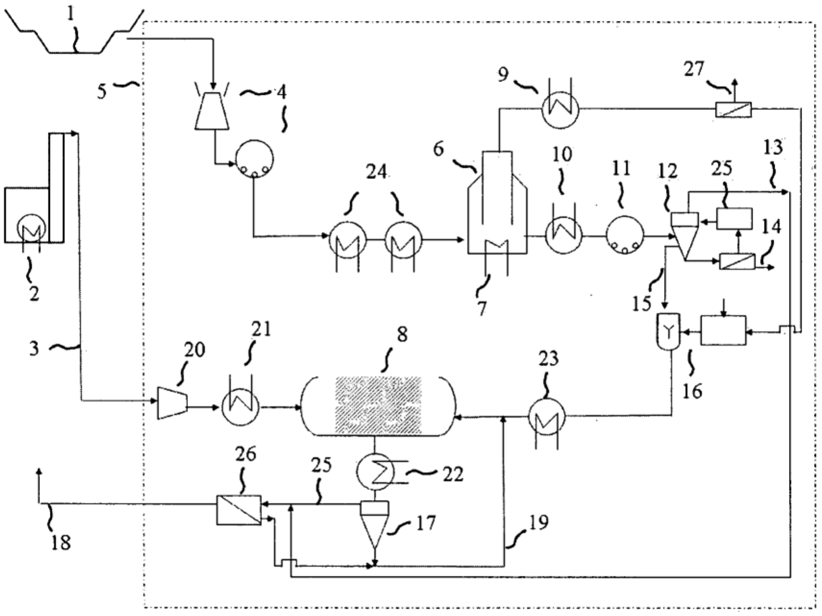


Figure 53 A flow diagram of invention for activation of serpentine ore and CO_2 sequestration [Brent, 2010]

Comments

- ✓ This is a modified Albany research centre (ARC) process scheme, apparently making better use of system heat.
- ✓ It may be hard to get the three feed materials in a close proximity hence fuel and CO_2 (in a pipeline preferably) must be transported to the mineral mining site.
- ✓ The author listed a list of additives that would possibly be used and not singling out a preferred one. However, ARC solvents be used basing on the reaction conditions given.
- ✓ A new process idea, for which neither experimental nor simulation work was reported.
- ✓ Valuable by-products such FeO and/or FeO(OH) can be obtained.

Final assessment:

Criterion	**Energy and efficiency**	**Material amounts**	**Products & additives**	**Simplicity & generality**	**Reliability, proven?**
Rating	B	C	B	A	B

14.3.8 Åbo Akademi staged (Fagerlund *et al.*, 2010a, b)

Feedstock	R_{real}	Pre-treatment	T_{max}	P_{max}	Additives	Conversion	CO_2 F.E.	Reaction time
S	5.83	M,T(250-425µm)	500- 550°C	20-… bar	$(NH_4)_2SO_4$	60%	73.26%	0.5 hour

CO_2 storage in magnesium silicate according to the ÅA team in Finland is done in two stages: first is the production of $Mg(OH)_2$ from serpentinite and second step is the carbonation of the produced $Mg(OH)_2$. This is done mainly because the reactivity of $Mg(OH)_2$ is much higher than that of serpentinite and MgO permitting for a faster carbonation while aiming at using the heat of reaction released during the carbonation.

In the process of extracting magnesium from serpentinite, a mixture of serpentinite is heated together with ammonium sulphate at a temperature of 450-500°C (may be higher, up to 550°C). This results in the formation of a magnesium sulphate (which unfortunately cannot be carbonated directly) that is dissolved in water. Adjusting the pH using ammonium hydroxide or ammonia leads to precipitation of $Mg(OH)_2$ while iron oxide is recovered as a by-product. The formed magnesium hydroxide is carbonated in a fluidised bed at 20 bar pressure (may be higher) and a temperature of 500-550°C. Figure 54 below shows the pressurised fluidised bed set-up used at ÅA, in which 50% conversion of ~200µm $Mg(OH)_2$ particles is achieved in (less than) 10min.

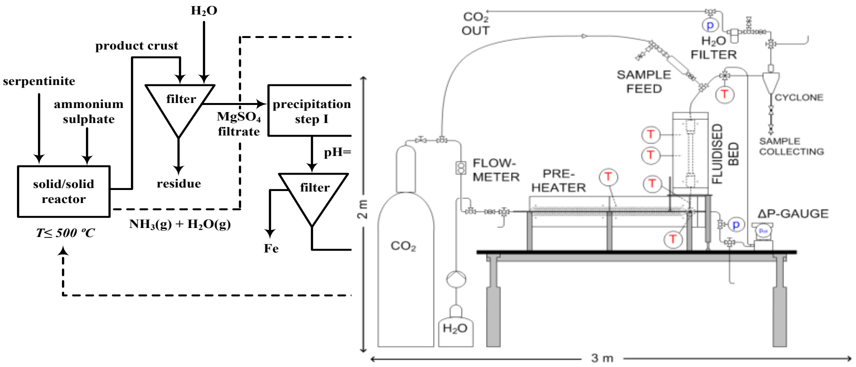


Figure 54 Schematic of $Mg(OH)_2$ production and figure of pressurised fluidised bed for $Mg(OH)_2$ carbonation set up at Åbo Akademi [Fagerlund *et al.*, 2010b]

Comments

✓ Possible losses of corrosive ammonia gas during Mg extraction from serpentinite

✓ It is thermodynamically feasible to cover heat used in the endothermic magnesium extraction by using the heat of reaction in the exothermic carbonation stage. However, combining the stages has not yet been practically done. Both stages operate successfully, however.

✓ Integration with other plant process valuable by-products such FeO and/or FeO(OH) is possible.

Final assessment:

Criterion	Energy and efficiency	Material amounts	Products & additives	Simplicity & generality	Reliability, proven?
Rating	B	D	B	B	B

14.3.9 W Huijgen (2007)

Feedstock	R_{real}	Pre-treatment	T_{max}	P_{max}	Additives	Conversion	CO_2 F.E.	Reaction time
W	4.06	M (38µm)	200°C	35.5 bar		69%	76.07%	0.25

This work involves direct aqueous carbonation of wollastonite (calcium silicate) mineral (besides steel slag and similar materials). Finely ground wollastonite to particle size 38µm was suspended in distilled water. A CO_2 stream is introduced into the reactor under continuous stirring to ensure dispersion of the gas. The carbonation reaction is occurring in the aqueous phase in two steps: calcium leaching from the $CaSiO_3$ matrix and nucleation and growth of $CaCO_3$.

A conversion of 69% is attained in 15 minutes at 200°C, 20 bar CO_2 partial pressure. Other work done by Huijgen involves aqueous carbonation of steel slag. Similar to carbonation of wollastonite, the carbonation reaction proceeds in two steps: leaching of calcium from steel slag particles and precipitation of calcite on the surface of these particles. A higher conversion of 74% is attained in 30 minutes at same partial pressure of CO_2 and at lower temperature of 100°C. In this report, wollastonite data is used for assessment. Figure 55 below shows a block diagram for the Huijgen process.

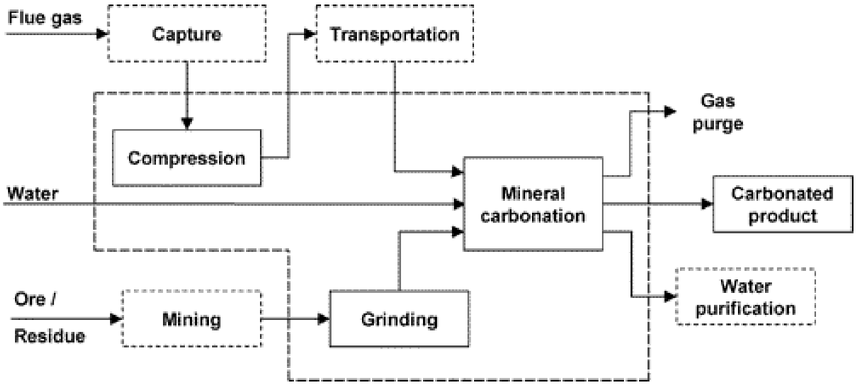


Figure 55 Block diagram of mineral carbonation [W Huijgen, 2007]

Comment

- ✓ Limited to availability of wollastonite or steel slag; calcium-based carbonation.

Final assessment:

Criterion	Energy and efficiency	Material amounts	Products & additives	Simplicity & generality	Reliability, proven?
Rating	B	B	C	B	C

14.3.10 Baldyga (Baldyga *et al.*, 2010)

Feedstock	R_{real}	Pre-treatment	T_{max}	P_{max}	Additives	Conversion	CO_2 F.E.	Reaction time
W	3.1	n.d	80°C	30 bar	Succinic acid	90%	n.d	1 hour

In this work, the author focuses on the first step of two-step mineral carbonation i.e. extracting of reactive component (Ca^{2+}) from mineral matrix (wollastonite). Extraction was conducted in a reactor where a mixture of wollastonite and succinic acid (extraction medium) reacts at temperature 80°C and pressure 30 bar. A calcium conversion of 90% is achieved after 1 hour.

Comments

- ✓Carbonation not addressed; partial process

Final assessment:

Criterion	Energy and efficiency	Material amounts	Products & additives	Simplicity & generality	Reliability, proven?
Rating	-	A	D	-	C

14.3.11 Munz (Muntz *et al.*, 2009)

Feedstock	R_{real}	Pre-treatment	T_{max}	P_{max}	Additives	Conversion	CO_2 F.E.	Reaction time
O	n.d	M (75µm)	250°C	150 bar	water	n.d	n.d	n.d

The paper aimed at demonstrating principles of separating magnesite and silica after dissolution of olivine in carbonated aqueous solutions. The process consists of three steps: 1) dissolution of finely ground olivine (particle size 75µm) in a reactor kept at 130°C and constant pressure 150 bar; 2) precipitation of magnesite which takes place a higher temperature 250°C; 3) precipitation of silica. Precipitation of magnesite and silica depends on pH and temperature. Figure 56 shows experimental set up of a flow-through column reactor.

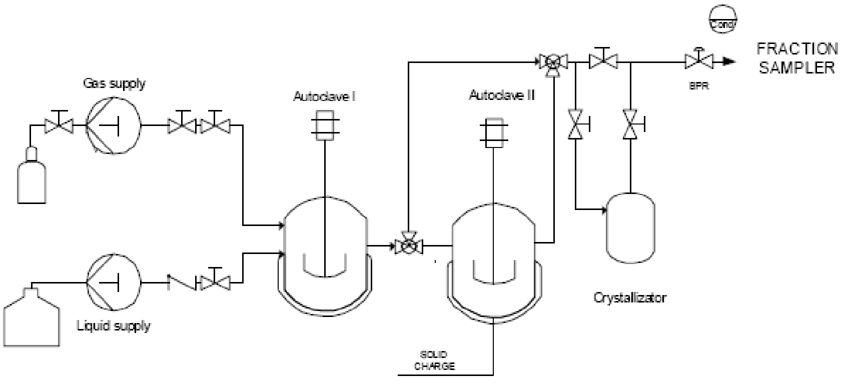


Figure 56 Experimental set-up of a continuously stirred reactor [Munz *et al.*, 2009]

Comments

- ✓ High dependence of reaction rates on high pressure. Long reaction times
- ✓ Not enough information for an assessment

Final assessment:

Criterion	**Energy and efficiency**	**Material amounts**	**Products & additives**	**Simplicity & generality**	**Reliability, proven?**
Rating	-	-	-	-	-

14.3.12 Lin (Lin *et al*., 2008)

Feedstock	**R_{real}**	**Pre-treatment**	**T_{max}**	**P_{max}**	**Additives**	**Conversion**	**CO_2 F.E.**	**Reaction time**
S	8.97	M,T (50µm:150)	325°C	1 bar	HCl/NaOH	26%	42.02%	26 hours

A two-staged process is proposed that employs hydrothermal treatment to decompose serpentine to magnesium hydroxide. Finely ground serpentine of particle size ca. 50µm is treated with 1N aqueous HCl at 150°C for 24h. After the hydrothermal treatment, the resulting mixture is neutralised with an appropriate amount of NaOH to precipitate dissolved silica (at pH ca. 8) and Mg to $Mg(OH)_2$ (at pH ca. 11). The resulting $Mg(OH)_2$ is carbonated isothermally in a fixed bed at atmospheric pressure and temperature of 325°C for 2 hours.

Comments

- ✓Decomposition of serpentine takes a very long time
- ✓Recovery of chemical use not addressed: this would add significant costs to the process

Final assessment:

Criterion	**Energy and efficiency**	**Material amounts**	**Products & additives**	**Simplicity & generality**	**Reliability, proven?**
Rating	E	E	D	C	C

14.3.13 Baciocchi (Baciocchi *et al*., 2009)

Wet carbonation

Feedstock	**R_{real}**	**Pre-treatment**	**T_{max}**	**P_{max}**	**Additives**	**Conversion**	**CO_2 F.E.**	**Reaction time**
IW	3.71	dna	30°C	3 bar	-	70%	n.d	1 hour

Dry carbonation

Feedstock	R_{real}	Pre-treatment	T_{max}	P_{max}	Additives	Conversion	CO_2 F.E.	Reaction time
IW	3.47	dna	400°C	1 bar	-	75%	n.d	0.16 hour

In their work, Baciocchi and co-workers carried out carbonation experiments with air pollution control (APC) residues from a waste incineration plant. Both dry and wet routes were compared under different conditions. In the dry route, carbonation was carried out in a thermo-gravimetric system where APC residues were placed on a holder heated up to an operating temperature of 400°C at atmospheric pressure. A mixture of CO_2 (10%) and argon was fed in to the system and a conversion of up to 75% was reached after few minutes. The wet process operates at a pressure of 3atm. and much lower temperature of 30°C. A liquid to solid ration of 0.2 at 30°C is optimal condition to speed up the reaction. Carbonation is done in a stainless steel reactor placed in a thermostatic bath to control the temperature. Dried ash samples were mixed with distilled water and treated in a continuous 100% CO_2 flow. A conversion of nearly 70% was attained in 1 hour.

Comments

- ✓Limited to availability of the APC residue, calcium based carbonation.
- ✓APC are in powder foam with little or no pre-treatment required.
- ✓A possibly of upgrading hazardous industrial waste to non-hazardous material
- ✓Primarily a waste-treatment process, limited CCS capacity as a result of limited feedstock

Final assessment:

Wet carbonation

Criterion	Energy and efficiency	Material amounts	Products & additives	Simplicity & generality	Reliability, proven?
Rating	-	B	C	C	C

Dry carbonation

Criterion	Energy and efficiency	Material amounts	Products & additives	Simplicity & generality	Reliability, proven?
Rating	-	B	C	C	B

14.3.14 K. J. Reddy (Reddy & Argyle, 2009)

Feedstock	R_{real}	Pre-treatment	T_{max}	P_{max}	Additives	Conversion	CO_2 F.E.	Reaction time
IW	n.d	(40µm)	150 $^{\circ C}$	1 bar	dna	4%	n.d	0.16 hour

In this invention, the inventor proposes a way to store CO_2 by reacting it with fly ash product of combustion. Flue gas from stack is coupled to a moisture control unit to reduce the moisture in the gas. The gas is blown through a fluidised bed filled with alkaline material (i.e. fly ash). The flue gas enters the fluidised bed at a temperature of 15-150°C and at a pressure of ca. 1 atm. The residence time of the solids in the bed is ca. 10min; a filter is positioned at the top of the bed to trap dust or solid particles from escaping to the atmosphere. Figure 57 below summarises the process described.

Comments

✓Fly ash couldn't be sufficient to store all the CO_2 generated. Calcium-based method.

✓Low absorption rate of the CO_2. 4% was recorded.

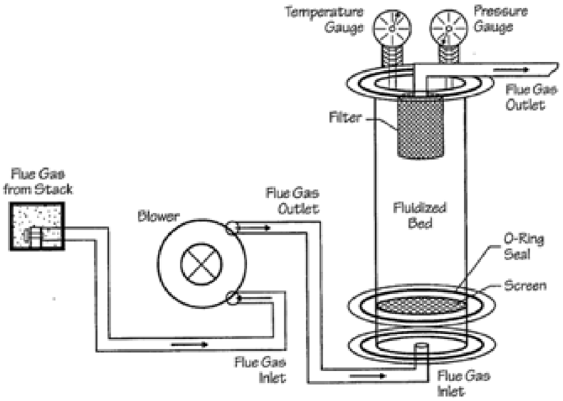


Figure 57 A schematic illustrating a fluidised bed reactor [Reddy & Argyle, 2009]

Final assessment:

Criterion	Energy and efficiency	Material amounts	Products & additives	Simplicity & generality	Reliability, proven?
Rating	E	-	C	C	D

14.3.15 Kodama (Kodama *et al.*, 2008)

Feedstock	R_{real}	Pre-treatment	T_{max}	P_{max}	Additives	Conversion	CO_2 F.E.	Reaction time
IW	5.93	M,T (440µm and 950°C)	950°C	1 bar	1N NH_4Cl	70%	82%	1.5 hours

In this process, a recyclable extraction solution is utilised to extract calcium ion from calcium silicates. The process consists of two steps. In the first step, the calcium ions are extracted from the calcium silicate by reacting with ammonium chloride solution:

$$4NH_4Cl(a) + 2CaO.SiO_2(s) = 2CaCl_2\ (a) + SiO_2(s) + 4NH_3(a) + 2H_2O(l)$$

When CO_2 – containing gas is contacted with the extraction solution, $CaCO_3$ is generated and the NH_4Cl solution is recovered for re-use.

Converter slag used as a source of calcium of particle size 20mm was ground to a size 440µm. The ground particles were calcined at 950°C for 30 minutes to remove CO_2 and H_2O that were adsorbed after the production of slag. Calcium was extracted by heating in ammonium chloride to the reaction temperature in a water bath. The slag sample was poured into the flask containing NH_4Cl. The sample is heated for an hour at 80°C and atmospheric pressure under continuous stirring. After an hour, 13% CO_2 (in N_2) is bubbled through the calcium extract solution. A block diagram of a process is shown in Figure 58 below.

Comments

- ✓ Significant yet limited availability of the steel slag for CO_2 sequestration
- ✓ Unreacted NH_3 needs to be cooled to avoid escape hence additional energy for cooling is required
- ✓ High cost for recovery and make-up supply of NH_3.

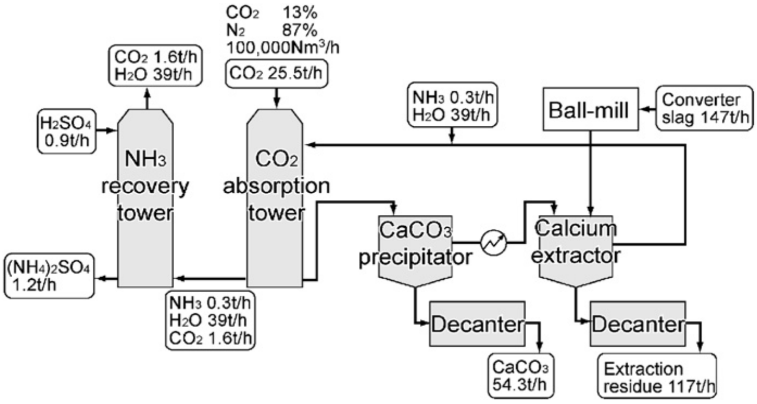


Figure 58 A block flow and material balance of the process [Kodama et al., 2008]

Final assessment:

Criterion	**Energy and efficiency**	**Material amounts**	**Products & additives**	**Simplicity & generality**	**Reliability, proven?**
Rating	B	C	D	C	D

14.3.16 Krevor (Krevor *et al*, 2009)

Feedstock	R_{real}	Pre-treatment	T_{max}	P_{max}	Additives	Conversion	CO_2 F.E.	Reaction Time
S	3.5	M (<75µm)	120°C	20 bar	0.1M citrate, EDTA	60%	n.d	2 hours

This mineral carbonation route involves direct carbonation of aqueous slurry of magnesium mineral with supercritical CO_2. Krevor and co-workers identified low dissolution rates of silicates as one of the reasons for slow carbonation reactions kinetics. In their process, finely ground serpentine of particle size less than 75µm is reacted in a solution with dissolved salts under a CO_2 atmosphere and at 120°C.

Salts (sodium citrate, sodium oxalate or sodium EDTA are the salts that gave highest conversion within 2 hours) is dissolved fully in a solution, after which serpentine is added to the reactor. The reactor, pressurized to 20bar is heated to 120°C. After 2 hours a conversion of 60% is attained, 80% in 7 hours and near 100% achieved at between 10 and 20 hours.

Comments

- ✓ According to recent communication with the author, they seek to improve their processes by exploring a possibility of finding a non-acidic catalyst (possibly a neutral salt and that it does not impact precipitation of carbonate phase) thus enhancing the overall carbonation process rate, potentially at low temperatures and pressures.
- ✓ Recovery or regeneration of additive salts has not been addressed
- ✓ Long reaction times

Final assessment:

Criterion	**Energy and efficiency**	**Material amounts**	**Products & additives**	**Simplicity & generality**	**Reliability, proven?**
Rating	-	C	D	D	C

14.3.17 Kwak (Kwak *et al.*, 2010)

Feedstock	R_{real}	Pre-treatment	T_{max}	P_{max}	Additives	Conversion	CO_2 F.E.	Reaction time
O	20	M (37µm)	80°C	97 bar	Water	8%	Up 46%	20 hours

Kwak and co-workers in their investigation on reaction pathways and reaction extent have set up experiments to carbonate forsterite under a range of geologic carbon sequestration (GCS) conditions. Finely ground forsterite mixed with water was fed into a batch reactor. The CO_2 channel connected to the reactor was used to feed CO_2 at pressure of 5atm. The reaction was kept at 80°C for 20h. A conversion of 8% was attained.

Comments

- ✓Reaction time is high, low conversion levels; not very successful…

Final assessment:

Criterion	**Energy and efficiency**	**Material amounts**	**Products & additives**	**Simplicity & generality**	**Reliability, proven?**
Rating	E	E	C	D	D

14.3.18 C Schiller (Schiller, 2006)

Feedstock	R_{real}	Pre-treatment	T_{max}	P_{max}	Additives	Conversion	CO_2 F.E.	Reaction time
S	2.33	M (100µm)	550°C	50 bar	Weak acid/NH_3	90%	102%	1 hour

In this process, a finely ground serpentine of particle size 75µm is dissolved in a medium-strong organic acid at 100°C. The dissolved magnesium can then be precipitated in three consecutive vessels by introduction of NH_3(g). The precipitated products from the three reactions (SiO_2, $Fe(OH)_3$ and $Mg(OH)_2$) can be separated from the residue by counter-current decantation.

The $Mg(OH)_2$ that is precipitated is dried, pre-heated to (nearly) reaction temperature 550°C and fed into a fluidized bed reactor. The reaction proceeds at a pressure of 50bar for an hour before separating the products for disposal. A recovery process suggested for the organic acid sorbent is by leaching with a volatile base such as trimethylamine (TMA). This would result in trimethyammonium carboxylate that can be recovered with heat input.

Comments:

- ✓ This process attempts to address the drawback of strong acid process: energy intensive dehydration and acid recovery requirements.
- ✓ The design assumes 100% heat transfer efficiency that is not realistic.
- ✓ Acid recovery process and the cost of additional acid and base (TMA) will affect the running costs.

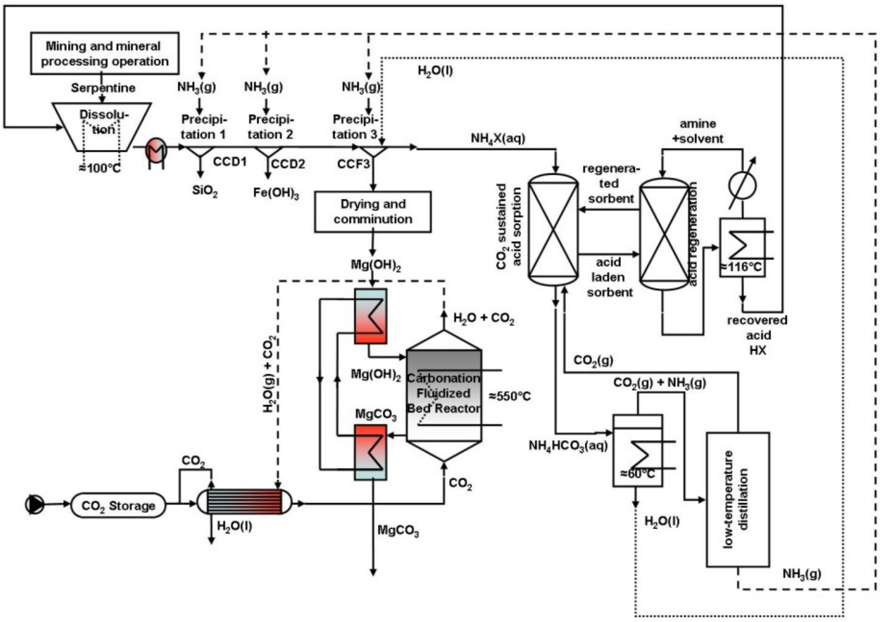


Figure 59 Process layout for the dissolution, precipitation, and carbonation of magnesium content of serpentine [Schiller, 2006]

Final assessment:

Criterion	**Energy and efficiency**	**Material amounts**	**Products & additives**	**Simplicity & generality**	**Reliability, proven?**
Rating	A	B	D	C	D

14.3.19 Maroto-Valer (Maroto-Valer *et al.*, 2005)

Feedstock	**R_{real}**	**Pre-treatment**	**T_{max}**	**P_{max}**	**Additives**	**Conversion**	**CO_2 F.E.**	**Reaction time**
S	5.38	M (100µm)	65°C	40 bar	H_2SO_4, NaOH	55%	95.54%	3hrs 10min

In this invention, silicate based materials are reacted with acid to form an aqueous suspension. Combining the suspension with CO_2 gives active carbonation resulting in metal carbonate, silica, and potential re-generable acid. In this process, the mineral (preferably serpentine) is chemically activated with sulphuric acid at temperature 20-65°C for 3-12 hours.

The resulting magnesium sulphate is reacted with sodium hydroxide to precipitate $Mg(OH)_2$ following an exothermic reaction. The $Mg(OH)_2$ subsequently reacts with CO_2 in aqueous suspension at 20°C and 40 bar. Conversion of 55% is achieved in 10 minutes under these mild conditions. In order to recover the spent acid, the inventor regenerates sulphuric acid by reacting CO_2 with $MgSO_4$. The chemical reactions below summarise all the steps the inventor presents:

1. $Mg_3Si_2O_5(OH)_4 + 3H_2SO_4 = 3MgSO_4 + 5H_2O + 2SiO_2 + 236kJ/mol$ __70%
2. $MgSO_4 + 2NaOH = Mg(OH)_2 + Na_2SO_4 + 139kJ/mol$
3. $MgSO_4 + H_2CO_3 = MgCO_3 + H_2SO_4 + 49kJ/mol$____54% at 20°C and 40 bar
4. $Mg(OH)_2 + CO_2 = MgCO_3 + H_2O + 300kJ/mol$___55%

Comments

- ✓ The cost of make- up acid and base would increase running cost
- ✓ Although a conversion of 55% is achieved, extraction reaction time is 3 hours which is high as compared carbonation with reaction time of 10 minutes

Final assessment:

Criterion	**Energy and efficiency**	**Material amounts**	**Products & additives**	**Simplicity & generality**	**Reliability, proven?**
Rating	A	D	D	C	B

14.3.20 Calera Corporation (Constantz, 2009; Constantz et al., 2009; Constantz et al., 2010a,b)

Feedstock	R_{real}	Pre-treatment	T_{max}	P_{max}	Additives	Conversion	CO_2 F.E.	Reaction time
IW	n.d	n.d	100°C	1 bar	Brine	70%	n.d	n.d

The invention involves contacting a volume of an aqueous solution of divalent cations (Mg^{2+}, Ca^{2+}) with a source of CO_2, then subjecting the resultant solution to conditions that facilitate precipitation. The alkaline-earth-metal-ion-containing water proposed include: seawater (35-50ppt salt), brackish water (0.5-35ppt salt), and brine (+50ppt salt) (ppt = parts per thousand). An alternative source of alkaline-earth-metal-ion-containing water may be prepared by adding one or more divalent metal ions (oxides or hydroxides of Ca or Mg) to water. A magnesium ion source added to initial water may be finely ground solids or aqueous solution including: serpentine, olivine, mafic and ultramafic minerals, and brucite (but not limited to this).

The dissolution of CO_2 into the aqueous solution of divalent cations produces carbonic acid. In order to produce carbonate – containing precipitate, protons (H^+) are removed from the solution to shift the equilibrium towards carbonate. The pH is important during precipitation since it prevents the shift back to acidic and precipitation of hydroxides. To attain this and to maintain a substantial constant pH value (9.5 – 11) or maximize the amount of CO_2 absorption the author proposed (Constantz et al., 2010a):

1. Natural occurring proton- removal agents e.g. lime (CaO), periclase (MgO), alkaline lakes

2. Electrochemical means - this comes along with acid generation stream such as HCl that could be used to enhance dissolution of Mg-bearing minerals.

3. Use of microorganisms and fungi that produce alkaline protease enzymes e.g. *aspergillus ustus* and *bacilluspasteulli.*

4. Synthetic chemical proton removal agents e.g. NaOH, KOH, $Ca(OH)_2$ and $Mg(OH)_2$

   The precipitation temperature may be 0-100°C (the inventors are not specific on the temperature range), pH of 9.5-11.

Process description

In Figure 60 below, water source 10 draws seawater into the precipitation reactor 20. Industrial flue gas containing CO_2 is charged into the reactor through source 30. The precipitation reactor may have a number of design features such as temperature regulators, chemical additives for raising pH, electrochemical components, mechanical agitation and monitoring parameters. The output from the reactor is directed to a separator 40. Precipitated carbonate mineral is separated from the mother liquor mechanically (mechanical pressing, vacuum filters, gravity sedimentation or centrifugation). The filter cake (precipitated carbonate) is washed to remove salt (50) and dried in drying station 60. The dried precipitate can further undergo milling 70 before use as a building material.

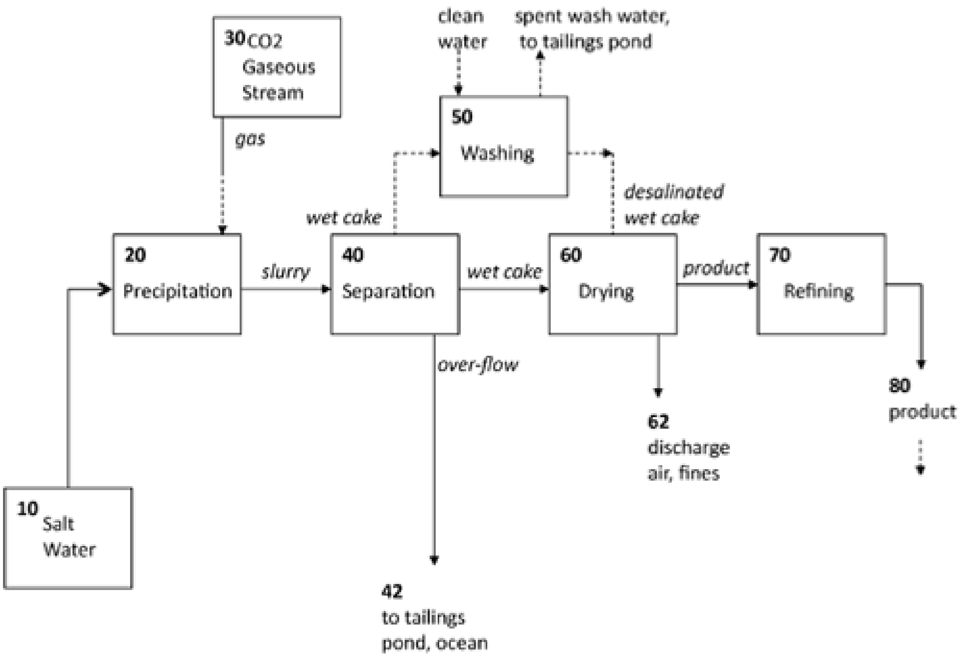


Figure 60 A block diagram of the Calera CO_2 sequestering process [Constantz et al., 2009]

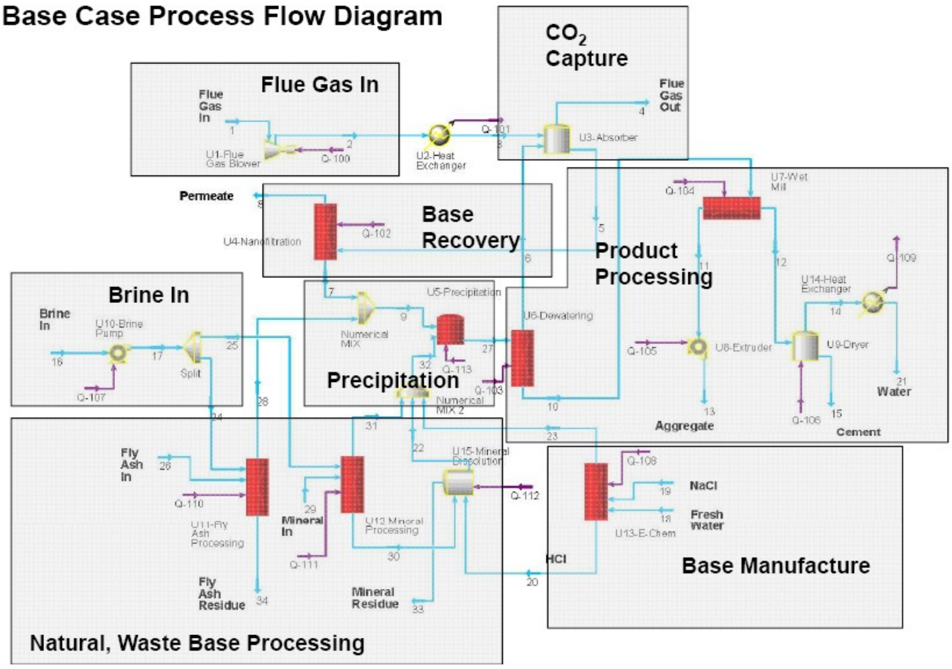


Figure 61 Process flow diagram showing varies blocks in Calera's invention [Constantz, 2009]

Comments

- ✓ The inventors state the source of pH raising agent to be NaOH that is expensive while $Mg(OH)_2$ is not naturally occurring in large amounts. The proposal of using HCl as dissolute serpentine for example will result in $MgCl_2$ hence the need for expensive hydroxide to convert this to $Mg(OH)_2$.

- ✓ Magnesium hydroxide is a rather uncommon mineral - because of its reactivity. The same holds for magnesium oxide. Therefore, aiming at producing magnesium hydroxide one typically takes magnesium carbonate and calcines this to an oxide, and then react this with water to the hydroxide. The reactions are:

$$MgCO_3 = MgO + CO_2$$

$$MgO + H_2O = Mg(OH)_2$$

CO_2 is released when calcining magnesium carbonate - thus producing CO_2 from the process

- ✓ One cannot react dolomite with seawater to form magnesium hydroxide. One has to calcine to dolomite to "dolime" (a mix of CaO and MgO) - this reacts with seawater to precipitate magnesium hydroxide (magnesium hydroxide is much less water soluble than calcium hydroxide). The reactions are:

$$CaCO_3/MgCO_3 = CaO/MgO + 2CO_2$$

$$CaO/MgO + 2H_2O + MgCl_2 = 2Mg(OH)_2 + CaCl_2$$

$$Mg(OH)_2 = MgO + H_2O$$

Again, this produces significant amounts of CO_2.

- ✓ An electrochemical approach could be energy intensive
- ✓ Although information in the patents gives less information about the process, the Calera process has been demonstrated and two pilot plants based in the USA and Australia have given promising results.

Final assessment:

Criterion	**Energy and efficiency**	**Material amounts**	**Products & additives**	**Simplicity & generality**	**Reliability, proven?**
Rating	-	-	-	-	A

14.3.21 D Vandor (Vandor, 2010)

Feedstock	**R_{real}**	**Pre-treatment**	**T_{max}**	**P_{max}**	**Additives**	**Conversion**	**CO_2 F.E.**	**Reaction time**
IW	n.d	n.d	148°C	1.1 bar	CH_3OH	n.d	n.d	n.d

This invention comprises mixing a non-aqueous solvent with alkali so as to form a suspension which is reacted with water-flue gas mixture such that a reaction occurs resulting in formation of carbonate, water and heat while substantially liquefying a portion of the nitrogen by compressing and chilling. The non-aqueous solvent (preferably an alcohol and more preferably methanol) is reacted in a mixing vessel with alkali (fly ash, bottom ash, or hydrides of K, Na or Mg) to form methoxide in mixing vessel (102, in Figure 62 below). (Methanol is used to avoid formation of salt water or carbonates in the solution and product.)

Flue gas enters the reactor at 1.1atm, so that the flue gas rises through the suspension. The unreacted gases (mainly methanol and nitrogen) leave the reactor via the top. The evaporated methanol is condensed (condenser, vessel 103) and recycled (stream 3) for mixing with the alkali (mixing vessel 102). The solid carbonate is withdrawn using an auger at the bottom of the reactor (stream 6). In the process diagram, capture and carbonation takes place at system boundary 100 and recovery of methanol at the boundary 200.

The inventor proposed three ways nitrogen is used though all of the nitrogen is first compressed. The first portion of nitrogen is used as refrigerant in the solvent regeneration process. A second portion is used to enhance the power output of a power plant (heated, compressed nitrogen is directed to a steam cycle of a power plant) and third portion is sold to off-site customers (used as a refrigerant and as a fluid). Further refining of nitrogen is can be done to remove liquid argon (0.9% volume of the recovered nitrogen stream) which is a high value product.

Comments

- ✓ Availability of fly ash could limit the scale of CO_2 storage.
- ✓ Alkalis such as KOH, NaOH, $Mg(OH)_2$ are more expensive than hydrides of potassium sodium, magnesium (KH, NaH or MgH_2 respectively) in which the author see a possible alternative for fly-ash

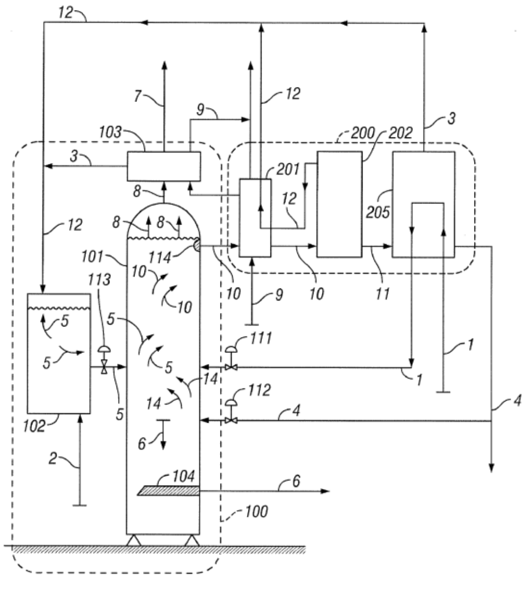


Figure 62 Flow diagram showing capture and sequestering CO_2 [Vandor, 2010]

Final assessment:

Criterion	**Energy and efficiency**	**Material amounts**	**Products & additives**	**Simplicity & generality**	**Reliability, proven?**
Rating	-	-	-	-	B

14.3.22 Caterpillar mineralisation process (Kwon *et al.*, 2009; Caterpillar, 2009)

Feedstock	R_{real}	Pre-treatment	T_{max}	P_{max}	Additives	Conversion	CO_2 F.E	Reaction time
O	2.8	M, C (10µm)	500°C	1.2	Base*	25%**	n.d	0.16

*it can be CKD, brines, wastewater from electrolysis processes, alkaline natural clay…**no process optimisation has been done.

The process developed Caterpillar is a single step direct carbonation of CO_2 from flue gases. Olivine mineral used in this process is mined and transported to the emission site. A mixture of olivine (75µm) and 'activator' (chemical additive) is ground (wet grinding) to 10µm before sprayed to SDA. The 'activator' is alkaline in nature (preferably from a waste stream, like cement kiln dust) and can be either liquid or solid. A conversion of 25% after 10 minutes has been so far though no optimisation of the process has been done. Figure 63 below shows a block diagram of the process, results achieved and some experimental conditions.

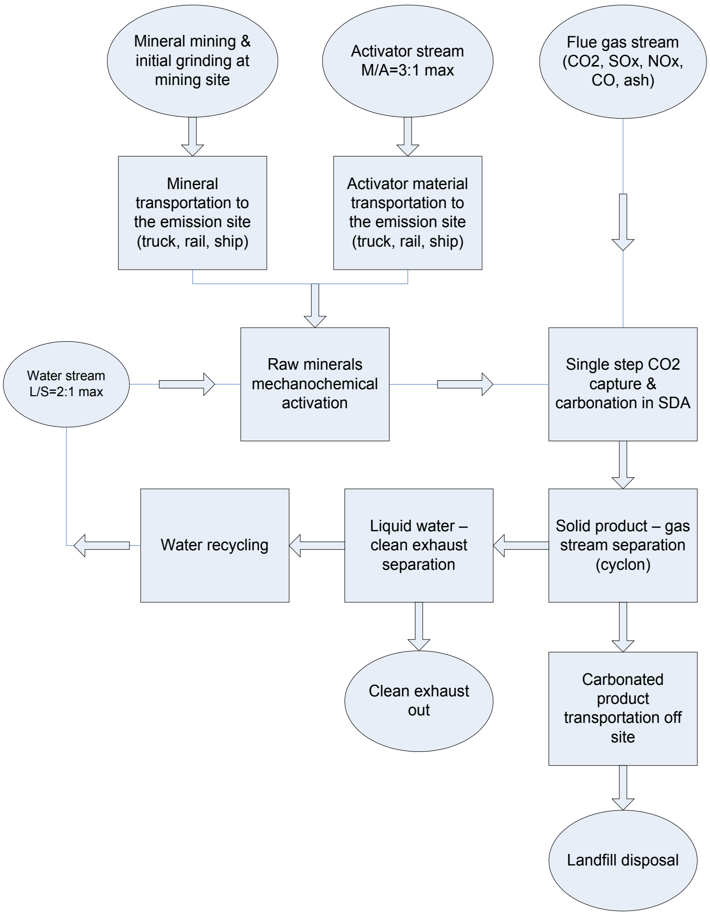


Figure 63 Caterpillar CCSM process scheme [see Appendix, Caterpillar Inc., 2009]

Comments

- ✓ CO_2 capture, separation and compression has been eliminated from the process.
- ✓ Mineralisation takes place at the CO_2 source, which means transportation of the mineral to CO_2 source.

✓ The process is aimed for relatively small CO_2 streams; for chemical processes rather than power plant

Final assessment:

Criterion	Energy and efficiency	Material amounts	Products & additives	Simplicity & generality	Reliability, proven?
Rating	B	B	C	B	B

Park (Park & Fan, 2004; Park et al., 2003)

Feedstock	R_{real}	Pre-treatment	T_{max}	P_{max}	Additives	Conversion	CO_2 F.E	Reaction time
S	3.23	M (75µm)	70°C	1 bar	1 vol% orthophosphoric*	65%	%	~1 hour

*1 vol% orthophosphoric acid +0.9wt% oxalic acid + 0.1wt% EDTA

Identifying dissolution of mineral as a limitation to mineral carbonation process, Park and co-workers set up experiments to identify a chemical additive/ catalyst to achieve magnesium silicate dissolution at low cost. Acidity coming from the dissolution of CO_2 in water is not sufficient to dissolve the mineral. Nine different additives were investigated. Of the nine, it was found out that a mixture of 1vol% orthophosphoric acid + 0.9wt% oxalic acid + 0.1wt% EDTA enhanced leaching of Mg at 70°C. Figure 64 below shows name, concentrations, and results of the different additives after 2 hours of leaching.

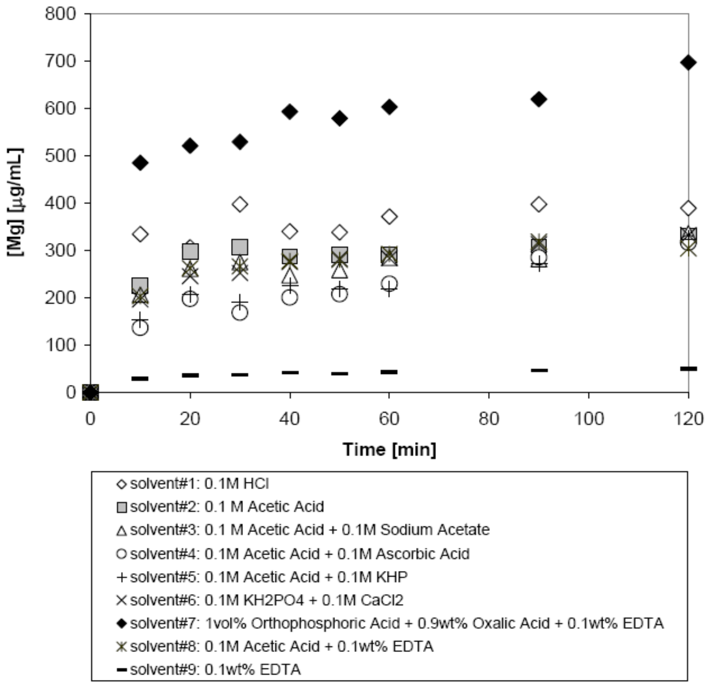


Figure 64 Dissolution of serpentine: Time vs. Mg concentration in filtrates of solvents at ambient temperature and pressure [Park *et al.*, 2003]

Based on dissolution of serpentine findings, ground serpentine (75µm) was dissolved in acidic solvent 1vol% orthophosphoric acid + 0.9wt% oxalic acid + 0.1wt% EDTA. After 1 hour, the slurry was filtered to remove SiO_2 undissolved matter. The filtrate rich in Mg^{2+} and Fe^{2+} was cooled to ambient temperature and pH raised by adding NH_4OH to precipitate iron oxide. Finally, on bubbling through CO_2, Mg^{2+} carbonated to $MgCO_3$ that precipitated at ambient temperature. Additional NH_4OH was added to raise the pH to counter the acidity caused by dissolution of CO_2 in the solution. Overall, conversion of 65% is achieved at low operating condition 70°C and 1atm.

Comments

- ✓Recovery of additive not addressed

Final assessment:

Criterion	**Energy and efficiency**	**Material amounts**	**Products & additives**	**Simplicity & generality**	**Reliability, proven?**
Rating	-	C	D	B	C

14.3.23 J D Jones (Jones, 2009; Layton, 2010)

Feedstock	**R_{real}**	**Pre-treatment**	**T_{max}**	**P_{max}**	**Additives**	**Conversion**	**CO_2 F.E**	**Reaction time**
NaCl		Electrolysis				98%	58.4	n.d

In this sequestration process, carbon dioxide is absorbed into an aqueous caustic soda mixture and reacts with hydroxide to form carbonate and/or bicarbonate products. Flue gas from power plant is cooled from 300°C to 30°C in a series of heat exchangers. CO_2 is introduced at the bottom of absorption chamber, which the gas is injected with an effect that causes bubbles to rise. The de-carbonated flue gas leaves the absorber at a top vent. Reaction taking place in the carbonation chamber are:

$$2NaOH + CO_2 = Na_2CO_3 + H_2O \text{ and } Na_2CO_3 + H_2O + CO_2 = 2NaHCO_3$$

The carbonate and bicarbonate formed are separated from the liquid solution by heating. Heating can be done by exchange of heat with the flue gas (93% purity of Na_2CO_3 is achieved) or heat derived from hydrogen produced in electrolysis. NaOH used in de-carbonation process is produced by brine electrolysis. In the membrane cell processing units, the following inputs and products are obtained:

At anode: 26% NaCl + 2,275 kWh/tonne $Cl_2 = Cl_2$ (g) + 24% NaOH

At cathode: $H_2O + e =$ 30-33% NaOH + H_2 (g)

Figure 65 below presents a detailed flow sheet of the process.

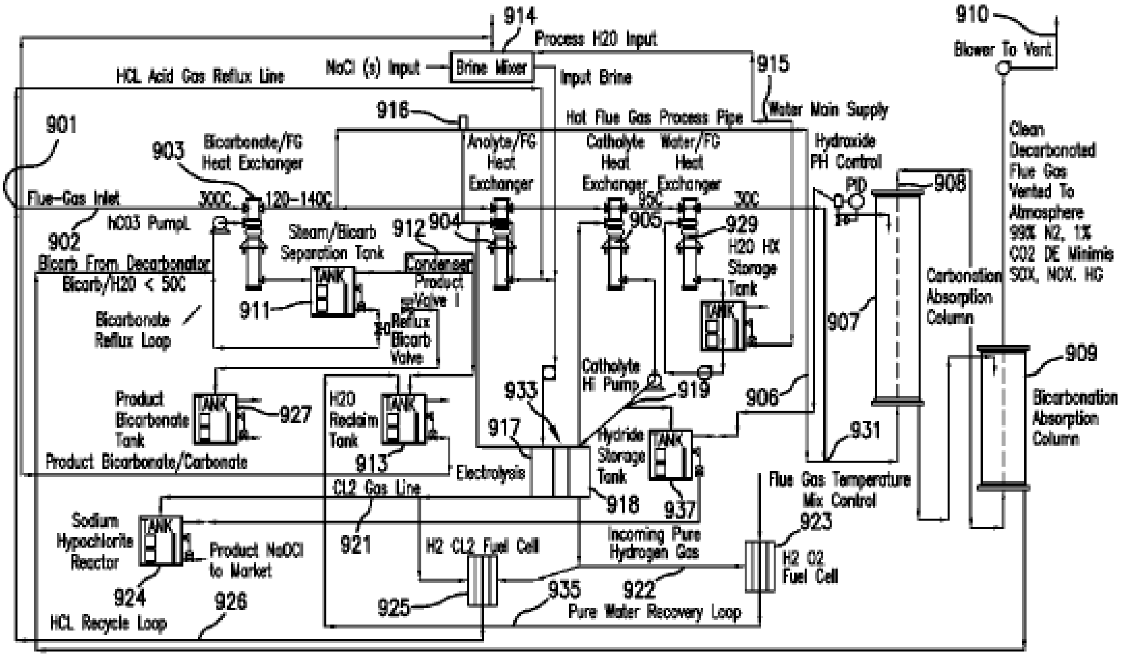


Figure 65 Carbonation process for producing baking soda with electrolytic production of caustic soda [Jones, 2009]

Flue gas enters the process at 901. Heat exchangers 903, 904 and 905 reduce the temperature of flue steam to 30°C. It enters absorption chambers 908 and 909 where carbonation takes place, and clean gas leaves the process via vent 910. Electrolysis that takes place in vessel 917 produces Cl_2 and H_2 that are stored in tanks 924 and 937, respectively. A simplification of the process is given below.

The process concept is also referred to as SkyMine.

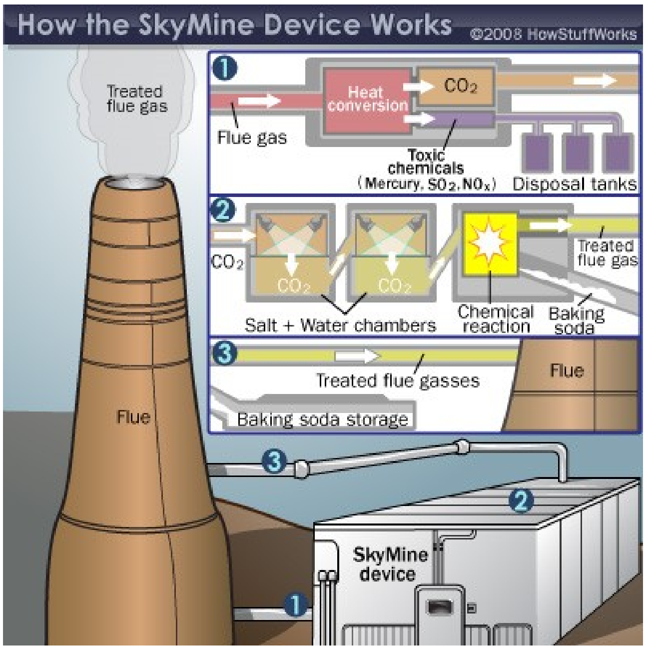


Figure 66 The SkyMine concept [Layton, 2010]

Comment

- ✓ This process uses large amounts of NaOH and /or electricity. Baking soda market soon saturated.
- ✓ Integration with chlorine production adds very much complexity, makes it energy-intensive, but may give revenues that can cover for costs. Balancing a set of objectives in combination with CCS may be a challenge in reality.

Final assessment:

Criterion	**Energy and efficiency**	**Material amounts**	**Products & additives**	**Simplicity & generality**	**Reliability, proven?**
Rating	C	-	-	-	A

14.3.24 DaCosta (DaCosta *et al.*, 2010)

Feedstock	**R_{real}**	**Pre-treatment**	**T_{max}**	**P_{max}**	**Additives**	**Conversion**	**CO_2 F.E**	**Reaction time**
Olivine	n.d	M	500°C		n.d	n.d	n.d	0.5

DaCosta and co-workers came up with a method for CO_2 sequestration where the flue gas containing CO_2 goes through a bed of finely ground particulate material (olivine, serpentine, wollastonite, bredigite, rankinite, spurrite or a combination thereof). The bed of material is positioned directly in the flue gas channel. As carbonation takes place, the mineral is replenished by either feeding fresh mineral with a pump or conveyer for vertical orientation (Figure 67) or other ways proposed by the author.

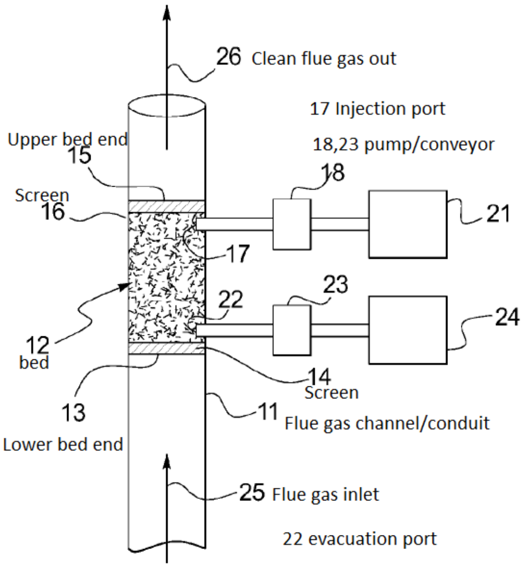


Figure 67 Flue conduit equipped with a bed of particulate material [DaCosta *et al.*, 2010]

Experimental results presented by the author (olivine ground to a surface area of 2.5m^2/g, at temperatures ranging from 100 to 500°C (+-10%) and flue composition 10% CO_2, 8.3% H_2O and balance N_2) indicated the capture capacity for 0.5g of olivine is 2g CO_2/g olivine and for 5g olivine is 0.12g CO_2/g olivine. Results presented in the Figure 68 below shows efficacy of using ground olivine in a bed for removing carbon dioxide gas stream with or without vapour.

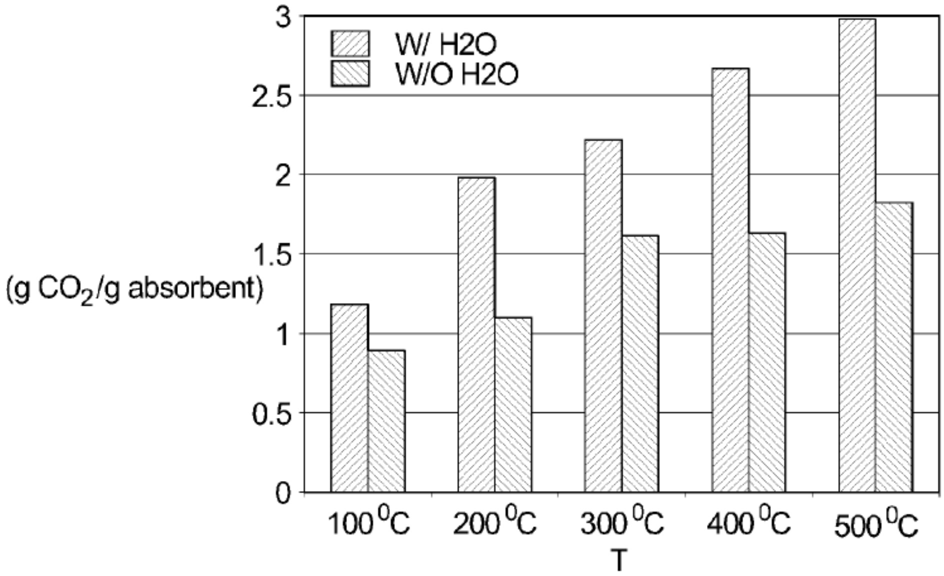


Figure 68 Olivine carbonation efficacy using flue stream with or without vapour [DaCosta *et al.*, 2010]

Comments

✓Most of the energy required will be for grinding to ca. 2.5-60μm

Final assessment:

Criterion	**Energy and efficiency**	**Material amounts**	**Products & additives**	**Simplicity & generality**	**Reliability, proven?**
Rating		-	-	-	B

14.4 TECHNOLOGY READINESS LEVEL ASSESSMENTS

In addition to the assessment of the 25 technologies identified above, the consortium also assessed the technology readiness levels of the processes. The technology readiness level (TRL) definitions described in Section 10.3 were used to assign the following TRL status values (Table 27) to the identified technologies based on the information available in the public domain about their level of deployment. Although not immediately apparent from their publications, for the Calera (Technology 20) and Jones (Technology 24) cases the consortium has assumed that, in order to qualify for their recently announced Department of Energy funding awards, they must be at least at TRL 4.

Technology	TRL
1ARC- Serpentine	4
2 ARC-Olivine	4
3 Shell- Serpentine	3
Shell- Olivine	3
4 Rau & Caldeira	1 / 2
5 N'ham process	3
6 Hunwick	2
7 Brent	2
8 Åbo Akademi	3
9 Huijgen	4
10 Baldyga	1 / 2
11 Munz *et al.*	2
12 Lin *et al.*	2 / 3
13 Baciocchi (wet)	3
Baciocchi (dry)	3
14 Reddy	3
15 Kodama	3 / 4
16 Krevor	3
17 Kwak	1
18 Schiller	2
19 Maroto-Valer	3
20 Calera Corp.	4
21 Vandor	2 / 3
22 Caterpillar	2
23 Park	3
24 Jones	4
25 DaCosta	2

Table 27 Technology Readiness Level Status of the Identified CCSM Systems

14.5 CONCLUSIONS

14.5.1 Summary of the assessment

Based on the assessment criteria described in section 10.2, the table below gives the weighted ranking of the processes, adding up points (A = 5 p.… E = 1 p) for the five criteria.

Assessment: processes marked ¤ most promising

Criteria process	Energy need[1]	Mineral req.[2]	Valuable products[3]	Apparent simplicity[4]	Apparent feasibility	CO_2 stream	Reaction time (minutes)	Scale of operation
1ARC- Serpentine ¤	B	C	D	A	A	Pure	120	Pilot
2 ARC-Olivine ¤	E	B	D	A	A	Pure	120	Pilot
3 Shell- Serpentine ¤	-	-	C	A	A	Flue	-	Pilot
Shell- Olivine	-	A	C	B	B	Pure	1,260	Pilot
4 Rau & Caldeira	-	-	-	-	-	-	-	-
5 N'ham process ¤	-	-	C	B	B	Flue	180 +	Lab
6 Hunwick ¤	B	C	B	B	C	Flue	60	No test
7 Brent ¤	B	C	B	A	B	Flue	60	Lab
8 Åbo Akademi ¤	B	D	B	B	B	Pure	30	Lab
9 Huijgen ¤	B	B	C	B	C	Pure	15	Lab
10 Baldyga	-	A	D	-	C	Pure	60	Lab
11 Munz *et al.*	-	-	-	-	-	Pure	-	Lab
12 Lin *et al.*	E	E	D	C	C	Flue	1,560	Lab
13 Baciocchi (wet)	-	B	C	C	C	Flue	60	Lab
Baciocchi (dry)	-	B	C	C	B	Flue	10	Lab
14 Reddy	E	-	C	C	D	Flue	10	Lab
15 Kodama	B	C	D	C	D	Flue	90	Lab
16 Krevor*	-	C	D	D	C	Pure	120	Lab
17 Kwak	E	E	C	D	D	Pure	1,200	Lab
18 Schiller ¤	A	B	D	C	D	Pure	60	No test
19 Maroto-Valer	A	D	D	C	B	Pure	190	Lab
20 Calera Corp.	-	-	-	-	A	Flue	-	Industrial
21 Vandor	-	-	-	-	B	Flue	-	No test
22 Caterpillar ¤	B	B	C	B	B	Flue	19	Lab
23 Park	-	C	D	B	C	Pure	~60	Lab
24 Jones	-	-	-	-	A	Flue	-	Industrial
25 DaCosta	-	-	-	-	B	Flue	30	Lab

1 CO_2 storage efficiency, 2 mineral input and products output stream, 3 valuable products versus not recovered chemicals additives, 4 apparent simplicity and generality, *further work is done to improve this process.

Table 28 Technology Assessments and Weighted Ranking [©Shell Global Solutions]

In the assessment of the processes, a key issue was availability of the relevant data. However, some of the processes could not be ranked because of a lack of information. It is worth highlighting that the assessment was based on the data found in the open literature, conference and journal papers, patents, newsprint and communication with the process developers (authors), besides documents (often confidential) kindly provided by the consortium partners. Some of the assumptions made are:

- Flue gas composition is the same for the processes although it varied from 10-20% depending on the source and some never mentioned the composition.

Minerals mentioned have the same carbonation potential (“serpentine” from Finland = “serpentine” from the U.S.).

When the TRL status assessment values are overlaid on the technology category figure shown in the introduction (as in Figure 69, overleaf) it can be seen that no one category is receiving more attention than the others nor are any technologies or technology categories accelerating ahead of the others in terms of rate of development.

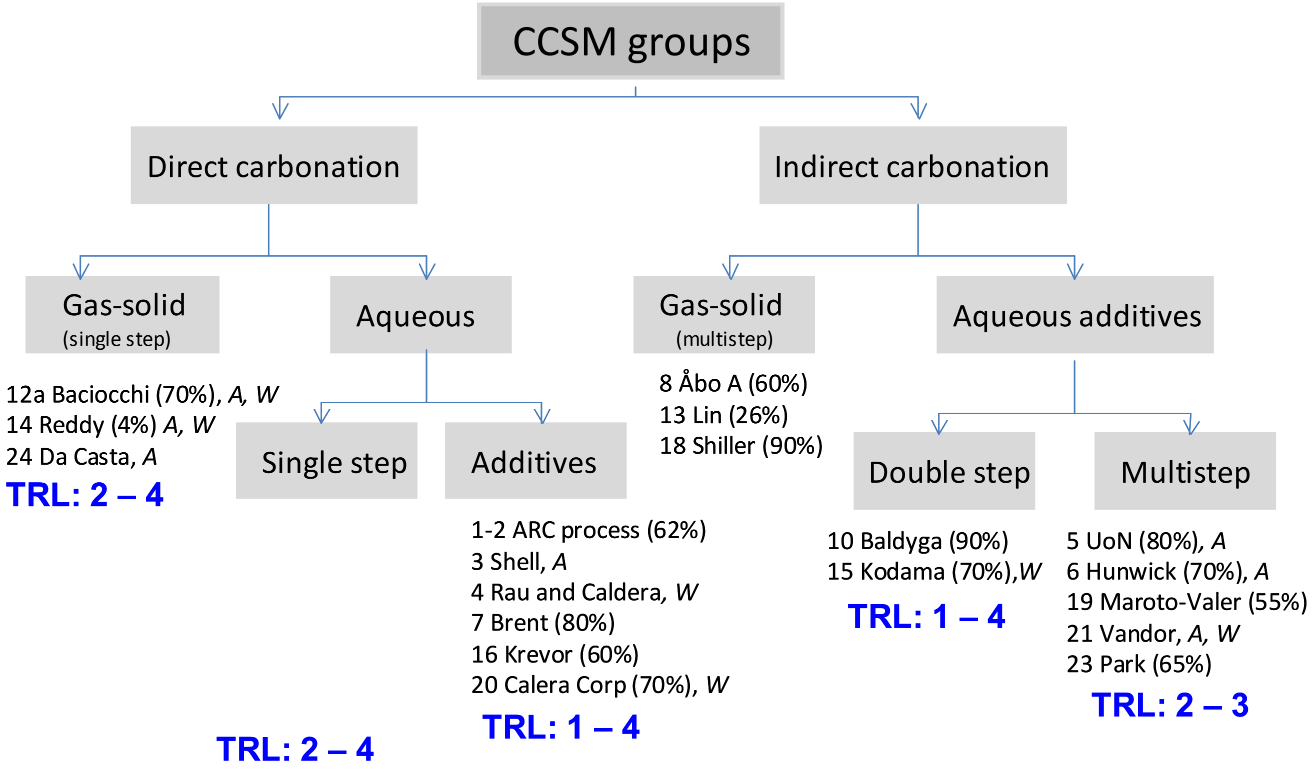


Figure 69 CCSM Technology Categories with TRL Status Value Ranges [Copyright University of Nottingham]

14.5.2 Summary of results

A first conclusion from an assessment of the processes listed above is that after the ARC process development, and the reporting of it, some progress was made in the form of promising new concepts for which claims are laid down in patents. A closer look that these, however, makes it in many cases difficult to assess the viability since crucial information to support the claims is missing, in most cases simply because no attempts were made to test the concepts experimentally. For example, amounts of material per unit mass CO_2, the use of special chemicals, time needed for high levels of carbonation conversion, pressure and temperature levels, water use, product type and quality, requirements for power and heat and the temperature of the latter are scarcely mentioned.

Below, several overview-figures show the energy requirements as heat, power, and the sum of the two as the useful energy (work), i.e. exergy, respectively. The many instances where a value = 0 is indicated presumably result from a lack of energy data (Rau, Baldyga, Baciocchi, Reddy, Krevor and Caterpillar) and for the ARC cases heat was penalised as power.

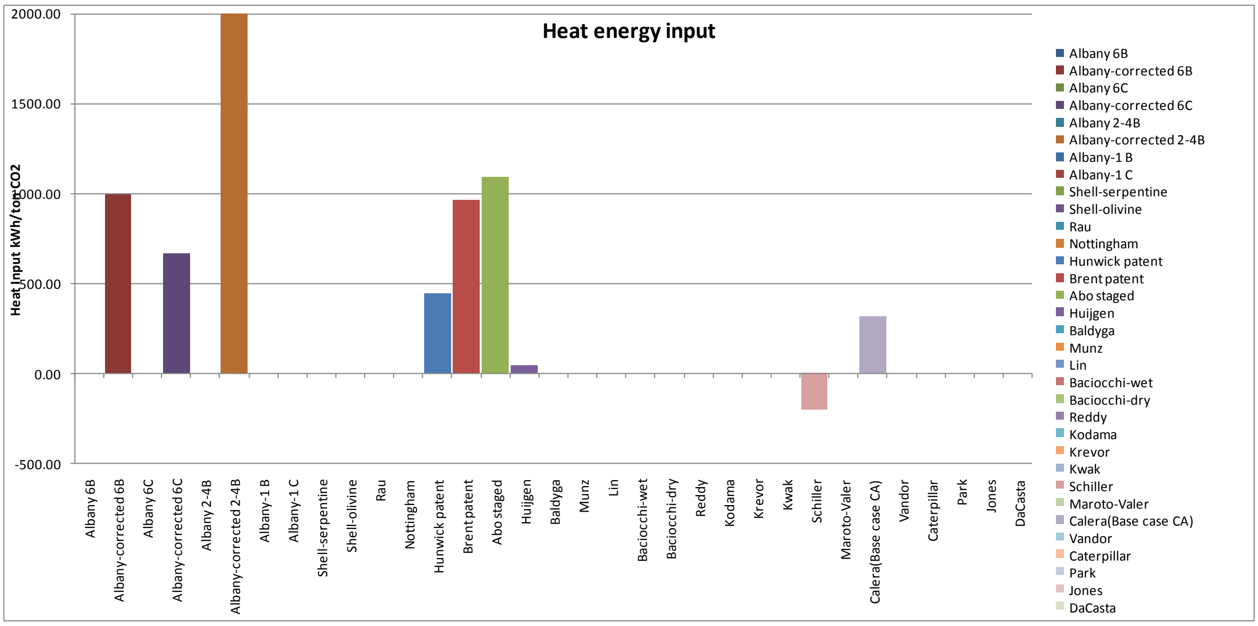


Figure 70 Heat Energy Input. [©Shell Global Solutions]

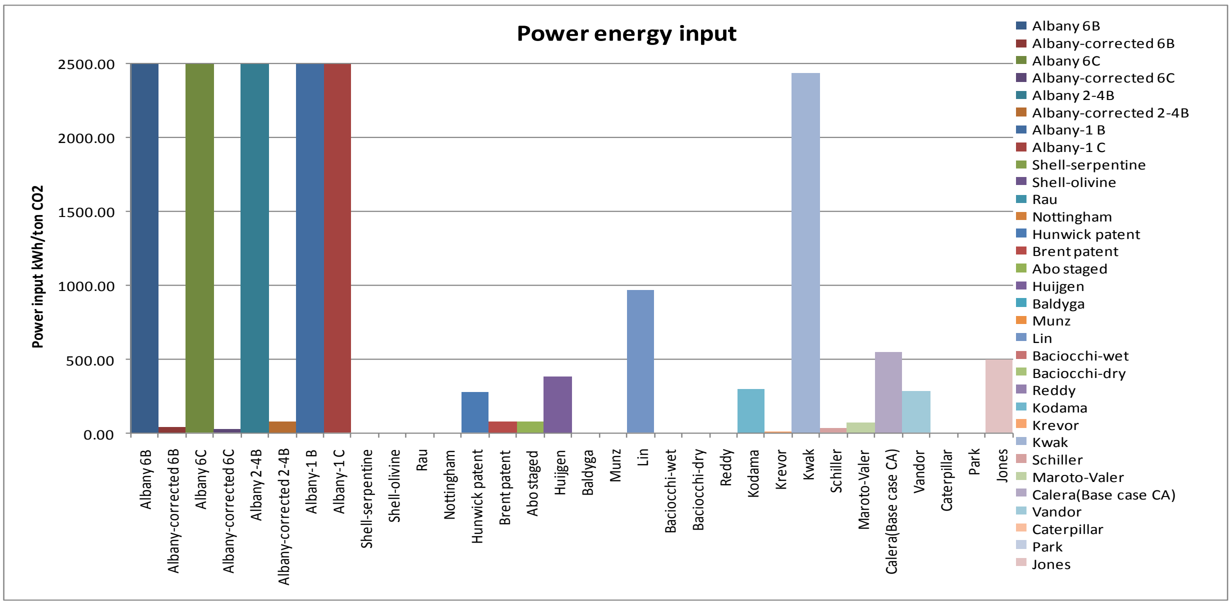


Figure 71 Power Energy Input. [©Shell Global Solutions]

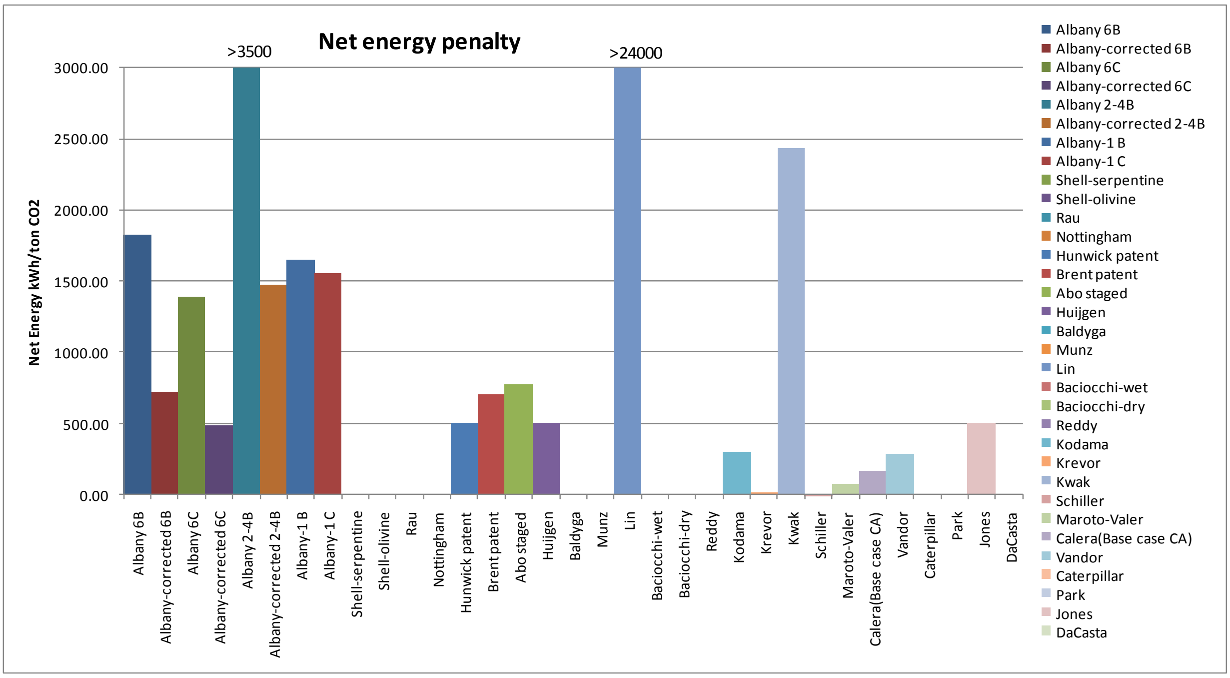


Figure 72 Combined exergy assuming a temperature of the surrounding to be 15°C (288 K). [©Shell Global Solutions]

The exergy of power P equals Ex(P) = P, while the exergy of heat Q equals Ex(Q) = Q·(1-T°/T), with surroundings temperature T° (K), temperature of the heat T (K).

The assessment shows that as well as the ARC concept several other processes have the potential to fix CO_2 at a similar overall energy requirement.

Moreover, note 1kWh heat from a fossil fuel typically generates 0.2kg CO_2, i.e. 1kg CO_2 per 5kWh, with a roughly three times higher number for power production. The data therefore shows that CCSM processes have net CO_2 reduction as long as energy requirements stay significantly below 1.5kWh/kg or 1,500kWh/tonne. (This then implies a CO_2 fixation efficiency of 70%).

The process routes by Schiller (18), Maroto-Valer (19), and Vandor (21) gave less information, making these processes look energy-efficient. However, process 19 (Maroto-Valer) operates at ambient temperature hence the bulk of energy needed is for pre-treatment of the mineral. Bond's equation is used to calculate the corresponding energy for grinding.

The CO_2 fixation efficiency is of the order of 60-80% for the most processes for which experimental tests have been done. Secondly, processes with CO_2 fixation efficiency above 90% are theoretical processes where no experiments have been done and it either assumes 100% heat recovery from a process (process19) or uses exotic additives (yet to be recycled, as in processes 17 and 20).

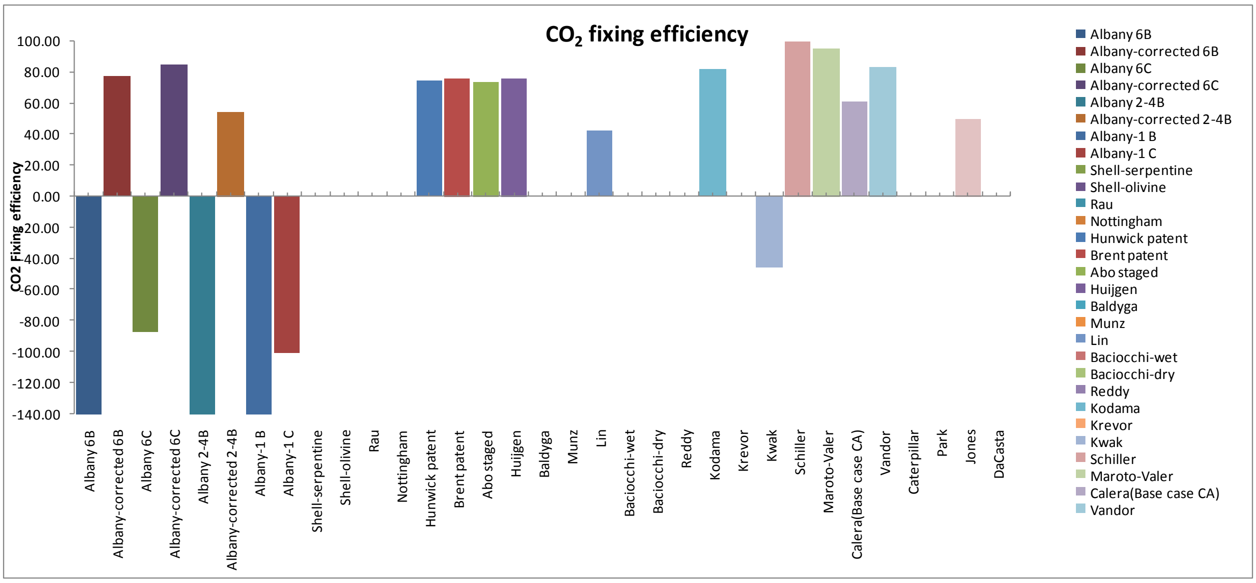


Figure 73 CO$_2$ Fixing Efficiency. [©Shell Global Solutions]

Mineral/rock input requirements, for as far reported show values below 6kg/kg CO$_2$ for the most feasible processes. Again, no data can be found for many processes.

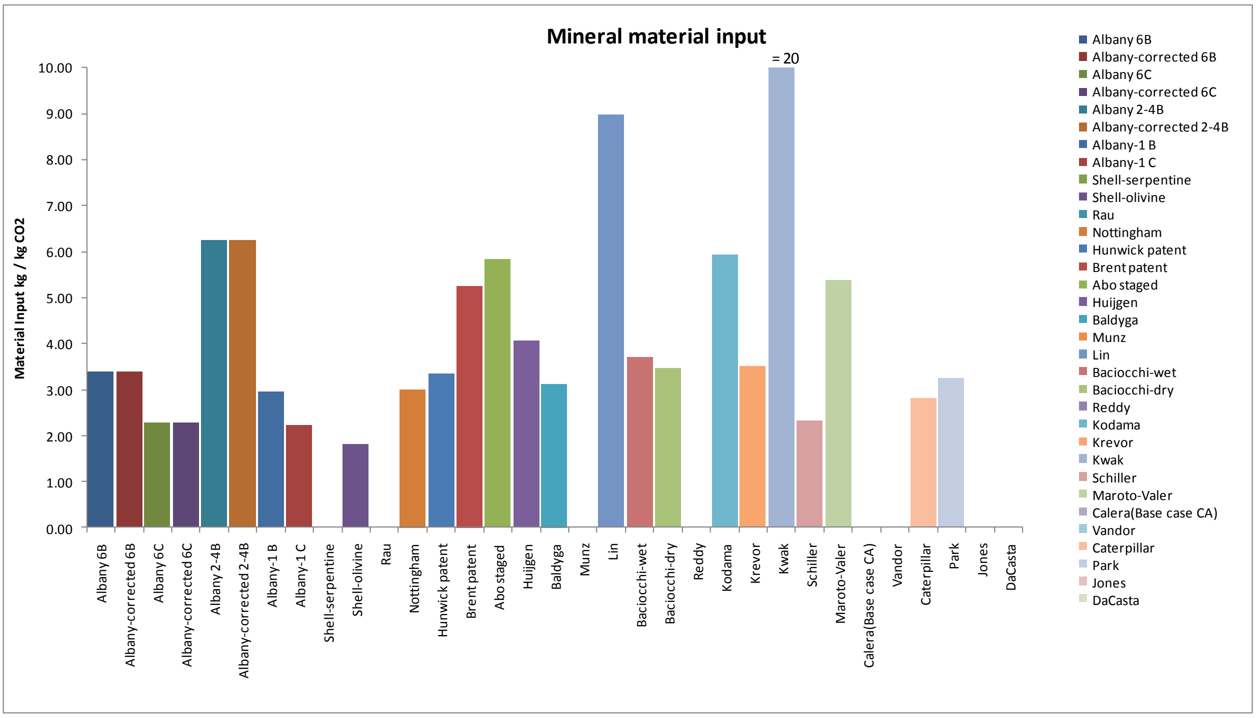


Figure 74 Mineral Material Input. [©Shell Global Solutions]

14.6 TECHNOLOGY ASSESSMENT CONCLUSIONS

It was discussed previously that the deployment of mineral carbonation is dependent on the development of low energy intensive processes with high mineral reaction conversion and fast reaction kinetics. The descriptions of 25 CCSM technologies above illustrate the various process routes created to provide potential solutions for capturing and storing CO_2. Although a number of processes are novel and no experimental work was done or made public, some processes look promising (marked ¤). The essential building blocks of described CCSM technologies include a mineral ***activation*** step (mechanical, chemical, thermal) and a ***carbonation*** step; the need for post-treatment of the carbonation products for either utilization or disposal has been discussed but not addressed at this stage of CCSM development.

Mechanical activation promotes structural and morphological changes in minerals via mechanical stress and in-situ generated heat. High surface area produced through size reduction and cracks significantly lower mass transfer limitations and accelerates follow up chemical reactions (dissolution, carbonation). High-energy penalty so far is an important drawback.

An alternative approach used in many CCSM technologies involves ***chemical activation*** of minerals in presence of various aqueous chemical additives. Type of additive controls not only mineral dissolution rate and degree of leaching, but also CO_2 dissolution rate, carbonation rate, and solid product precipitation rate in aqueous media. Chemical consumption, cost, and regeneration are the main challenges.

Thermal activation (also called dehydroxylation) of minerals, namely serpentines, has also been explored, and nearly an order of magnitude increase in dissolution rates has been demonstrated after heat exposure. Meanwhile, important detailed information on the cost/energy balance for thermal activation is not available.

All three types of mineral activation methods were considered as stand-alone, and no consideration for their integration (thermo-mechanical, mechano-chemical, etc.) has been considered thus far. Meanwhile, it should be mentioned that all three methods are well-established large-scale mineral processing technologies.

With regard to the ***carbonation*** step, a low reaction rate due to significant mass transfer limitations, sub-stoichiometric mineral utilization, as well as substantial energy consumption (in terms of temperature, pressure and process duration) requires further improvement and optimization. In order to achieve this, the following gaps in carbonation fundamentals will have to be addressed:

- Insufficient knowledge of indirect (gas-liquid-solid) carbonation fundamentals (optimum particle size distribution, P, T, pH, ionic strength to promote CO_2 transfer from flue gas and ion-exchange, etc.)
- Insufficient knowledge of carbonation fundamentals using flue gas
- Lack of assessed large scale carbonation reactor technology options and cost studies
- Carbonation tests were not verified on representative raw minerals
- Process performance data incomplete and inaccurate
- Integration options CCSM with CO_2 emission point source largely overlooked

Since a number of processes are new and lack sufficient evidence of feasibility, further experiments to generate complete data sets and some simple analysis using tools such HSC (Gibbs energy minimization) should be made to ascertain claims of various authors using their reaction conditions. It is clear that further applied research is required to advance promising process concepts into a commercially viable and executable mineral carbonation system that operates at industrial scales. The suggested path forward will be discussed in Chapter 17.

15 Current Estimated Costs of CCSM and Potential Cost Reduction Opportunities

The overall costs of the CCSM technologies available currently range from £160/tonne CO_2 to £300/tonne CO_2, therefore the mineralisation state of the art currently has higher costs compared to geological sequestration. However, geological sequestration is geographically limited to certain areas, requires a significant pipeline system investment, and may not be appropriate for small or medium emitters, while CCSM can overcome its cost penalty by focussing on mitigating CO_2 from small emitters and in areas where geological CCS cannot be deployed.

The available sequestration costs for the CCSM technologies are summarised in Table 29 where the data reported in a previews economic comparison (Huijgen et al, 2007) have been updated with new economic assessments. It is important to highlight that these assessments were done using different methods and the aim is to establish the wide range of costs involved in the mineralisation technology and not to compare single technologies. The estimated cost of geological sequestration (GS) was considered as a base to establish the penalty cost of CCSM. About £45-55/tonne CO_2 avoided were assigned to GS considering the values reported in the IPCC report (£1-6/tonne CO_2) and the energy cost of the amine capture stage of £45/tonne CO_2 (Kothandaraman, 2010). CCSM using Ca-silicate rocks or waste materials shows an average cost of £94/tonne CO_2 while the CCSM cost increases to £155/tonne CO_2 in average if Mg-rocks are used as feedstock. The recent industrial assessments made by Shell and Caterpillar indicate a most likely cost ranging from £200-300/tonne CO_2 for direct carbonation using flue gases instead pure carbon dioxide. The ARC process usually considered as the mineralisation state of the art shows costs between £80 and 180/tonne CO_2. Other processes such as the UoN, Kodama show promising estimated energy cost between £65-70/tonne CO_2, but capital and operational costs were not assessed. Åbo Akademi processes has an estimated cost of £70-100 CO_2.

The economics laid out below refers to the mineralisation technology and capture stage but does not include post-processing, landfilling and transport of material in/out from the conversion site. Therefore, it was made an effort to estimate the possible overall costs involved in the mineralisation technology by a generic economic evaluation of the Albany Research Centre (ARC) single-step wet carbonation process using serpentine as reported in Table 29. The ARC process was chosen for the serpentine assessment, because considered the state of the art of the technology (IPCC, 2005). A large values variation has to be account in the interpretation of the following data, considering all the caveats and the absence of a complete and specific economic evaluation in literature due to the early development stage of the mineralisation technology.

Process or reference	Feedstock	Cost (£/t CO_2)	Capture cost (£/t CO_2)	Tot Cost (£/t CO_2)
Geologica sequest. (IPCC, 2005)	/	[1] 1-6	[2] 45	46-51
Oceanic sequest. (IPCC, 2005)	/	3-21	[2] 45	48-66
Huijgen et al, 2007	Wollastonite	87	[2] 45	132
Huijgen et al, 2007	Steel slag	65	[2] 45	110
Iizuka et al, 2004	Waste cement	[4] 21	[2] 45	66
ARC, 2000	Olivine	38	[2] 45	83
ARC, 2000	Serpentine	50-135	[2] 45	95-180
IEA, 2000	Mg-silicate (direct)	80	[2] 45	125
IEA, 2000	Mg-silicate (indirect, HCl)	> 127	[2] 45	> 173
UoN. 2010	Serpentine	[4] 47	[3] 20	67
Kodama et al. 2008	Ca-silicate	[4] 24	[2] 45	69
Abo Akademi, 2010	Serpentine	32-55	[2] 45	77-100
Shell, 2010	Serpentine	[5] 218-313	[7] 0	218-313
Caterpillar, 2010	Olivine	[6] 20-205	[7] 0	20-205
Most probable range				150-250

* These economic analyses were not done on the same basis; Exchange rate of $1 = £0.64

1 IPCC reports costs ranging from £1 to 6/tonne CO_2 without consider the capture costs. Other studies show an energy penalty of 364kWh/tonne that gives ~£ 45/tonne CO_2 of energy cost (Kothandaraman, 2010).

2 Based on capture stage energy requirement of 364 kWh/tonne CO_2 for amine stripping and considering £ 0.08 / kWh. Costs do not include injection underground and transport of CO_2 on site (Kothandaraman, 2010).

3 Chilled ammonia capture process requires 477 kWh/tonne CO_2 of which 60% is absorbed for compression and desorption stages that are not required for the UoN process. Therefore, only 191 kWh/tonne CO_2 (£ 20/tonne CO_2).

4 Only energy costs are included, capital and operational costs not available.

5 Capital and operation costs included, products are not dried, and used/disposed wet.

6 Max value with technology well developed (90% CO_2 capture efficiency), Min value with early stage technology (25% CO_2 capture efficiency). Capital costs (£7-117/tonne CO_2); Operational costs (£ 13-88/tonne CO_2).

7 They use directly flue gas. No capture stage is required.

Table 29 List of the available CCSM technologies sequestration costs using different feedstock and other CCS technologies costs

The overall mineralisation process was divided in 9 different blocks: rocks mining, crushing, transport, grinding, CO_2 capture, carbonation, post processing, transport and landfill of products. Some of the economic blocks are reported in Table 30 while the others were roughly assessed here.

Two extreme scenarios were considered:

- In the *worst* case we considered the ARC process economics assuming the average cost of the technology (£135/tonne CO_2)(IPCC, 2005), a CO_2 capture stage, no value generated by the powders produced with transport and 4.4 tonnes of products landfilled. The carbonation reaction was considered at 70% efficiency (3.4t Serpentine + 1 tonne $CO_2 \rightarrow$ 1.5 tonnes SiO_2 + 2.6 tonnes $MgCO_3$ + 0.1 tonnes FeO), Transport was assumed as £4/tonne rock (by sea) plus £12/tonne CO_2 (by truck for a distance lower than 10 miles).
- In the *best* case we assume that mature carbonation processes would be able to decrease the cost of the pre-treatment and conversion costs, to work with flue gas instead of pure CO_2, to decrease the transport costs and finally, to sell part of the powders produced (100% of silica sand and iron ore pellets for steel production). The carbonation reaction was considered at 90% efficiency (2.2 tonnes Serpentine + 1 tonne $CO_2 \rightarrow$ 1.1 tonnes SiO_2 + 1.9 tonnes $MgCO_3$ + 0.07 tonnes FeO. Transport

was assumed as £4/tonne rock (by sea) plus £1/tonne CO_2 (by rail for a distance lower than 10 miles). Carbonation costs of £40/tonne CO_2 was used representing the cost average of Kodama, ARC (olivine), Åbo A., and UoN processes (£40/tonne CO_2). Capture stage was not considered speculating that the mature technology will not require it (Processes such as Shell and Caterpillar are already exploring this pathway). It was assumed to landfill 1.95 tonnes of $MgCO_3$ and to produce 1 tonne of silica sand (£13/tonne value and £6/tonne production cost) and 0.1 tonnes of FeO for steel works as a feedstock (£33/tonne value and £3/tonne cost).

Serpentine was chosen to assess the carbonation technology being the main resource in the UK among the usable minerals.

The worst case indicates that the mineralisation costs of ARC process using serpentine is around £250/tonne CO_2 when costs of material extraction and transport of products and landfill costs are added to the cost provided in Table 29. In comparison, the geological storage can be done at £72/tonne CO_2. The overall costs of mineralisation using serpentine would decrease to about £85/tonne CO_2, if the technology would be able to use directly flue gas, significantly decrease the pre-treatment and carbonation costs from £110 to about £40/tonne CO_2 and sell part of the products (100% of silica and iron products). Instead, geological storage costs about £40/tonne CO_2 in its best case.

This rough assessment indicates that about £75/tonne CO_2 need to be added to the values shown in Table 29 to consider the overall costs involved in the CO_2 sequestration under the worst scenario. In the best case, only about £30/tonne CO_2 would be required in addition to the costs shown in Table 29. However, this scenario would not involve a CO_2 capture stage, would involve lower pre-treatment and conversion costs and the commercialisation of the silica and iron ore products.

	Mining[1]	Crushing	Transport	Grinding	CO_2 Capture[2,3]	Carbonation[4]	Products[5]	Transport	Landfill		
		2 kWh/t		(100 kWh/t)	(364 kWh/t CO_2)					**CCSM**	**Geolog. Storage[3]**
Energy (kWh/t CO_2)		6		220-340	0-364						
Cost (£/t CO_2) Worst case	6.8	0.5	26	27	45	108	0	30	11	**254**	**72**
Cost (£/t CO_2) Best case	4.4	0.5	10	18	0	40	-7	14	5	**85**	**39**

Table 30 Approximate economic evaluation.

[1] M Styles et al, 2010, [2] Kothandaraman A, 2010, [3] GCCSI, 2009, [4] Carbonation costs of £135/tonne CO_2 (IPCC, 2005) including pre-treatment in the worst case; in the best case costs of £40/tonne CO_2 (average of UoN, Kodama, Åbo and ARC olivine processes) were considered, [5]Assuming 100% of silica and iron oxide sold at the following prices: SiO_2 (13 £/tonne), Iron ore pellets (33 £/tonne).

The overall costs of the CCSM technologies available currently range from £85/tonne CO_2 to £254/tonne CO_2, therefore the mineralisation state of the art shows higher costs compared to the geological sequestration costs that range from £50 to £100 per tonne of CO_2. However, geological sequestration is geographically limited to certain areas, requires a massive pipe system and it is not appropriate for small or medium emitters, while CCSM can overcome its energy penalty sequestrating CO_2 from small emitters and in areas where GS cannot be deployed.

CCSM costs can be significantly reduced. For example Shell can compress the costs of his process by reducing flue gas pressure drop hence reducing booster requirements, capital expenses for dehydroxylator and by the integration of different plant sections (e.g.

dehydroxylator coupling with power plant), even if the reduction quantification has not be done yet. Similarly, Caterpillar indicates that the costs of his process might be significantly reduced if the CO_2 capture efficiency will reach 90%. Overall, capture, grinding and carbonation are the step that can suffer high cost reduction. For example, the energy required for grinding calcium carbonate to <2μm for PCC production has dropped from 250kWh/tonne in 1995, 0.5 tonnes/h and 180kWh/tonne in 2003, to reach 2.0 tonnes/h and 90kWh/tonne in 2005 (Zheng, 2007). Similarly, the energy required for the CCSM might significantly drop at technology maturity.

Important caveats:

- CO_2 capture is not included in the mineralisation assessment found in literature. The cost of capture was considered in £45/tonne CO_2 based on CO_2 capture energy requirement of 364 kWh/tonne CO_2 for amine stripping and considering £0.08/kWh. Costs do not include injection underground and transport of CO_2 on site (Kothandaraman, 2010).

- In WP1 it is reported a cost of £2/tonne for the extraction of the silicate rocks.

- WP1 and Caterpillar report an average transport cost by sea of £4/tonne of rock transported that was considered in the calculations. In addition, £12/tonne of transporting materials by truck for 10 miles was accounted for the worst case and £1.2/tonne of transport <10 miles by rail in the best case.

- Conversion and mineral activation were assessed together. Conventional rod and ball milling techniques plus thermal activation at 630°C with an energy consumption of about 100kWh/tonne were considered in the serpentine calculations (d < 37μm) with an average CO_2 conversion of 70%. The conversion step was performed at 155°C and 115 bar (IPCC, 2005).

- The assessment considered the capacity to separate the high valuable products such as iron oxides and silica at the end of the process. It was assumed that silica phase can be extracted from the CCSM mineralised product with purity not less than 90% permitting to enter the market for supplying these basic material commodities (e.g. silica sand) and iron oxide with 60% purity to be used as feedstock for steel production.

- Assumes a non-significant cost from the drying process. Silica sand can be sold dump after a dewatering step.

- Post processing was assessed assuming serpentine was main resource, the material mass balance of the reaction ($Mg_3Si_2O_5(OH)_4 + 3CO_3 \rightarrow 3MgCO_3 + 2SiO_2 + 2H_2O$), and an efficiency of 70% (average of efficiency considered in the ARC evaluation, IPCC, 2005). Two final conditions were: the products are buried (£0/tonne) in the worst case; the majority of the products are sold (£/tonne variable) in the best case. The mass balance using the above conditions indicates that 3.4 tonnes of serpentine are needed to fix 1 tonne of CO_2, producing 2.6 tonnes of $MgCO_3$, 1.55 tonnes of SiO_2 and 0.1 tonnes of iron oxide. The values of the commodities used for the best case were: iron ore pellets (£33/tonne) (Cardero, 2004), SiO_2 (£13/tonne). In addition, 100% of silica and iron oxide and 0% of $MgCO_3$ were considered marketable.

- The post-processing cost for the silica sand and iron ore pellets was estimated in £6/tonne CO_2 and £3/tonne CO_2, respectively.
- Approximate commodity market values are given (or converted to) in Pounds Sterling per tonne at current exchange rates which, at the time of writing, were taken as \$1 US = £0.64, and Euro 1 = £0.85 on 21st September, 2010.

16 Possible scenarios for CCSM implementation

This analysis shows that the logical target markets for CCS Mineralisation deployment in the UK are power producers up to 300MW capacity and industrial processes with emissions up to 1Mt CO_2 per year. In both cases, the target deployment site should ideally be within 2km of the coast or, if inland, co-located with a suitable waste or process by-product stream.

16.1 INTRODUCTION

This section gives some possible examples of the implementation of CCSM in three regions of the UK and discusses the proposed deployment scenario, targeting smaller (< 300MW or < 1Mt CO_2 per annum) emitters located within 2km of the coast.

16.2 NORTH-EAST SCOTLAND

There is a large resource at the coastal location of Belhelvie, just north of Aberdeen and at Portsoy (Figure 75).

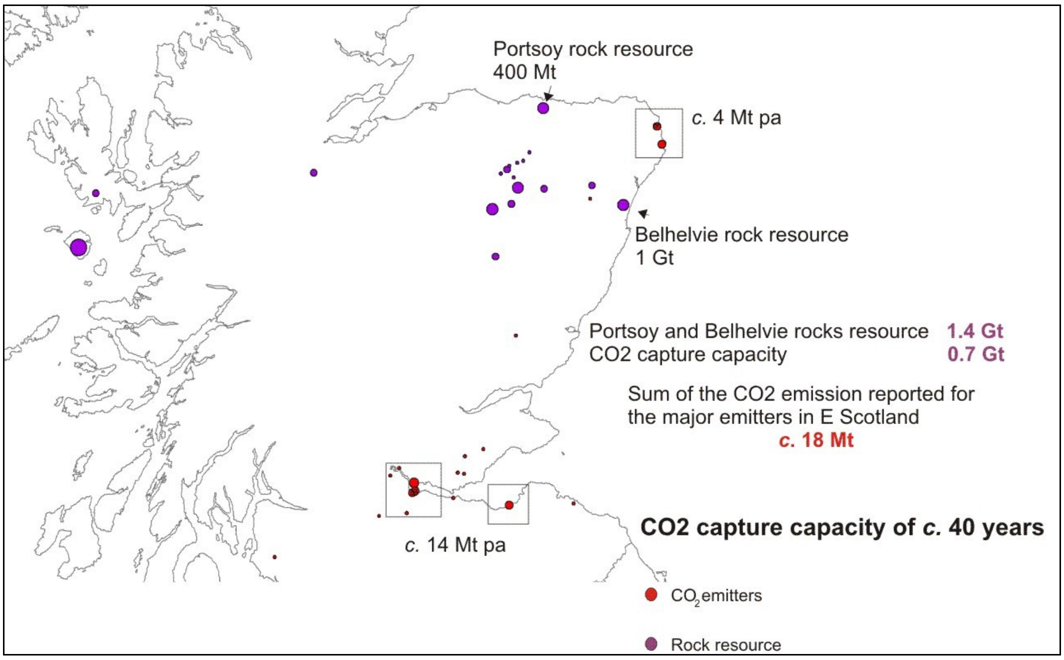


Figure 75 The location of the resources and emitters in eastern Scotland. [Based on OS topography, © Crown copyright]

The 1Gt Belhelvie resource and the smaller resource at Portsoy have the capacity to capture 700Mt of CO_2. This could be utilised at the gas/oil-burning power station immediately south of Peterhead (emitting 3.6Mt CO_2 per year), with a capture capacity of 150 years. In this instance, transport by road, rail or sea might be possible. Sea transport would also make the group of coastal emitters located around the Firth of Forth an outlet for Belhelvie-Portsoy rock. There is the capacity to capture **all** the major emissions for eastern Scotland about 40 years or part for a much longer period.

16.3 SOUTH-WEST SCOTLAND

There is a large resource of 2.5Gt at Ballantrae in southwest Scotland (Figure 76).

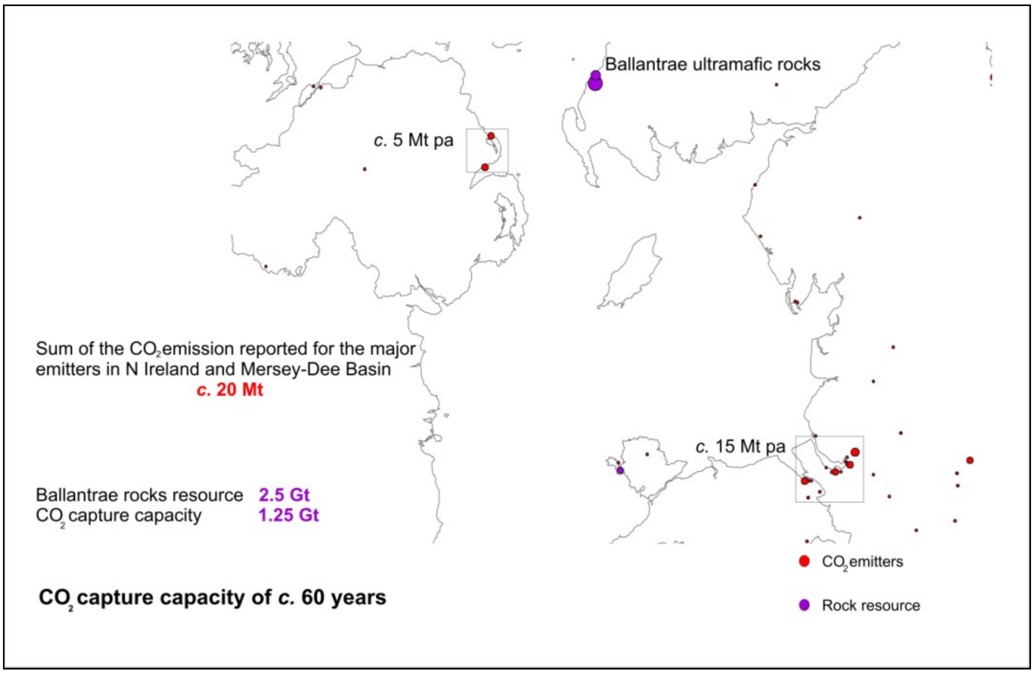


Figure 76 The resource at Ballantrae and possible uses. [Based on OS topography, © Crown copyright]

The Ballantrae resource would most likely be exploited using sea transport. There are relatively local sources such as the power stations on the coast of Northern Ireland and the small industrial sources near Glasgow. Further afield, there are numerous coastal emitters in northwest England, particularly those located within the Mersey-Dee Basin. The resource has the capacity to capture **all** the major coastal emissions for 60 years or part for a much longer period.

16.4 SOUTH-WEST ENGLAND

There is a very large (5Gt) resource centred on the Lizard peninsula in SW England (Figure 77).

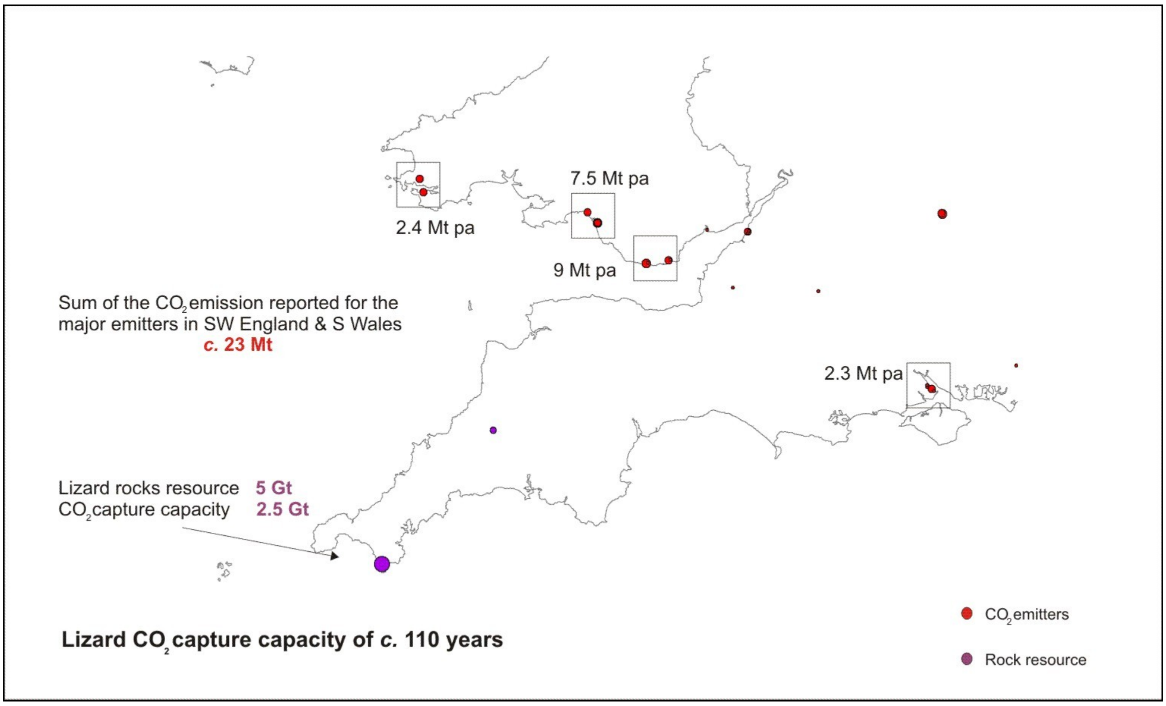


Figure 77 The resource at the Lizard and possible uses. [Based on OS topography, © Crown copyright]

The coastal location of the Lizard resource, and its remoteness with respect to emitters, makes sea transport essential. There are numerous emitters with coastal locations relatively nearby, such as the power stations and steel works in South Wales, and the oil refineries in Pembrokeshire and Southampton. The Lizard resource could capture the CO_2 from all these sources for over 100 years. Further afield, there are numerous coastal emitters located within the Thames Basin, amounting to an additional 20Mtpa that could use Lizard rock.

16.5 POSSIBLE DEPLOYMENT SCENARIO

In addition to these 3 specific locations where deployment of CCSM has been highlighted as attractive from the point of view of conveniently proximate location of minerals and emitters the more general scenarios for deployment are discussed here.

Analysis of the CO_2 emissions data used to generate Figure 23 shows that emitters can be categorised into 2 main groups:

1. Power (or CHP) producers
2. Industrial processes

Power producers in turn were grouped by capacity into the following 4 bands:

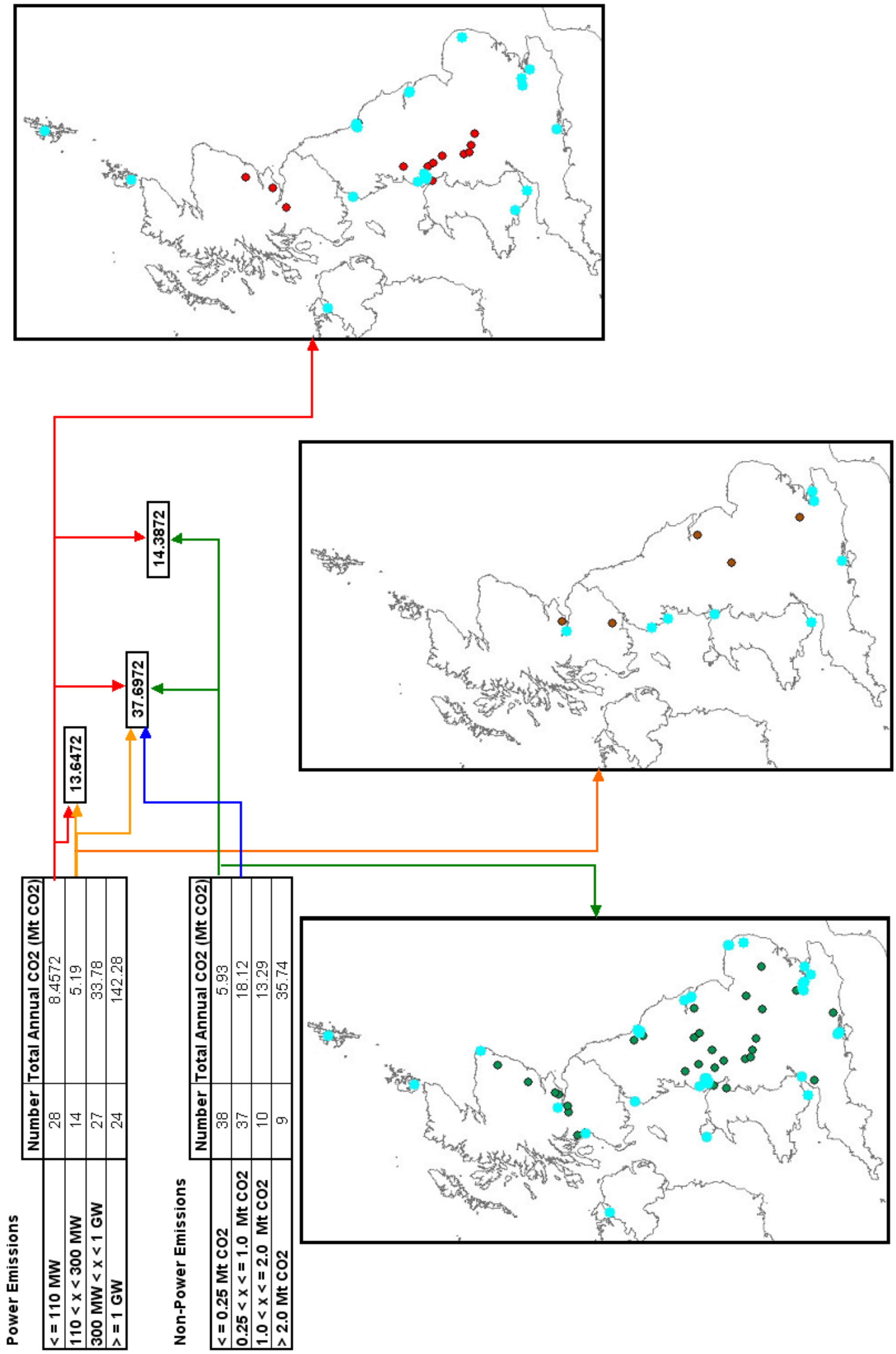
- 110MW and smaller

- 110 – 300MW
- 300 – 1,000MW
- 1,000MW and greater

Industrial processes were grouped by reported annual CO_2 emissions in the following 4 bands:

- 0.25Mt CO_2 and less
- 0.25 – 1.0Mt CO_2
- 1.0 – 2.0Mt CO_2
- 2.0Mt CO_2 and more

It can be seen from Figure 78 that the 29 power producers of 110MW capacity or less produced 8.45Mt CO_2 in the year reported. The 38 smallest industrial emitters reported produced a total of 5.93Mt CO_2 in the year reported. The total CO_2 from the smallest power producers and industrial emitters is therefore 13.65Mt CO_2 per annum, which is greater than the 11 Mt CO_2 set as a target for this project.



Power Emissions

	Number	Total Annual CO2 (Mt CO2)
< = 110 MW	28	8.4572
110 < x < 300 MW	14	5.19
300 MW < x < 1 GW	27	33.78
> = 1 GW	24	142.28

Non-Power Emissions

	Number	Total Annual CO2 (Mt CO2)
< = 0.25 Mt CO2	38	5.93
0.25 < x < = 1.0 Mt CO2	37	18.12
1.0 < x < = 2.0 Mt CO2	10	13.29
> 2.0 Mt CO2	9	35.74

Figure 78 Emissions Bands and Locations of Emitters by Band (Blue dots represent emitters within 2km of the coast. [Copyright BGS, NERC]

It can also be seen that the 2 smallest bands in both category is 37.7Mt CO_2 which is 3 times as much as the project is required to target. It can be seen from the location images that a substantial number of these emitters are within 1km of the coast. In the case of the larger 110 – 300MW power producers, the majority are within, or just over, this 1km distance.

16.6 CONCLUSION

The conclusion of this analysis is that the logical target markets for CCS Mineralisation deployment in the UK are power producers up to 300MW capacity and industrial processes with emissions up to 1Mt CO_2 per year. In both cases, the target deployment site should ideally be within 2km of the coast or, if inland, co-located with a suitable waste or process by-product stream.

17 Pathway for CCSM Technology Development

This chapter analyzes the gaps in CCSM technology and discuses the opportunities for further developments. With regard to mineral resources, no CCSM studies have been completed utilizing UK feedstock minerals. CCSM process fundamentals require better understanding of the interplay between the major control parameters (particle size, chemical additives, temperature, pressure, reactor design, etc.). Detailed techno-economic analysis of the selected CCSM technology in a specific UK scenario(s) and comparison with the alternative CCS options are the essential building blocks for the implementation pathway.

17.1 Gaps and development needs

17.1.1 Rock resources

The data on the testing of carbonation of ultramafic rocks is inadequate for a realistic assessment of any natural body of rock of sufficient size to be considered as a resource. The range of rock types tested is narrow, and the characterisation of starting materials is poor. The experiments were carried out in a number of laboratories all using different conditions of temperatures, pressures, fluid compositions, and additional chemical reagents. The result is that the significance of the data from many experimental studies cannot be readily compared and cannot be used to guide the resource assessment, only to establish the principles of the carbonation process. This situation has probably arisen from the fact that the technologists carrying out the experiments have been unaware of the extensive variation in natural rocks and have not appreciated the necessity to fully characterize the starting material. It is apparent that the tests, such as XRD analysis, were carried out by people with little knowledge of the special sample preparation required and the interpretation of geological materials. The interpretation of data is simplistic and inadequate.

In the UK context, it has been established, from desk studies only, that there are substantial resources of ultramafic rocks far in excess of the project target and that these are all essentially serpentinites. In the published literature, there is contradictory evidence about the reactivity of the serpentine polytypes lizardite and antigorite. Some studies show that antigorite has a high reactivity, similar to olivine, while lizardite is inferior; however, other experiments show the opposite. Carefully controlled comparative tests of lizardite and antigorite are essential. It is known from previous unpublished studies that serpentinites are heterogeneous and their reactivity can vary significantly. There are no published data on the carbonation of UK serpentinites. The Phase 2 activities on the detailed characterisation of UK ultramafic rocks must be accompanied by carbonation experiments. These experiments will be made on rocks that have a full mineralogical and geochemical characterisation carried out by experts in the field at BGS. This has not been done for previous experimental studies.

The review of the global context showed that there are huge resources of ultramafic rocks. These cover a wide range of combinations of the proportions of constituent minerals but experimental testing is confined to simple, single mineral compositions, pure olivine or pure serpentine.

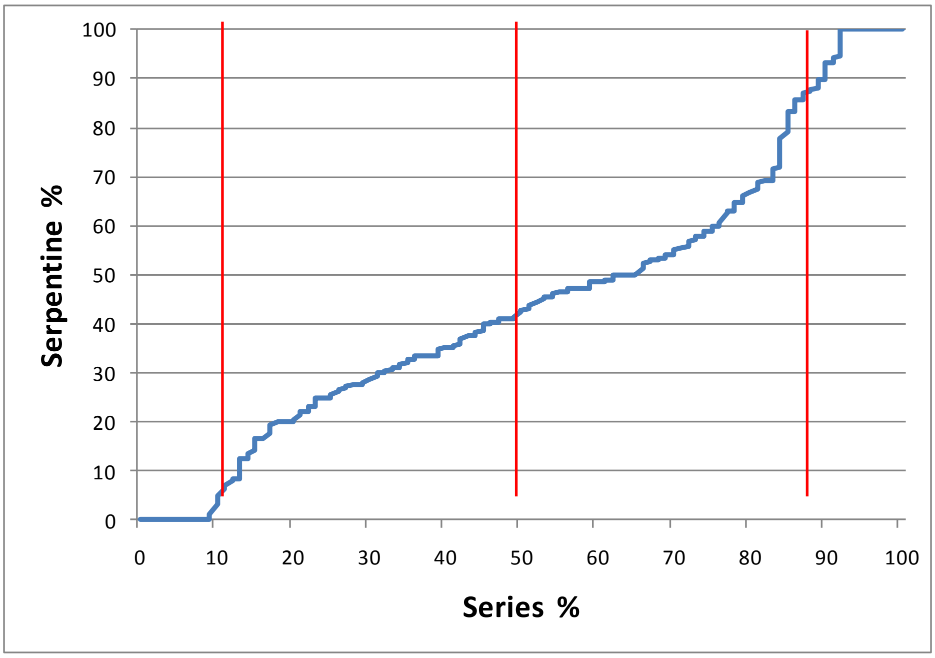


Figure 79 A plot of the degree of serpentinisation of 400 ultramafic rocks from the UAE ophiolite. [Copyright BGS, NERC]

Figure 79 shows data from ca 400 ultramafic rocks from the UAE studied during previous BGS projects. The samples are from an area covering over 1,000km^2 in the UAE. This data is used as an example as it is the most extensive and comprehensive data set to our knowledge; there is nothing comparable from the UK. The data arranged so that the degree of serpentinisation of each sample is shown as a proportion of the whole sample suite. The data shows that only 10% of the samples could be considered as an olivine resource and similarly around 10% as a serpentine resource. The median value is 40% serpentinised and the majority of samples (70%) lie between 20-70% serpentinised. This rock type forms a major part of the global resources. If the huge amount of potential resource is to be utilised a process that can use a mixture of olivine and serpentine is vital and experiments to test such mixtures are essential.

- Need for a set of experiments of various mineral mixtures, such as olivine-serpentine, all under identical conditions, to establish the variation in carbonation efficiency that is solely due to the variation in mineralogy of the starting material.
- Need to carry out a set of carbonation experiments from the highly rated UK sources identified in this report to confirm that they follow the general trends established from the first experiments.

17.1.2 CCSM Technologies.

Chapters 14.5 & 14.6 summarize the assessment of various CCSM technologies published up to date in open literature. The major conclusions are the following:

- The overall technology is still in the R&D stage (TRL level below 4), although the pre-treatment sub processes (mechanical, chemical or heat treatment) are well established within the large-scale mineral engineering industries.

- Most experiments have not properly characterized the materials used or products produced.
- No testing on rocks consisting of more than one mineral such as olivine-serpentine or olivine-pyroxene mixtures has been reported.
- Mineral activation was not tuned to starting mineral characteristics.
- The focus of most research has been on the optimization of mineral utilization rather than CO_2 capture.
- The ability of minerals to react directly with flue gas has not been fully investigated.
- There is a lack of complete CCSM process performance data (mineral characteristics, mineral utilization, CO_2 capture, energy usage, etc.).
- The total process integration to optimize energy usage has not been investigated and/or demonstrated thus far.
- Only three 'in-depth' techno-economic analyses are published in the open literature (ECN, ARC/NETL, IAE). Detailed economic assessments of all other CCSM technologies described in the literature was not feasible at this time due to the lack of appropriate data.

The following options for the path forward can be considered and shall be revised at the end of each stage.

Option	Pros	Cons
Evaluate only the technologies that are developed up to TRL 4	Major fundamental challenges were identified and resolved. High level cost analysis was completed.	Higher TRL means only an advanced stage of development, and does not define any advantage of a particular CCSM in terms of performance or cost. Emerging prospective CCSM technologies are eliminated. Do nothing and revisit CCSM area after at least 5 technologies are demonstrated at TRL 4 - the timeline is unknown.
Illustrate the performance of a composite, optimized CCSM technology that combines high performing elements from several documented technologies.	Can be initiated now. Opportunity to realize a novel, low cost CCSM process, generating new Intellectual Property	The compatibility of various "building blocks" from different CCSM will have to be analyzed and validated. Might take up to 5-10 years to demonstrate.
Continue development of one specific, well-documented credible	Allows creating realistic CCSM application scenario(s).	Might be not the best CCSM in terms of performance characteristics Cost might be high but scope for improvement will be indicated

technology (eg. Shell)	Allows performing detailed techno-economic analysis in realistic application(s). Can be completed in 12-18 months.	

The third option was chosen to proceed. The proposed path forward is outlined in Figure 80 and includes the following activities:

- Select a well-documented baseline CCSM technology at its current state of the development (TRL 2-3). Perform its fundamental review: process risks (pre-treatment, carbonation, final disposal); CAPEX/OPEX and operability; final products; time to get process to market; integration with process plant; initial outline for a full life cycle analysis.
- Complete high-level TEA for the selected technology in application to specific UK scenario(s) (feedstock mineral, transport logistics, full chain HSE compliance, etc.).
- Identify areas of potential performance improvements and cost reduction at least 10% against the selected baseline CCSM technology.
- Create an experimental plan to validate the proposed improvements (optimize pressure/temperature/time balance, evaluate chemical additives, mineral-water-additive balance, etc.); the execution of the experimental plan should provide the essential data for a follow up detailed TEA.
- Complete the next iteration of TEA to verify improvements.
- Finalize the layout for the improved CCSM integrated with the emission source and mineral deposit site (explore, define and analyze heat and power integration options, etc.)
- Pilot improved integrated CCSM.
- Develop roadmap from TRL 4 to TRL 9 (define and specify unit operations and integrations, estimate time required for development; benchmark against alternatives at that time; etc.).
- Perform full LCA and make final Go/No Go decision.

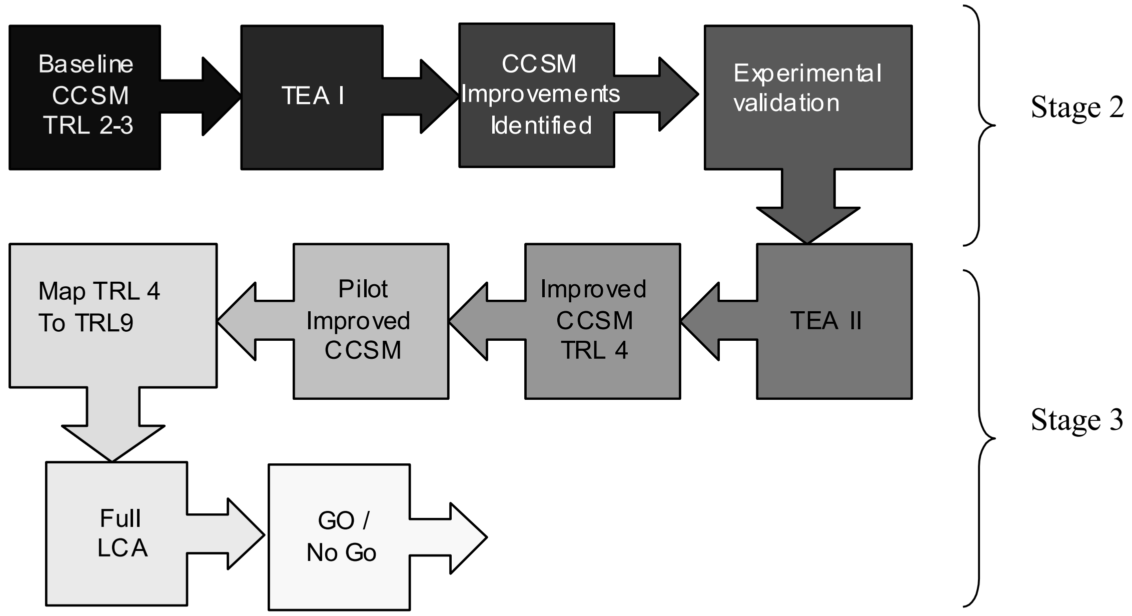
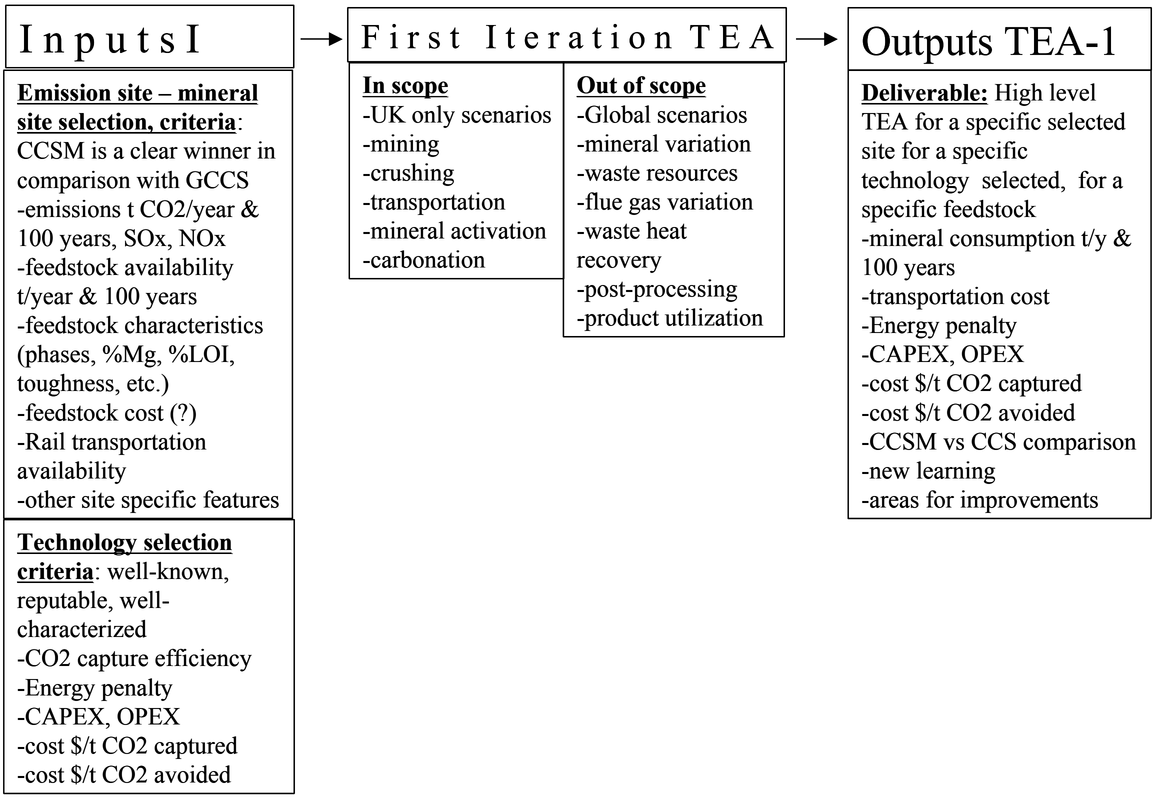


Figure 80 Outline of the proposed path forward. [Copyright Caterpillar Inc.]

The detailed inputs, outputs, and scope of the TEA-1 and TEA-2 are presented in Figure 81 and Figure 82, respectively.



InputsI → First Iteration TEA → Outputs TEA-1

<u>Emission site – mineral site selection, criteria</u>: CCSM is a clear winner in comparison with GCCS
-emissions t CO2/year & 100 years, SOx, NOx
-feedstock availability t/year & 100 years
-feedstock characteristics (phases, %Mg, %LOI, toughness, etc.)
-feedstock cost (?)
-Rail transportation availability
-other site specific features

<u>Technology selection criteria</u>: well-known, reputable, well-characterized
-CO2 capture efficiency
-Energy penalty
-CAPEX, OPEX
-cost $/t CO2 captured
-cost $/t CO2 avoided

<u>In scope</u>
-UK only scenarios
-mining
-crushing
-transportation
-mineral activation
-carbonation

<u>Out of scope</u>
-Global scenarios
-mineral variation
-waste resources
-flue gas variation
-waste heat recovery
-post-processing
-product utilization

<u>Deliverable:</u> High level TEA for a specific selected site for a specific technology selected, for a specific feedstock
-mineral consumption t/y & 100 years
-transportation cost
-Energy penalty
-CAPEX, OPEX
-cost $/t CO2 captured
-cost $/t CO2 avoided
-CCSM vs CCS comparison
-new learning
-areas for improvements

Figure 81 Process flow for the high-level TEA-1. [Copyright Caterpillar Inc.]

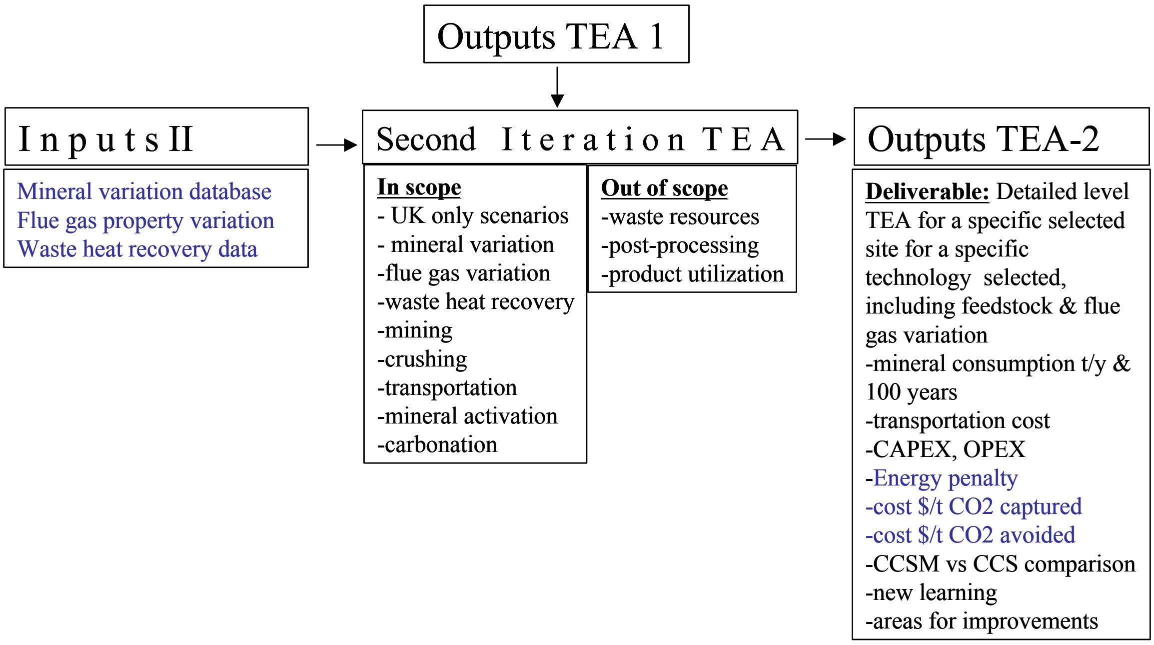


Figure 82 Process flow for high-level TEA-2. [Copyright Caterpillar Inc.]

In the first high-level techno-economic assessment (TEA-1) using the baseline CCSM technology, it is assumed that the outlet stream from the carbonation process will have net zero value (ie no income stream, but no disposal cost). This analysis will be included in the follow up, detailed techno-economic assessment (TEA-2), and into a full life cycle analysis. TEA-1 assessment of the baseline CCSM technology will provide additional justification for the required experimentation. In turn, the objective for the experimentation work is to provide the essential data for TEA-2.

The detailed objectives and deliverables for the tasks are described below.

Task 1. CCSM technology selection.

Objective: Select a well-documented, credible CCSM technology as the baseline technology for application in UK specific scenarios; document selection criteria. Perform additional review of the selected process. The full techno-economic analysis for the following technologies is well documented in the literature:

- aqueous, single-step, no additives (ECN)
- aqueous, single-step, additive enhanced (ARC/NETL)
- aqueous, multi-step, additive enhanced “pH-swing” (IEA)

In addition, Shell Global Solutions has provided documentation for full techno-economic analysis for its aqueous, multi-step, additive enhanced CCSM technology. Shell’s technology is the most suitable candidate as a baseline technology for the high level CCSM techno-economic analysis.

Deliverables:

- Techno-economic analysis of a baseline CCSM technology is documented (Shell’s report)

- Additional fundamental review of the process is completed covering process risks (pre-treatment, carbonation, final disposal); time to get process to the market, integration with the process plant; initial outline for a full lifecycle analysis.

Task 2. Selection of specific UK scenarios: Emission site – Mineral deposit site.

Objective: Analyze data described in SG1 report related to UK mineral deposit sites and emissions sources; select "emitter location – mineral deposit location" combinations where CCSM implementation is favourable. These will be medium-small emitters where GCCS is less favoured. The selected sites will be used for high-level techno-economic analysis of CCSM and GCCS including alternative options for CO_2 transport (pipeline or liquid CO_2 transportation by truck or ship).

Deliverable: Two scenarios selected and selection criteria justified and documented; best available data on mineral cost and mineral transportation cost (truck, rail, and ship) collected and documented including source(s) of information.

Task 3. Cost estimation of GCCS for the selected UK scenarios.

Objective: provide cost analysis for the conventional GCCS for 2 selected UK scenarios. The data will be used for comparative analysis of CCSM and GCCS including options for CO_2 transport to underground injection site

Deliverable: up-to-date best available data on CO_2 emissions, CO_2 transportation cost (pipeline, ship, truck), collected and documented including source(s) of information; detailed description of a conventional GCCS cost for the same 2 scenarios documented; GCCS cost for the selected UK scenarios estimated as £/CO_2 captured and £/CO_2 avoided.

The information from Tasks 1-3 will be used as input data for TEA-1 (Task 4).

Task 4. High level TEA-1 estimation of the selected CCSM (Shell) for 2 selected UK scenarios.

Objective: Perform high-level techno-economic analysis of well-documented credible CCSM technology in application to 2 specific UK scenarios. Perform comparative analysis of selected CCSM technology against 2 alternative options applied to the same scenarios – conventional GCCS (pipeline) and alternative CCS option (liquid CO_2 transportation by truck). Identify cost reduction areas for CCSM technology.

Deliverables:

- in scope and out of scope boundaries, criteria definitions documented
- areas of uncertainties (data gaps) that significantly impact the confidence level of the techno-economic analysis specified and documented
- assumptions for the data gap areas documented
- detailed description of CCSM techno-economic model and analysis of the results for 2 scenarios documented
- comparative analysis of the selected CCSM technology against GCCS and an alternative CCS option documented
- preliminary cost reduction options for CCSM identified and documented

- high quality technical professional report provided

The results of the TEA-1 analysis will be used as inputs for the detailed techno-economic analysis (TEA-2) along with the additional inputs such as mineral variation data and flue gas variation data. It should be mentioned that the impact of variation of these important parameters on CCSM cost has not been investigated previously and is unknown thus far.

The possibility of utilization of waste heat from various industrial processes has been mentioned in the open literature, but has not been fully analyzed. This presents an attractive option for energy penalty reduction through overall CCSM technology integration with the primary industrial or power generation processes. The inputs, outputs, and the scope of the second detailed TEA-2 is presented in Figure 82. Text in blue colour shows the list of data required for TEA-2 but not available in the literature. Therefore, the data will have to be generated through experimentation described below.

Task 5. Develop a detailed experimental plan.

Objective: Develop and justify a detailed experimental plan to address the data gap/uncertainty areas and cost reduction options identified in Task 4. Execution of the experimental plan will create a dataset required for validation of improved CCSM and its Detailed Techno-Economic assessment (TEA-2).

Deliverables:

- comparative analysis of major CCSM groups revisited (single-step vs. multi-step; direct mineral - flue gas vs. CO_2 pre-separated; no additives vs. additive enhanced, etc.)
- 1-2 most promising groups selected, selection criteria justified and documented (CO_2 capture efficiency, mineral conversion efficiency, additive consumption and recyclability, process energy intensity in terms of T/P, etc.)
- essential experimental data demonstrating the correlation between CCSM process fundamentals (mineral type, particle size, additive types, dissolution rates, carbonation rates, etc.) and CCSM economics (cost, energy penalty, reduction options) identified and documented
- detailed description of the technical approaches, experimental methods & techniques that cover mineral characterization, mineral pre-treatment (mechanical, thermal, chemical) and carbonation steps; post-processing is out of scope for Stage 2b
- general layout of the improved CCSM technology (TRL 4)

The experimental objectives with the justification will be provided in a separate document (SG 2a report) along with the detailed Microsoft Project Plan.

Task 6. High-level Stage 3 project plan.

Objective: Develop high-level project plan for Stage 3.

Deliverables: Microsoft project plan describing timeline, resources, and documentation required for the successful execution of the following tasks:

- TEA-2 for the improved CCSM technology based on the experimental data collected
- Detailed layout of the improved CCSM technology at TRL 4
- Pilot site selection (ECN, CAT UK, CPI suggestion?)
- Detailed pilot plan
- Pilot demonstration & post pilot data analysis
- Full LCA of the integrated CCSM
- Comparative analysis with the alternative CCS options
- Detailed roadmap TRL 4 – TRL 9
- Final recommendations and documentations
- Project wrap up

At the project closeout, a report detailing the CCSM technology layout, development, and deployment roadmap will be presented. The key ETI focus areas for Mineralisation CCS will be analyzed, so that the ETI can decide where best to invest in this technology. A technical report will be provided as the final output of this project.

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List of Acronyms

ACC	amorphous calcium carbonate
ASR	alkali silica reaction
BET	specific surface area of a material (m^2/g)
CCSM	carbon capture and storage by carbonation
CEM	cement
CFRRPC	Carbon-fibre reinforced RPC
CKD	cement kiln dust
CMC	ceramic matrix composites
CVD	Chemical vapour deposition
FGD	flue gas desulphurisation
GCC	ground calcium carbonate
HIP	hot isostatic pressing
LECA	lightweight expanded clay aggregate
LOI	loss on ignition
MAP	mineralization via aqueous precipitation
MPC	magnesium phosphate cement
MSW	municipal solid wastes
PC	Portland cement
PCC	precipitated calcium carbonate
SCC	self compacting concrete
SiC	Silicon Carbide
VOCs	volatile organic compounds

Appendix 1

This appendix contains information about the nature of ultramafic rocks and the serpentine mineral group. This is given in relatively simple terms and should be comprehensible by scientists and engineers who do not have specialist geological knowledge. It provides the background to the interpretation and conclusions made by the specialist geologist that are part of the main body of the report.

THE NATURE OF ULTRAMAFIC ROCKS

The classification diagram shows that there is a wide range of possible compositions of ultramafic rocks. The following sections describe in more detail some of these rocks and the mineralogy of the serpentine group of minerals to assist the understanding of those less familiar with geological aspects. The properties of rock types that have actually been studied in the laboratory as to their suitability for mineral carbonation.

OLIVINE ROCKS

Dunite is the name for rocks composed entirely of olivine. In addition, in this category are olivine mineral grains separated out of a rock (e.g. Figure 83), which have been used for laboratory studies. These fall in field 1 of the classification.

Peridotite xenolith in basalt from San Carlos.

San Carlos olivine from Lopaki Co. Mineral suppliers

Figure 83 Example Olivine Rocks. [Copyright BGS, NERC]

One type of olivine that has been used widely in experiments is from the San Carlos location in Arizona (Figure 6). This is a place where a basalt volcano has brought up fragments of the mantle directly from its source region as inclusions (xenoliths) within the basalt magma. These fragments tend to be very fresh and can produce gem quality olivine (peridot), as at

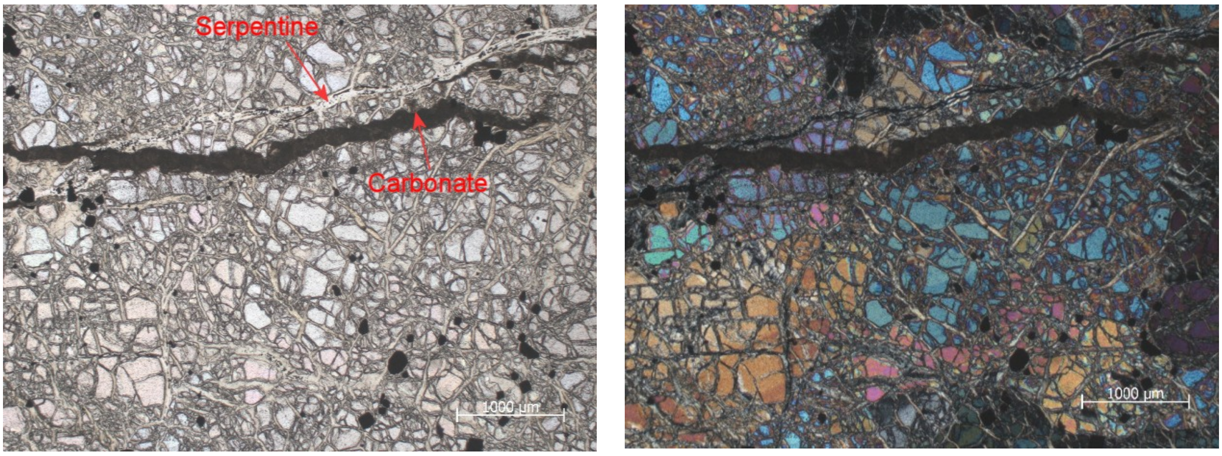
San Carlos, which gives a very clean, pure starting material for an experiment. However, the xenoliths are small, usually only a few centimetres in diameter, and these types of volcanoes are quite rare. It would be difficult to fill more than a few trucks with olivine from locations such as San Carlos.

The main source of olivine is from dunite, and the main types that have been used for laboratory testing are from the Twin Sisters Complex in Washington State, just northeast of Seattle and the Green Mountain peridotite in North Carolina. Both bodies have been quarried for use as foundry sand and Twin Sisters is also used as an international geochemical standard for rock analysis, hence its composition is well known. These peridotites occur in large intrusions; Twin Sisters is a large body around 90km^2 in area.

Figure 84 Dunite from the United Arab Emirates. [Copyright BGS, NERC]

Rocks very similar to these are found in the United Arab Emirates (UAE) and have been studied in detail by BGS (Styles et al., 2006). Samples from there will be described as examples. Figure 84 shows a sample of dunite from the UAE, it shows the typical green colour of an olivine rock but with paler areas indicating slight alteration to serpentine and numerous small fractures also showing alteration.

The features of the rock can more clearly be seen by using a polarizing light microscope to view a thin (30μm) section of the rock through which light is able to pass.



Photomicrograph of dunite from the UAE, plane-polarised light (ppl).

In cross-polarised light (xpl).

Figure 85 Dunite from the UAE. [Copyright BGS, NERC]

The thin section depicted in Figure 8a shows that the dunite is very fresh and little altered and that the olivine is cut by a network of thin serpentine veins that have formed along micro fractures. The black crystals are chromite, a Cr, Al, Mg, Fe-oxide, and are 100 – 200µm in size. The rock is also cut by a thin vein of carbonate. The view in cross-polarised light (Figure 83) shows the presence of abundant fresh olivine (showing blue, pink and orange colours). The original grain size of the olivine is indicated by the areas of similar colour, each of which represents one olivine crystal. The original grains are fractured and the serpentine (pale grey) forms in these fractures. This fresh rock contains 5 – 10% serpentine, but most dunites will contain more. The serpentine is intimately intergrown with the olivine and would be difficult to separate.

Peridotites

Peridotites are rocks that consist dominantly of olivine but contain up to 40 % pyroxene. When fresh, they will fall in field 6 of the classification.

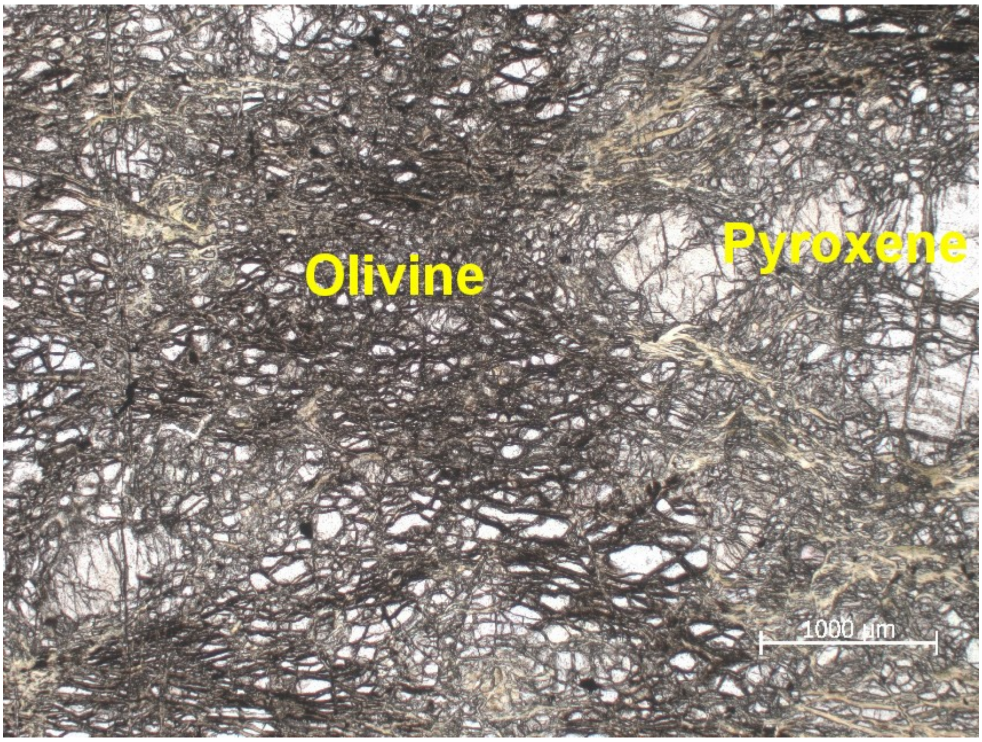


Figure 86 A fresh peridotite from the UAE (ppl). [Copyright BGS, NERC]

The fresh peridotite (Figure 86) shows the intimate intermixing of olivine and pyroxene on a millimetre scale, with minor amounts of serpentine alteration. When a rock like this is crushed the resulting particles are likely to be mixtures of olivine and pyroxene as well as some single mineral grains, and both of these minerals will contain some serpentine.

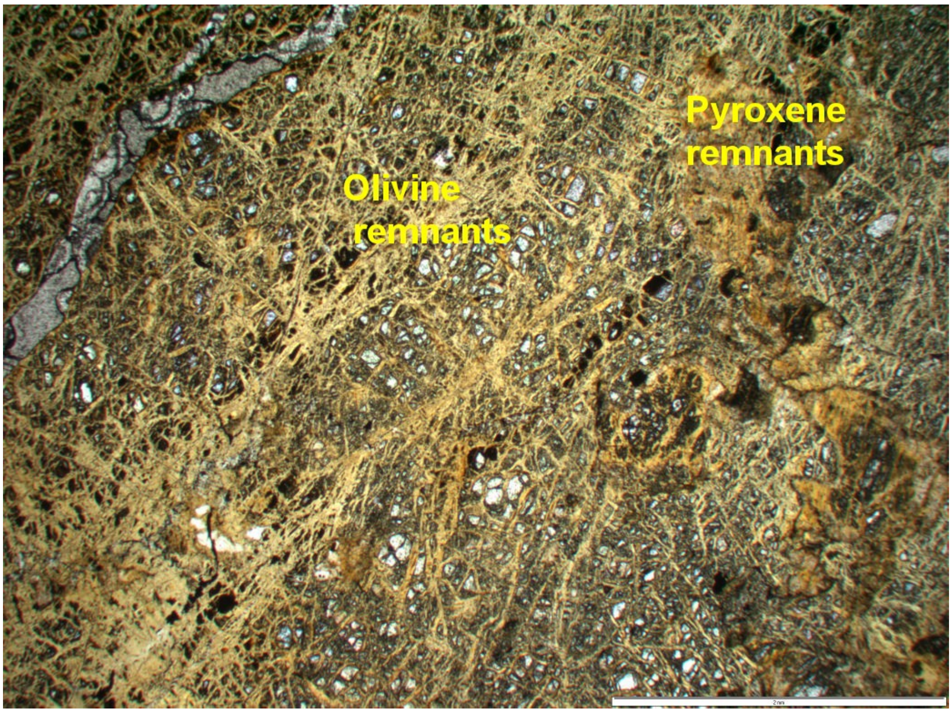


Figure 87 Typical partially altered peridotite from UAE, scale bar 2 mm. (ppl). [Copyright BGS, NERC]

Figure 87 shows a typical peridotite from the UAE that originally consisted of olivine and pyroxene, in which 50 – 60% of these minerals have been altered to serpentine. The olivine and pyroxene now exist as small remnants, mostly 100µm or less, within a matrix of serpentine. These minerals will be difficult to separate if a rock such as this is used as a resource. A rock like this would plot in field 8 of the classification scheme.

Serpentinites

Serpentinites are formed when ultramafic rocks such as dunite and peridotite are affected by hydrous fluids at temperatures below 500°C, and the unstable, anhydrous, high temperature minerals olivine and pyroxene are converted to the hydrous mineral serpentine.

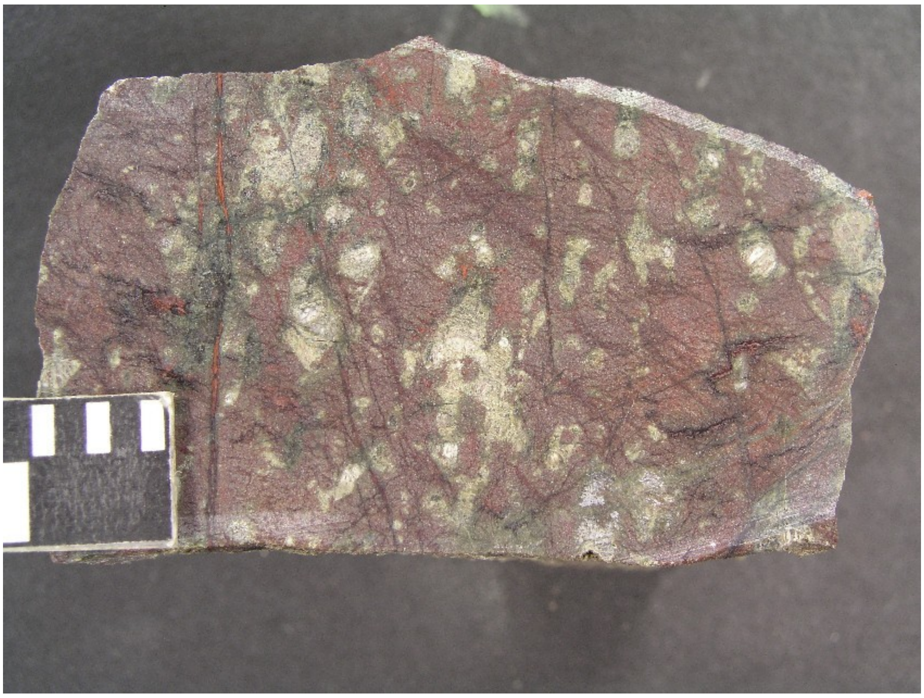
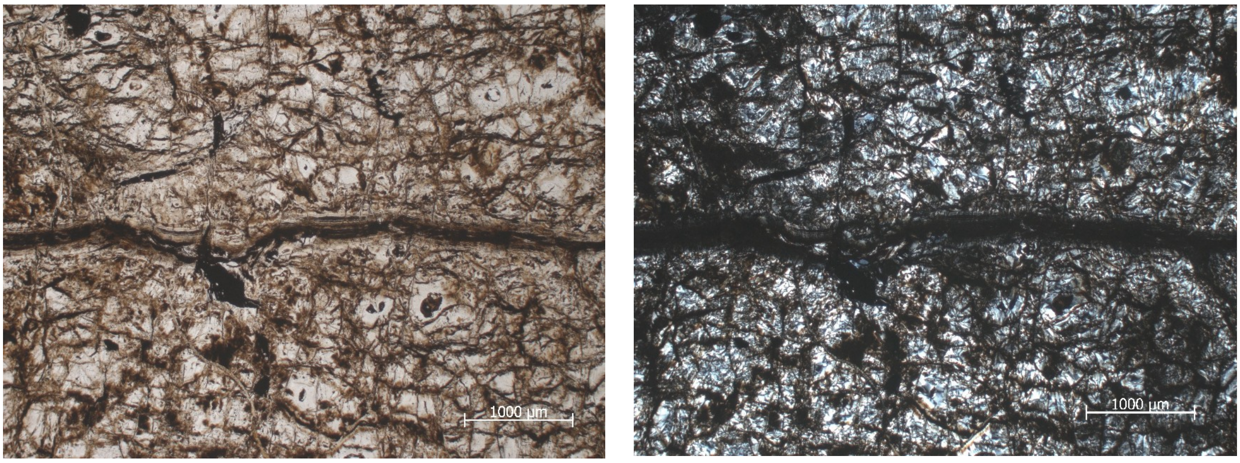


Figure 88 A serpentinite from the Lizard, Cornwall, showing red hematite-stained serpentine replacing olivine and pale-green serpentine replacing pyroxene. [Copyright BGS, NERC]

Figure 88 shows a typical serpentinite from the Lizard in Cornwall. This rock is largely composed of the serpentine variety lizardite and still preserves the texture of the parent peridotite although all the minerals have completely changed. The rock is cut by red veins rich in iron oxides and oxyhydroxides.

When serpentinites are studied in thin section, more features of the rock can be seen.



Serpentinite formed from dunite, UAE, ppl. **Serpentinite formed from dunite, UAE, xpl**

Figure 89 Serpentine derived from Dunite. [Copyright BGS, NERC]

Figure 89 shows a serpentinite derived from a dunite. The rock is relatively homogenous and still preserves a 'ghost' texture of the original rock. The outlines of the original olivine grains are now outlined by reddish-brown secondary iron oxides. This is the simplest type of serpentinite and is largely composed of lizardite.

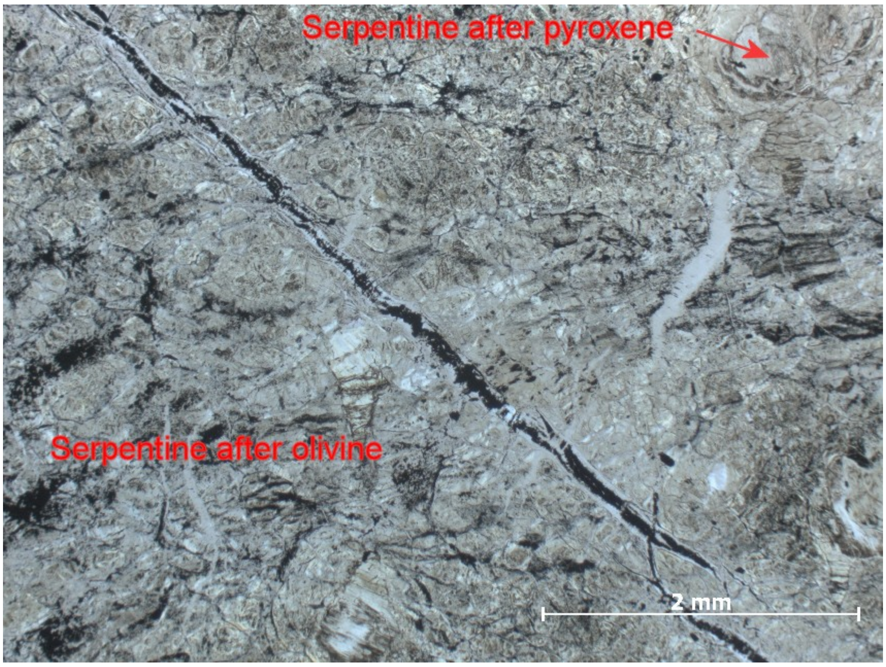


Figure 90 A serpentinite formed from a peridotite, Lizard, Cornwall. [Copyright BGS, NERC]

Figure 90 shows a serpentinite derived from a peridotite. The outline of the original pyroxene crystals can still be seen and contrasts with the massive serpentine from the matrix olivine. There are also distinct veins of secondary serpentine, and the largest one (top left to bottom right) contains iron oxides. This rock is mostly composed of lizardite but the serpentine in the matrix, veins, and pyroxene pseudomorphs is likely to have slightly different compositions that could affect its reaction properties. The vein may well contain the fibrous serpentine chrysotile.

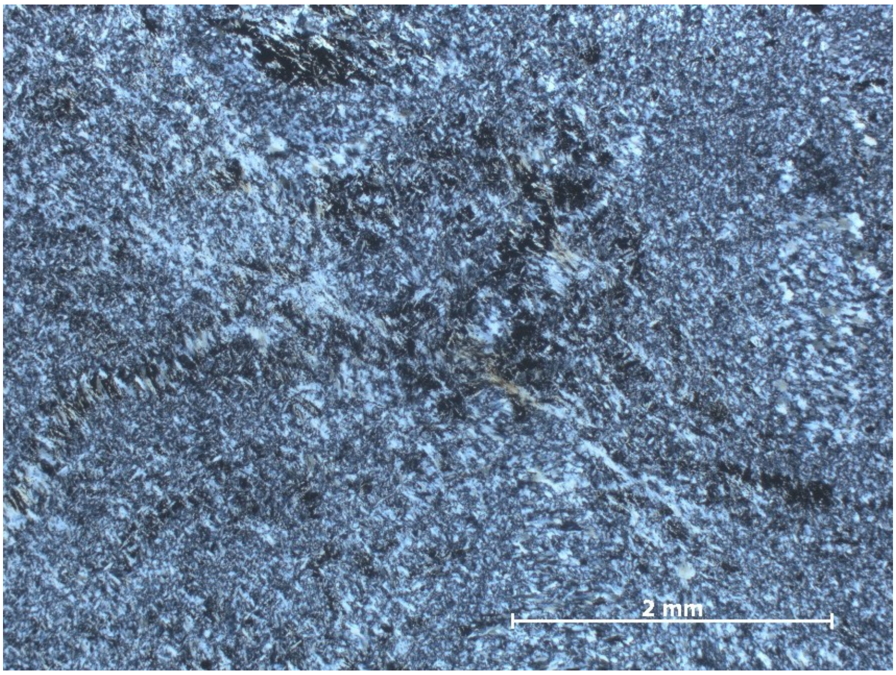


Figure 91 Recrystallised antigorite serpentinite from N Italy. [Copyright BGS, NERC]

Some serpentinites are affected by metamorphism (heating and deformation) and if the temperature is between about 300 and 500°C the lizardite serpentine recrystallises to antigorite, the higher temperature form of serpentine. This destroys most or all of the remnant features of the original rock and can form a fine-grained massive rock as shown in the example from Italy Figure 91.

The serpentine mineral group

Serpentinites are likely to be one of the main feed materials for CCSM but as their mineralogy is complex it will be described in some detail in this section. The serpentine mineral group comprises three main polymorphic forms: chrysotile, lizardite and antigorite. These have the approximate composition $Mg_3Si_2O_5(OH)_4$ with, in natural specimens, comparatively little substitution of other ions. Of these polymorphic forms, chrysotile, in all European Union and North American legislation, is classed as an asbestos mineral. Below is a general description of the serpentine mineral group taken mostly from Clinkenbeard et al. (2002)

Serpentine minerals are phyllosilicates (“sheet” or “layer” silicates) and have a structural unit comprising one tetrahedral sheet bonded to one octahedral sheet (Figure 15). In the tetrahedral sheet, four oxygen atoms surround a silicon atom. The silica tetrahedra share three basal oxygen atoms with adjacent tetrahedra and are arranged in hexagonal rings to form a continuous sheet. The fourth oxygen is each orientated in the same direction, occur on the top of the tetrahedral layer, and are shared with the octahedral layer. The octahedra comprise six oxygen and hydroxyl ions surrounding a magnesium atom. They are shared with adjacent octahedra and form a continuous sheet. Linking of the tetrahedral and octahedral layers is through sharing of oxygen atoms to form a two-layer structure having the ideal formula $Mg_3Si_2O_5(OH)_4$. Chemical substitution is limited as only small amounts of a few other elements, mainly iron and aluminium, can utilise magnesium or silica sites. The dimensions of the octahedral (magnesium) and tetrahedral (silicon) sheets are slightly different. This gives rise to a misfit between the tetrahedral and octahedral sheets that needs to be accommodated for the serpentine tetrahedral–octahedral layer to be stable. There are three main ways that this accommodation occurs, and this results in the three principal types (polymorphs) of serpentine: lizardite, chrysotile, and antigorite. In lizardite, the difference is taken-up by in-plane rotation of the tetrahedra within the planar structure of the layer. Chrysotile accommodates the misfit by curling the tetrahedral–octahedral layer into scrolls or hollow cylinders. In antigorite, alternating parts of curved layers are periodically inverted to create a wave-like or corrugated structure that accommodates the misfit (Figure 16).

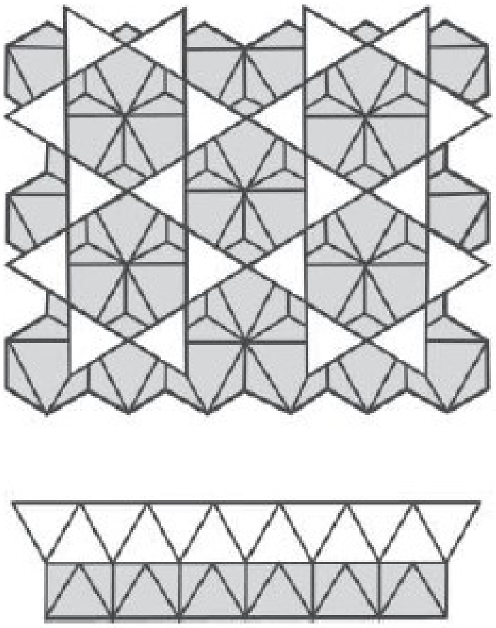


Figure 92 Illustration of the structure of the serpentine group minerals—the octahedral sheet is shaded in the plan and end views above [after Veblen and Wylie, 1993]

Of the three main serpentine minerals, lizardite is the most abundant (Wicks and O'Hanley, 1988). The misfit between the tetrahedral–octahedral sheets in the lizardite layer is relieved by in-plane rotation of the tetrahedra in the tetrahedral sheet. This gives rise to a planar structure. In addition, Al or Fe^{3+} in small amounts probably helps to stabilize the planar structure. Although the lizardite layer is planar (Figure 92), it can, near the edge of the layer, exhibit some curvature. Lizardite is rarely found in the asbestiform habit, commonly occurring as massive or scaly aggregates. Lizardite chemistry is very similar to chrysotile.

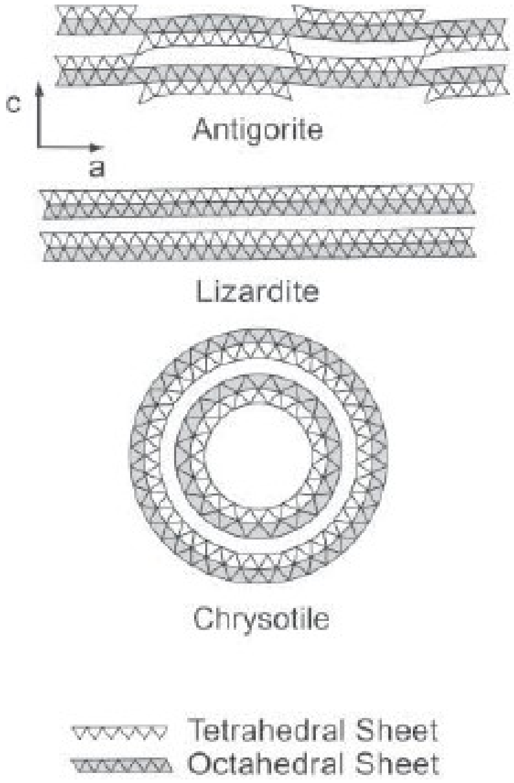


Figure 93 Simplified diagrams of the structures found in antigorite, lizardite, and chrysotile [after Livi and Veblen, 1987]

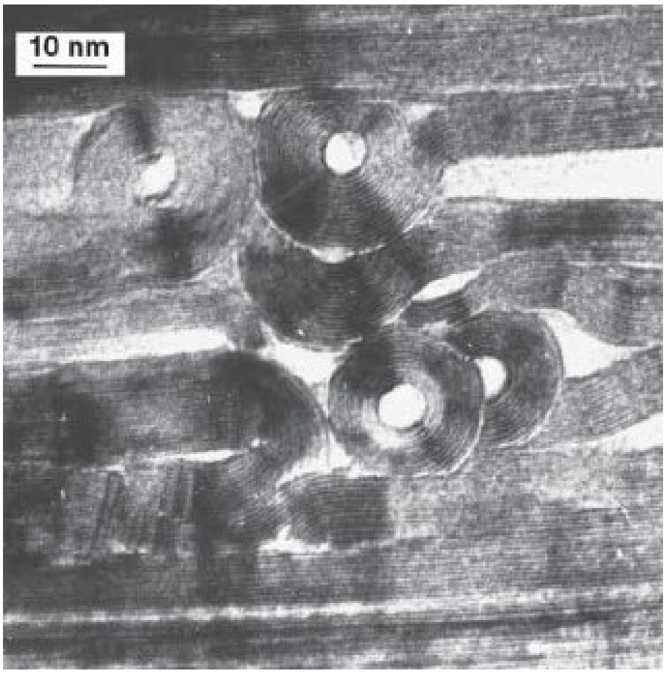


Figure 94 Transmitted electron microscope (TEM) image of lizardite and chrysotile, showing the different structures between the polymorphs. Chrysotile has a coiled or scrolled structure and lizardite is predominantly planar [after Dodony, 1993]

Chrysotile is probably the least abundant serpentine mineral. However, its characteristically fibrous habit means that it is easily recognised (Wicks and O'Hanley, 1988). The structure of asbestiform chrysotile is such that the tetrahedral–octahedral layers are curved into cylinders or spirals (scrolls) (Figure 93). It typically occurs in cross-fibre and slip-fibre veins and sometimes as mass fibre deposits (Figure 94). Chrysotile can also occur in a massive form (polygonal chrysotile). This cannot be distinguished from lizardite or antigorite without X-ray diffraction (XRD) or electron diffraction studies and occurs as a non-fibrous component of cross-fibre and slip-fibre veins, or as the sole component of veins or as coatings on shear surfaces in serpentinites (Wicks and O'Hanley, 1988).

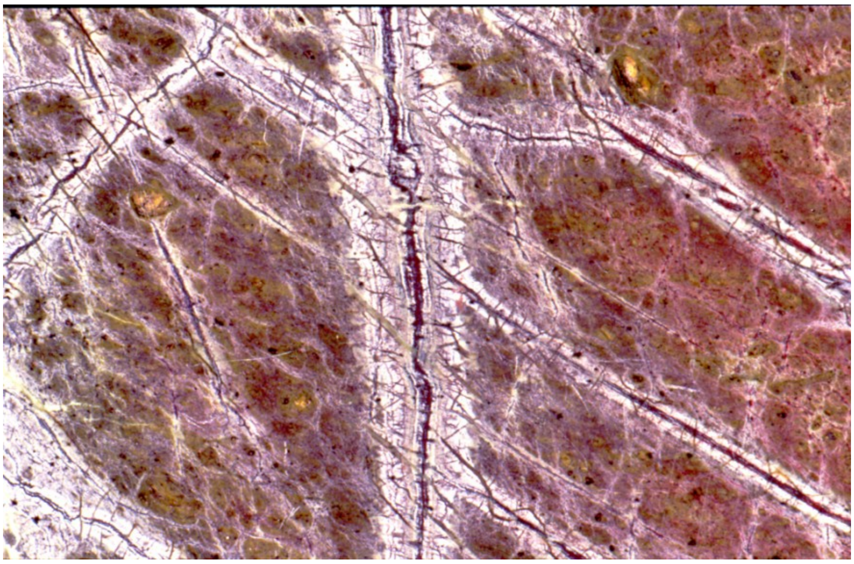


Figure 95 Serpentinised peridotite from the Lizard, Cornwall, showing multiple generations of crack-fill serpentine and a central portion rich in hematite (red). Field of view 10 cm [Copyright BGS, NERC]

Antigorite is intermediate in overall abundance between lizardite and chrysotile (Wicks and O'Hanley, 1988). Its structure consists of tetrahedral–octahedral layers. Periodic inversions of the sheets create a wave-like shape (Figure 96). In addition, the inversions give rise to missing octahedral sites. This causes antigorite to have slightly higher SiO_2 and lower MgO and H_2O contents than either lizardite or chrysotile. Antigorite can be massive, acicular, or pseudofibrous in habit.

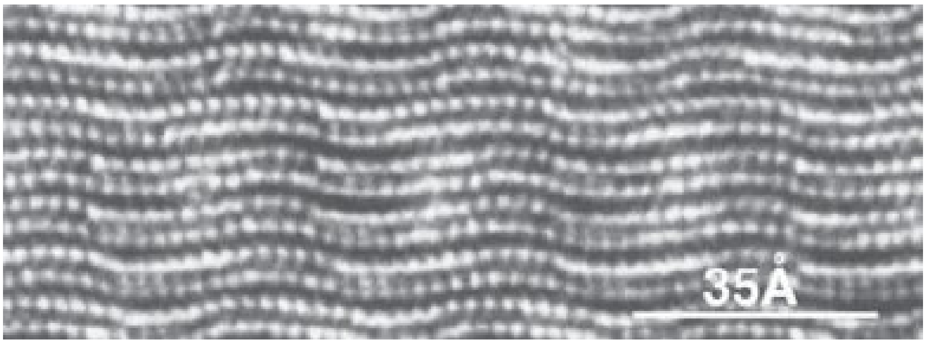


Figure 96 HRTEM image of antigorite showing the wave-like structure of the layers [Dodony et al., 2002]

STABILITY OF SERPENTINE MINERALS

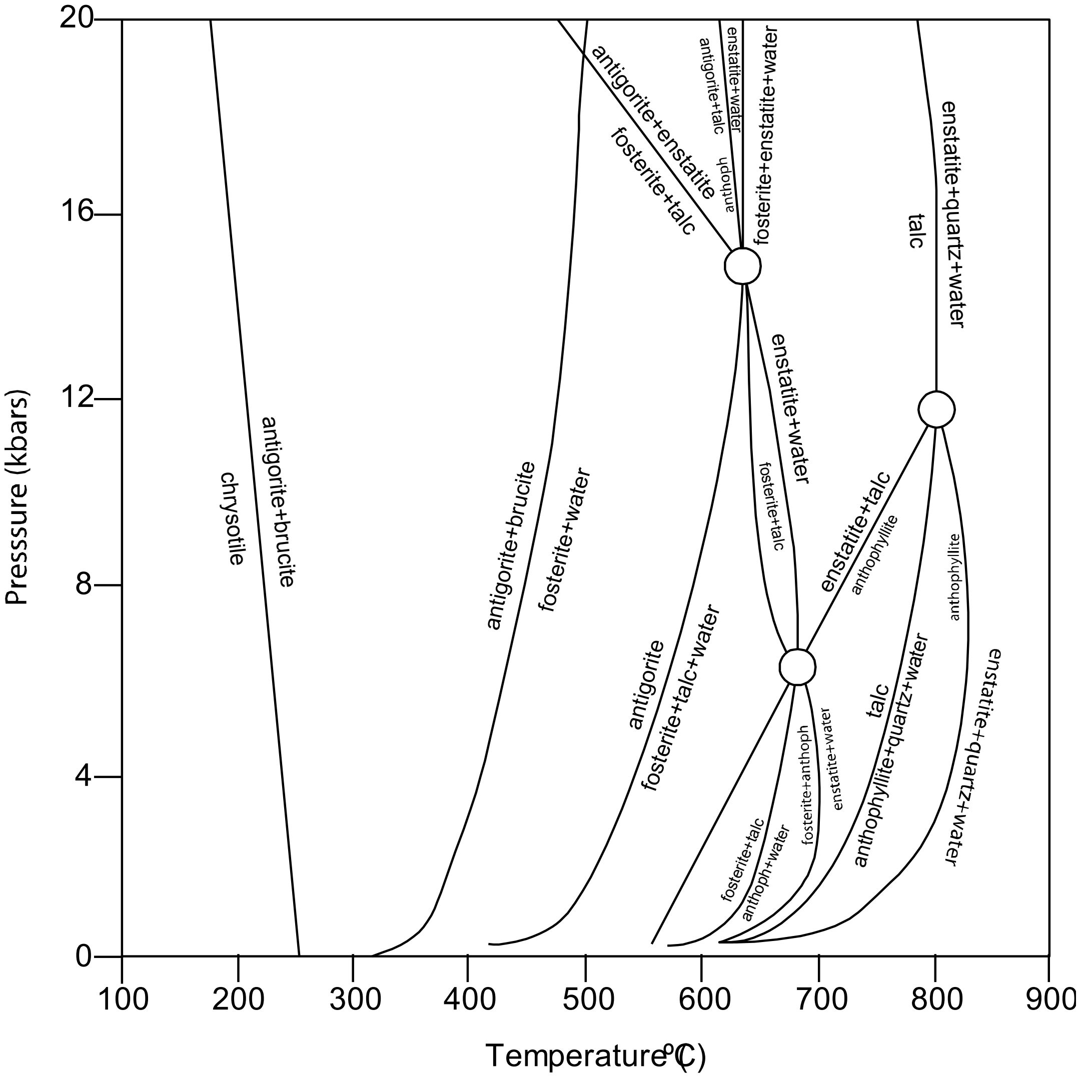


Figure 97 Pressure–temperature relationships amongst chrysotile, antigorite and other magnesium silicates in the system MgO–SiO_2–H_2O [after O'Hanley, 1996].

As stated above, serpentine minerals form by the hydration of a variety of magnesium silicates under a range of pressure–temperature conditions. Figure 97 shows that, depending on pressure, at temperatures less than about 250ºC, chrysotile is stable compared with antigorite. Regarding lizardite, the stability relations for the equilibrium *chrysotile = lizardite* are poorly constrained. However, experimental data (Chernosky et al., 1988) suggest that lizardite is stable with respect to chrysotile at temperatures below 420ºC and 2 kbar. In addition, lizardite has a slightly smaller molar volume than chrysotile and is therefore stabilised at higher pressures. This is illustrated schematically in Figure 21 and can be used to explain the formation of serpentine minerals during serpentinisation. Qualitatively, at the highest temperatures hydration would produce antigorite + brucite [($Mg(OH)_2$)], at intermediate temperatures chrysotile + brucite, and at the lowest temperatures lizardite + brucite. In terms of geological processes this means that serpentinisation of deeply seated (hot) ultramafic rocks first forms antigorite + brucite. Then during uplift (cooling) and eventual percolation of surface-derived fluids, antigorite is progressively altered to lizardite and chrysotile to form a mixed antigorite–lizardite–chrysotile rock. The dominant type of serpentine mineral formed depends on the temperature of the major influx of water and this is often in the lizardite–chrysotile stability field. As all serpentinites at the Earth's surface are exposed to low temperature aqueous fluids it is difficult to envisage a geological situation that would produce a completely chrysotile-free serpentinite. However, the phase equilibria do allow predictions to be made as to the type of geological environment where the conditions are such that the formation of chrysotile is minimised. A key geological process is prograde metamorphism (heating-up) of serpentinites. Here, serpentinites that comprise mainly lizardite and chrysotile can be changed into rock that is dominantly composed of antigorite due to later burial and heating, though it should be stressed that subsequent uplift and fluid ingress has the potential to alter this antigorite-rich rock back to chrysotile.

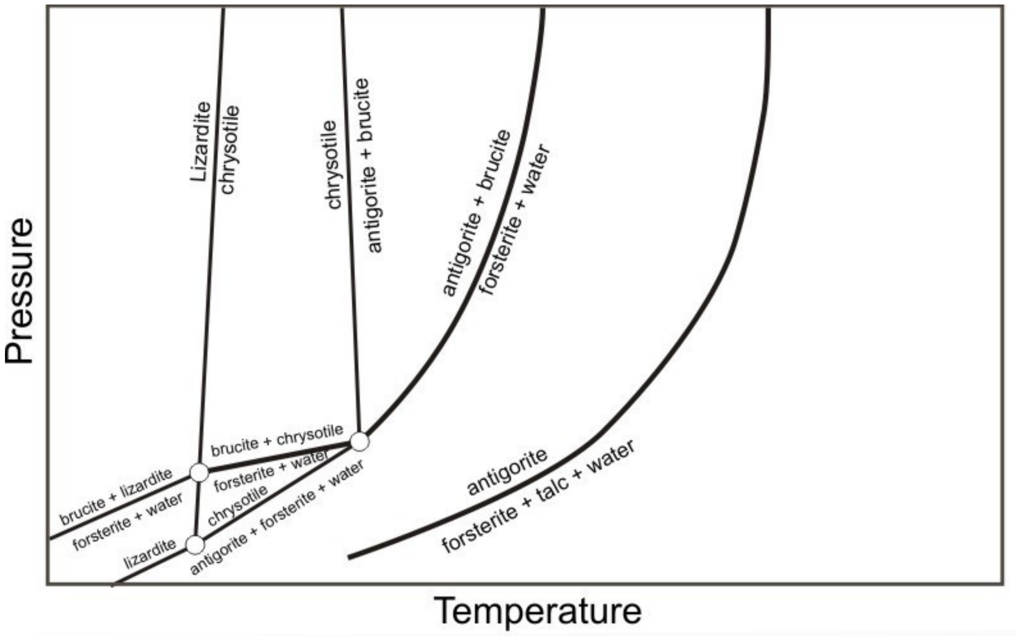


Figure 98 Schematic pressure temperature relations among various serpentine minerals brucite, forsterite and water in the system magnesium silicate MgO–SiO_2–H_2O [after O'Hanley, 1996]

There is very little information about the worldwide distribution of the serpentine types and this needs to be investigated during Phase 2 of the project. From the existing sparse data we make a very rough estimate of the worldwide distribution of serpentine types, giving lizardite as the most abundant, perhaps 70%, antigorite around 25% and chrysotile only 5%.

SERPENTINE ASBESTOS

Chrysotile, the fibrous variety of serpentine, is an asbestos mineral according to H&S regulations throughout the world. Chrysotile only constitutes a few percentage of all the serpentine in the world and very rarely forms a significant proportion of the rock. In most serpentinites it occurs as vein fills, formed by late alteration and fluid flow along fractures in rocks largely composed of lizardite or antigorite as shown in Figure 18. This means that every serpentinite sample and other partially serpentinised ultramafic rocks have to be considered as potentially hazardous material.

In practice this is only a real hazard in situations where dust is created and airborne particles are produced that could be inhaled, such as during the crushing and milling of samples and handling of powders during experiments. Previous projects by BGS studying serpentinites have established safe working practices for crushing and milling samples and subsequent use on the assumption that they are hazardous. All samples that are processed are sent for testing at a certified testing laboratory for the presence of asbestos. Asbestos has only been found in a small proportion of samples and then at the lowest detectable levels. These samples are not used for experimental work.

It should be noted that all rock dust poses some health hazard and similar measures should be taken to prevent inhalation.

A quarrying operation producing large volumes of serpentinite will be subject to H&S regulations equal to or greater than those for standard quarrying. Serpentinites are mined and quarried for nickel and asbestos in countries such as the USA, Canada, Australia, and Finland where there are rigorous H&S regulations, but it does not prevent the activities, as safe working practices have been established.

The range of compositions of ultramafic rocks

There is a wide range of compositions of ultramafic rocks, but most studies in the geological literature are details of one particular intrusion or area. The more mundane rocks, such as serpentinite, that rarely have value for economic metal deposits or building materials have received little study. Hence there is very little information about the variation on a regional or global scale.

The BGS carried out a project making geological maps of the Hajar mountains of the UAE on behalf of the UAE Federal Government (Styles et al., 2006). This mapping included about 1,000km^2 of ultramafic rocks from the Oman–UAE ophiolite, a slab of oceanic crust and mantle that has been thrust onto the Arabian continental margin (see section 7 for more information). Around 400 rock thin sections were examined as part of the study, which is one of the most comprehensive investigations of such a large area of ultramafic rocks anywhere in the world. The compositions of the ultramafic rocks from the UAE are plotted on Figure 99.

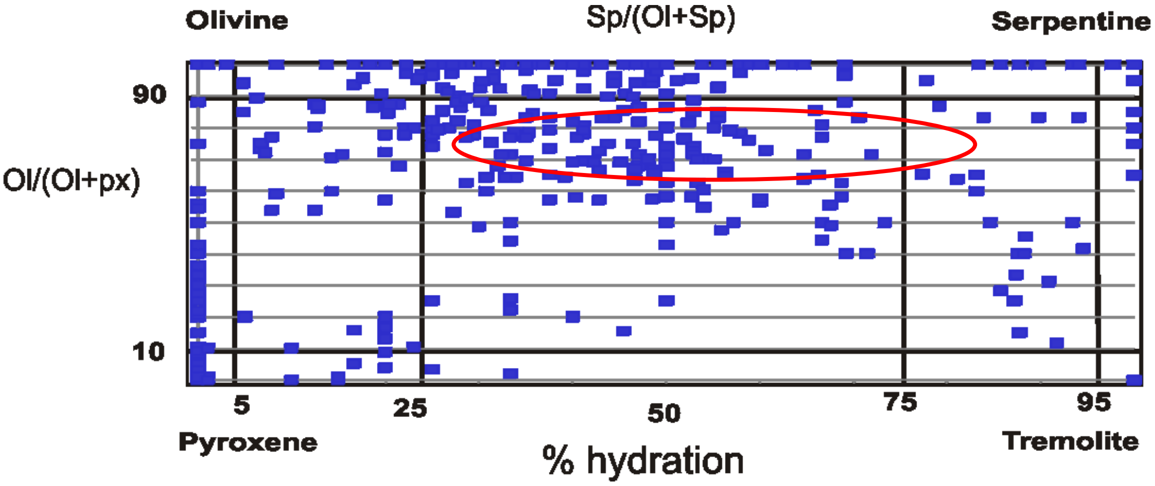


Figure 99 The compositions of 400 ultramafic rocks from the UAE ophiolite, the commonest compositions are outlined by the red ellipse. [Copyright BGS, NERC]

The diagram shows that there is a wide range of compositions both in terms of olivine–pyroxene ratio and the degree of serpentinisation. Because several data points can plot on top of each other, the concentration of compositions with minor (< 20%) pyroxene and around 50 % serpentine is clear but underemphasised. This is by far the commonest composition and shown by red outline.

The global occurrence of ultramafic rocks is covered in Section 8. To give an impression of what that global distribution might be, a very rough estimate of possible global compositions has been made here. However, it is stressed that this will need substantial work during Stage 2 to make the data more robust. The estimate is shown in Figure 100. An explanation of the different geological settings and terminology is given in section 7, but is not of great importance here.

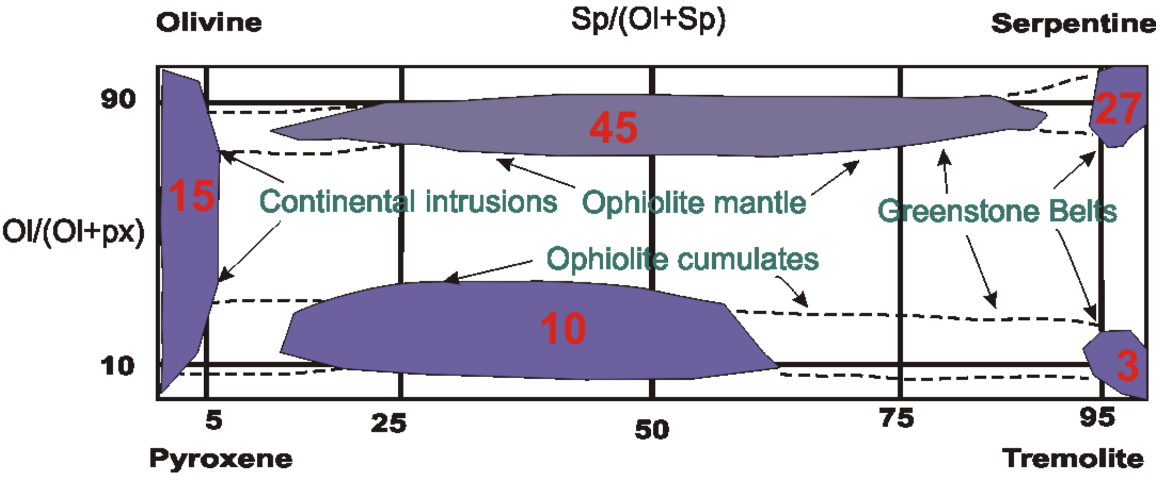


Figure 100 An estimate of the possible global distribution of ultramafic rocks in volume percent (shown in red). [Copyright BGS, NERC]

The estimate shown in Figure 23 indicates that the commonest type of source rock is likely to be ophiolite mantle rocks, similar to those studied by BGS in the UAE. These rocks consisted originally of olivine with 10 – 20% pyroxene but are now in various states of hydration. Very fresh rocks and particularly olivine-rich rocks are likely to be relatively rare, as are rocks rich in pyroxene and amphibole. Serpentinites are probably one of the commoner rock types.

Appendix 2 UK rock resources

This appendix describes the detail of the geology and aspects of the location that are summarised in Chapter 3. This product includes mapping data licensed from Ordnance Survey with permission of the Controller of Her Majesty's Stationery Office © Crown Copyright and/or database right 2007. All rights reserved. 100037272

ENGLAND LIZARD

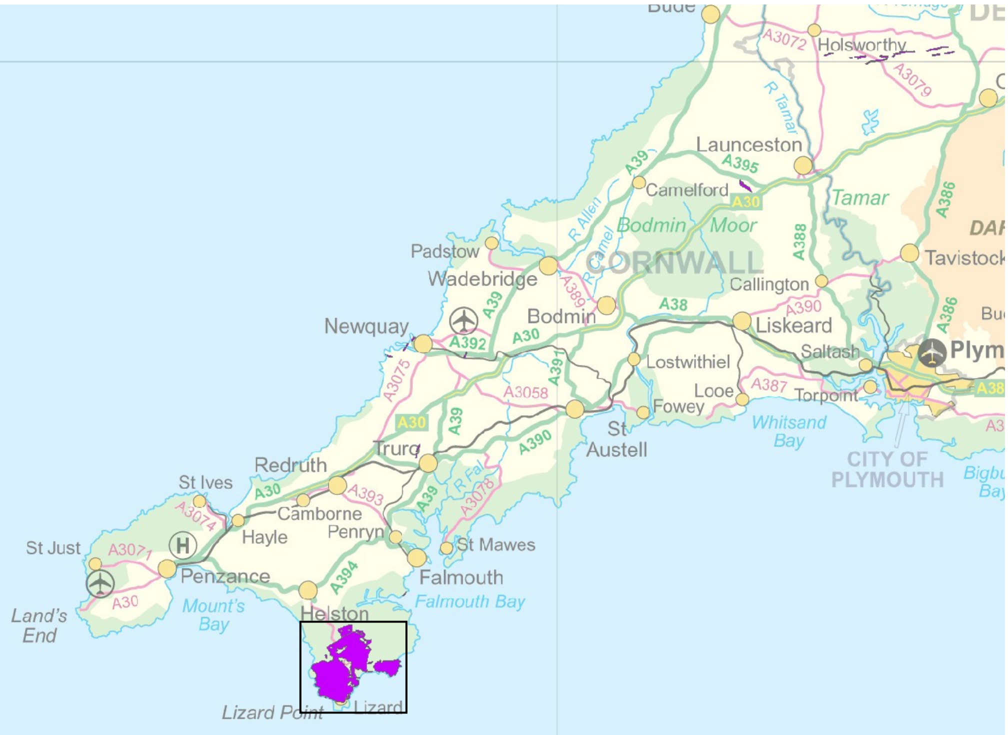


Figure 101 Map showing the location of the Lizard Complex, grid squares are 100km. [Based on OS topography, © Crown copyright]

The ultramafic bodies of Lizard [SW 701 115] belong to the Lizard Ophiolite Complex and are located in southwestern Cornwall, in the Lizard peninsula, the most southerly point of the British mainland. It is *c.* 13km southwest from the town of Falmouth and consists of two main, large ultramafic bodies that collectively cover an area of *c.* 60km^2.

Lithological description (Cook, 1999 & Chandler et al, 1984)

The ultramafic rocks of Lizard are peridotites that have suffered pervasive serpentinisation. The degree of alteration falls into the range of 20 - 100% for the majority of peridotites but most are greater than 80%, and only a small minority (< 5%) are within the 1 - 20% serpentinisation range *i.e.* relatively fresh. The most serpentinised peridotites are located in the western area (between Vellan Head and Ogo Dour Cove), in the northern area (between Trevassick Quarry and Trelan), at Poldowrian, Carrick Luz and Coverack in the eastern area. At Porthkerris the peridotite is extremely serpentinised, most sections showing 100%

serpentinisation. Dunite is the most serpentinised peridotite. Serpentinisation is influenced by the presence of faults.

Degree of alteration classification: 5 & 4 for Lizard. (see Figure 101)

SG: no known published data for Lizard, thus 2.7t/m^3 estimated.

Mineral composition (Cook, 1999)

Olivine is replaced by mesh texture serpentine dominated by a lizard +/- chrysotile and/or antigorite assemblage and bladed-mat texture serpentine consisting of an assemblage of antigorite +/- lizard +/- chrysotile. Orthopyroxene is pseudomorphed by the serpentine mineral bastite, which is composed of lizardite and chrysotile. Spinel alters to magnetite and also ferrit chromite. Plagioclase is altered to a saussuritic assemblage of fine-grained masses of epidote and mica.

The less altered rocks have mineral compositions as follows: olivine is Mg-rich and has the average composition of $Fo_{87.9}$ in ultramafic Traboe cumulates to $Fo_{90.6}$ in spinel lherzolite, showing intermediate values for the remaining subdivisions of Lizard peridotite. The orthopyroxenes plot in the enstatite, bronzite or hyperstene fields with Mg# ranging from 48.5 to 91. CaO contents vary from 0.13 to 2.31wt% and Al_2O_3 contents from 0.63 to 5.84wt%. The clinopyroxene compositions range between diopside and augite with wollastonite contents ranging from 42 to 49.6. CaO contents range from 18.5 to 25.6wt%. Al_2O_3 contents vary from 0.9 to 7.0wt%.

Comments and description of access etc.

The Lizard bodies occur at the southernmost part of the mainland of Britain and therefore they have very good access for transport by sea (English Channel). Onshore the access is somewhat limited and could only be provided by a combination of SW-NE trending A390 - A394 with minor A and B roads.

Overall amount of resource, suitability rating,

The Lizard peridotite covers a large area that, with the assumption of 35m depth of a quarry, provides a large resource (*c.* 5,073 Mt) of potentially highly desirable rocks (high degree of uniformity due to extensive serpentinisation). In addition, the costal location makes them suitable for marine transport.

Lizard peridotite has a suitability rating of **A**.

SCOTLAND SHETLANDS

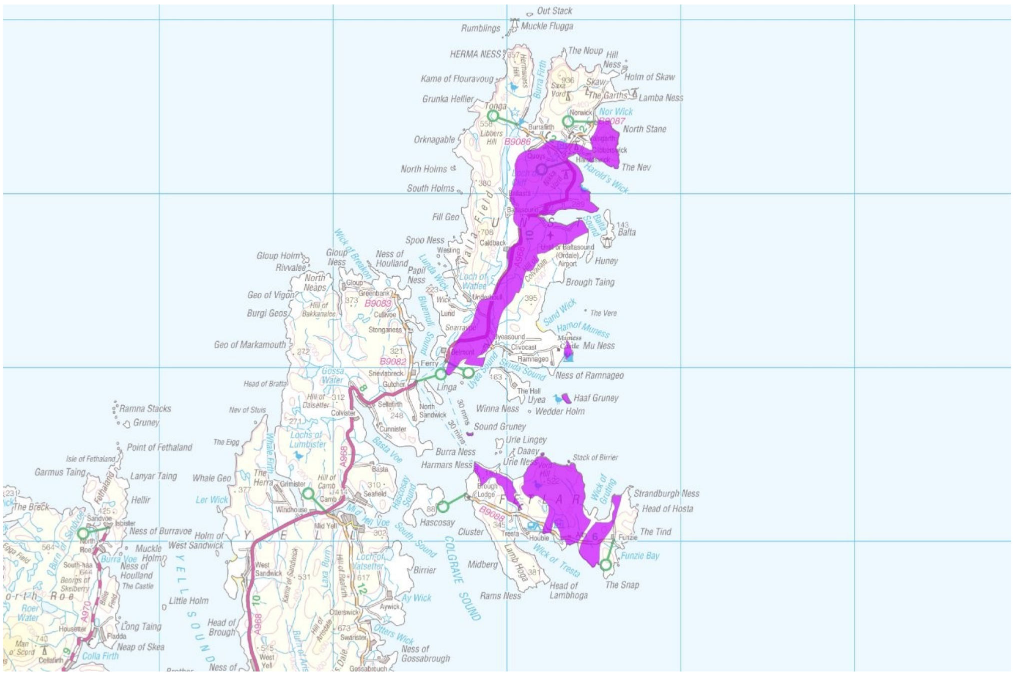


Figure 102 The location of the Shetland ultramafic bodies, grid squares 10km. [Based on OS topography, © Crown copyright]

The main ultramafic bodies of the Shetland Islands belong to the Shetland Ophiolite Complex and crop out in the northernmost two of the larger islands of the group, Unst and Fetlar. The rocks extend over a large area of *c.* 38km^2 on Unst and *c.* 16km^2 on the island of Fetlar. There are also smaller bodies that are irregularly scattered on the island of Mainland, with the biggest (*c.* 0.9km^2) located in the southeastern part near the town of Cunningsburgh.

Lithological description (Prichard, 1985)

The ultramafic part of the ophiolite is represented by variably serpentinised harzburgite, dunite, wehrlite and clinopyroxenite. In places serpentinisation is pervasive, with no more than few percentage by volume of original phases (Flinn, 1996). Harzburgite is characterised by a phase zoning that is distinguished by varying proportions of orthopyroxene and olivine. On Unst the harzburgite is overlain by the dunite. On Fetlar there are no large areas of dunite exposed but numerous lenses of dunite outcrop in the centre of harzburgite. On Unst, the base of magmatic-layered sequences is represented by dunite that gradually gives way upwards to wehrlite and pyroxenite.

The ultramafic body near the town of Cunningsburgh is a large serpentinised and steatised (talc-rich) mass.

Degree of alteration classification: 5

SG: 2.63 tonnes/m^3 for serpentinites (*Flinn, 2000*)

Mineral composition (Prichard, 1985)

The degree of serpentinisation of olivine varies from 75% fresh to completely serpentinised. The olivine in harzburgite has a composition $Fo_{90.5}$ whereas in dunite it is slightly less magnesian Fo_{90} - Fo_{88}. The orthopyroxene in the harzburgite is $En_{90.5}$ – $En_{91.5}$. Clinopyroxene from wehrlite is richer in CaO and MgO and poorer in FeO than pyroxene in gabbro.

Comments and description of access etc.

The virtually treeless islands lie about 180km northeast of the Scottish mainland. Despite its geographical isolation the road network is fairly good on Unst (a combination of A and B roads) but less satisfactory on the island of Fetlar, where there is only one B road running NW-SE across the island. There is an existing quarrying industry on Unst but not on the scale envisaged for CCSM.

Overall amount of resource, suitability rating, with reasons

Given a theoretical depth of quarry of 35m, the ultramafic rocks from Unst would provide *c.* 3,500Mt and Fetlar *c.* 1,500Mt of potentially highly suitable material. The large volume of what is likely to be a suitable resource rock, together with its coastal location, allows a high suitability rating for the Shetlands ultramafic mass.

Shetland mass has a suitability rating of **A**.

SCOTLAND BALLANTRAE

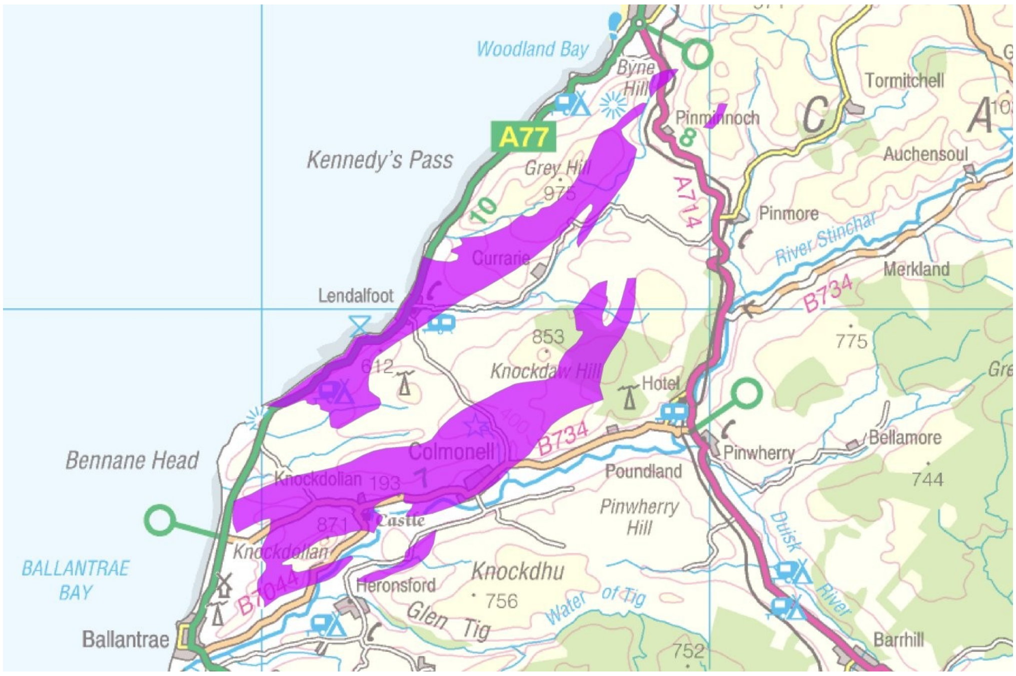


Figure 103 The location of Ballantrae ultramafic bodies, grid squares 10km. [Based on OS topography, © Crown copyright]

The ultramafic bodies of the Ballantrae Ophiolite Complex are located on the coast, *c.* 75km southwest of Glasgow, in between the towns of Girvan and Ballantrae. There are two SW-NE trending belts: a) the north belt [NX 1810 9487] – up to 1.5km wide, extending over an area of 12.8km^2. Within this area the topography is subdued and undulating except to the south and east of Cairn Hill where the serpentinite crops out in a series of crags (*Stone, Smellie, 1988*). b) the southern belt [NX 092 859 – NX 183 905] that is larger, occupying *c.* 19.1km^2. It is up to 2km wide.

Lithological description (Stone, Smellie, 1988)

The Ballantrae ultramafic rocks are largely serpentinised harzburgites, where olivine is replaced by serpentine and orthopyroxene (originally enstatite) is replaced by either bastite (platy serpentine) or, more rarely, pale green actinolitic amphibole. Relics of both olivine and enstatite are preserved in the centres of incompletely altered pseudomorphs. The northern serpentinite outcrop also contains a range of mineralogically and texturally diverse pyroxenites.

Degree of alteration classification: 5

SG: no known published data, thus 2.65 tonnes/m^3 is assumed

Mineral composition (Stone, Smellie, 1988)

The great majority of serpentinite is pseudomorphic after olivine and orthopyroxene. Both lizardite and antigorite are likely to be present. Relict olivine survives in the centre of some mesh cells, but hourglass texture is more common. Bastite pseudomorphs after orthopyroxene, generally enstatite, are widespread. Because of calcium metasomatism that was probably associated with serpentinisation, grossular garnet (rarer andradite) has formed after clinopyroxene. The bastite pseudomorphs in the southern serpentinite belt tend to be both larger and more numerous than those seen in the northern outcrop. The pyroxenites vary principally in their relative proportions of diopside and enstatite, and the presence or absence of significant accessory phases, notably olivine. In comparison with serpentinite, they are characteristically little altered: diopside may show marginal or patchy replacement by actinolite or chlorite and enstatite is often pseudomorphed by bastite, but olivine is invariably completely serpentinised.

Comments and description of access etc.

The Ballantrae ultramafic rocks are situated on the west coast of Scotland, neighbouring the waters of the Irish Sea. The network of roads in the area of Girvan-Ballantrae is reasonable and the use of a combination of A and B roads would provide a fairly good access to the site of interest. There are ports around Troon and Ayr a few kilometres to the north.

Overall amount of resource, suitability rating, with reasons

The amount of rocks that could potentially be exploited from a quarry of a theoretical 35m is *c.* 881mT for the northern belt and *c.*1,540mT for the southern belt. The extensive serpentinisation (high degree of homogeneity) puts the Ballantrae masses as potentially highly desirable source material. These facts together with the coastal location allow a high suitability rating for the Ballantrae serpentinites.

Both belts of the Ballantrae mass have a suitability rating of **A**.

SCOTLAND BELHELVIE

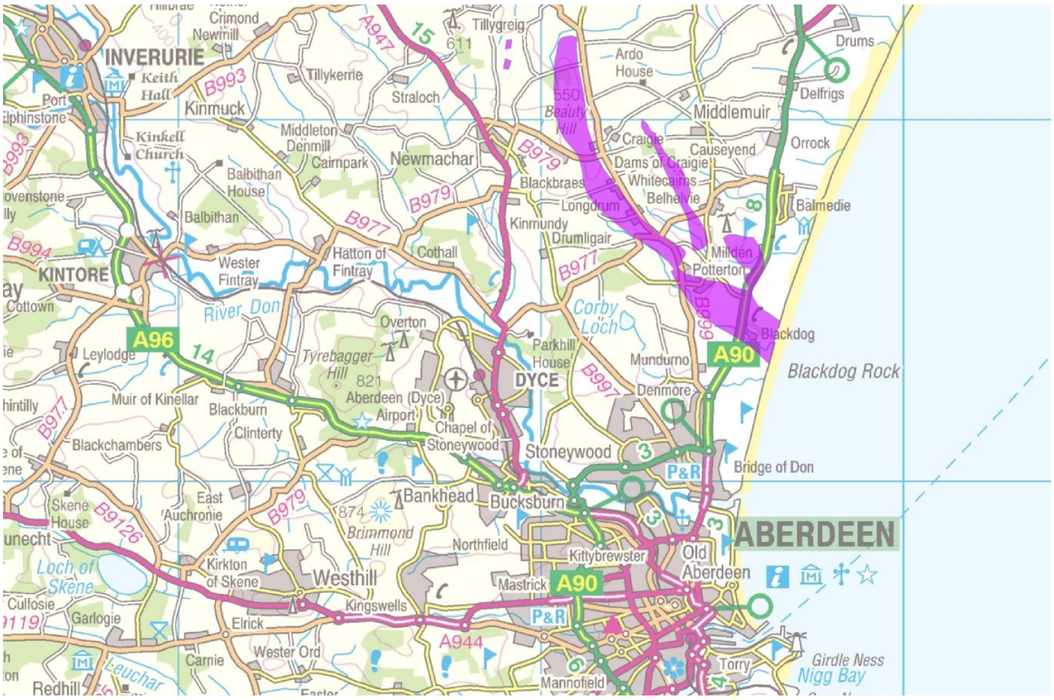


Figure 104 Location of the Belhelvie intrusion, grid square 10km. [Based on OS topography, © Crown copyright]

The Belhelvie intrusive mass, located around 10km to the north of Aberdeen, occupies an onshore area of *c.* 25km^2. Of this 25km^2, just over 10km^2 are accounted for by ultramafic lithologies. The ultramafic rocks occur principally as two NW–SE trending strips, one lying along the southern flank of the intrusion, with the second being found towards its centre.

Lithological description (Munro 1986)

The Belhelvie ultramafic rocks are largely peridotites composed of 70–80% olivine. In general, the olivine has been almost completely replaced by serpentine; fresh olivine only occasionally survives in relict kernels. Larger crystals of orthopyroxene or augite poikilitically enclose the olivine in some areas. Altered plagioclase is relatively abundant locally, notably near boundaries between the Belhelvie ultramafic and mafic components.

Degree of alteration classification: 4 & 5

SG: no known published data, thus 2.65 tonnes/m^3 is assumed

Mineral composition (taken from Munro 1986 and references therein)

In the ultramafic rocks of the northern part of the Belhelvie mass, the surviving olivine has a composition of $Fo_{85–89}$. The occasional orthopyroxene crystals have a composition of En_{83}.

Comments and description of access

The Belhelvie mass occurs within low-lying, undulating terrain. A network of B and unclassified roads provide access to those areas underlain by ultramafic rocks. These minor roads link with the A90 trunk road at several points. The city of Aberdeen lies a short distance to the south, while the town of Peterhead and the oil-/gas-fired Peterhead Power Station lie *c.* 30km to the north.

Overall amount of resource and suitability rating (with reasons)

The Belhelvie mass could potentially supply in the region of 1,000Mt of highly suitable ultramafic rock. Road access is reasonable to good, and the area lies in close proximity to a major CO_2 emitter. Pre-existing settlements will likely preclude full exploitation of this resource.

Belhelvie has a suitability rating of **A**.

SCOTLAND PORTSOY

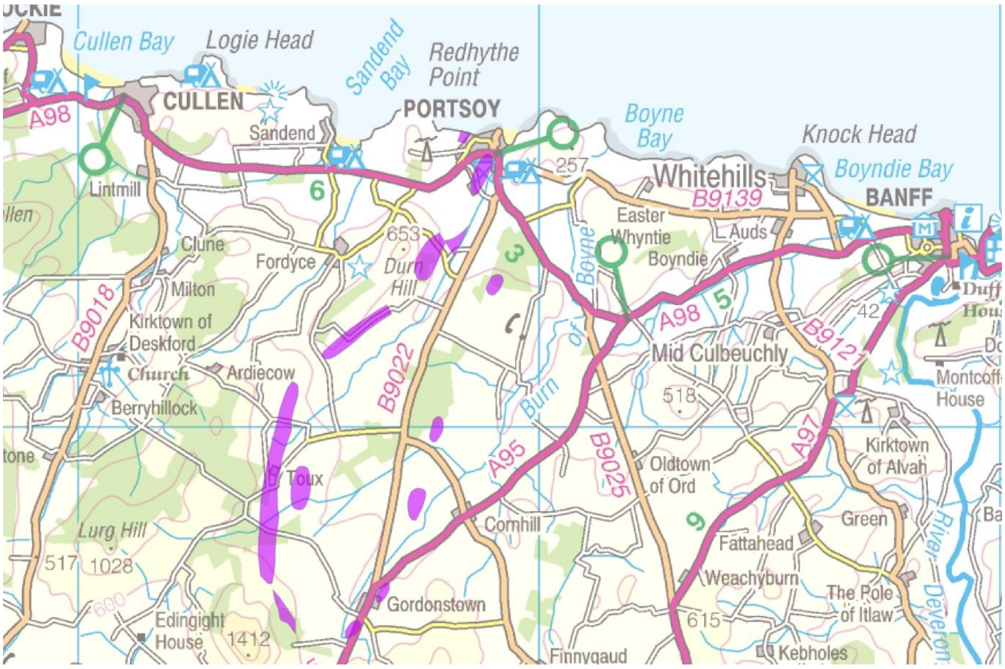


Figure 105 The location of the Portsoy ultramafic bodies, grid squares 10km. [Based on OS topography, © Crown copyright]

The Portsoy ultramafic bodies exist as a discontinuous NNE–SSW trending belt that extends for around 10km inland from the Moray Firth coast. Estimating the true extent of these bodies is problematic due to poor exposure, but together they could occupy an area of *c.* 4.7km^2.

Lithological description (Styles, 1999)

The Portsoy ultramafics are predominantly serpentinised harzburgites, lherzolites or dunites, but include some pyroxenites. Evidence of shearing is commonly observed, and, indeed, many of these rocks possess a mylonitic texture.

Degree of alteration classification: 4 & 5

SG: no known published data, thus 2.65 tonnes/m^3 is estimated

Mineral composition (Styles, 1999)

The Portsoy ultramafic rocks are extensively, if not completely, serpentinized. Remnants of the earlier mineralogy are rarely preserved, and examples have been analyzed by electron microprobe. Relict olivine has a composition of $Fo_{90–93}$, while orthopyroxene gives Mg# of 91–95, tremolite Mg# of 90–95 and Mg-hornblende Mg# of 90–92.

Comments and description of access etc.

The Portsoy area is readily accessible by a network of A, B and unclassified roads. The ground actually underlain by ultramafic rock is, overall, fairly low-lying, undulating farmland. There is, however, a notable exception to this viz. the ultramafic rocks located close to the Moray Firth coast, which underlie the town of Portsoy itself.

Overall amount of resource, suitability rating

Based on assumed quarrying depth of 35m, the Portsoy bodies could provide some 400Mt of highly suitable rock. Further investigations would, however, be required to assess the extent of the ultramafic rock in this area, as exposure is notably poor away from the coast. Road access is reasonable, and to the south of Portsoy no sizeable settlements would be lost as a result of the exploitation of this potential resource.

The Portsoy ultramafics have a suitability rating of **A/B**.

WALES ANGLESEY AND HOLY ISLAND

Figure 106 The location of the Anglesey ultramafic bodies, grid squares 10km. [Based on OS topography, © Crown copyright]

The main ultramafic bodies of Anglesey and Holy Island are located *c.* 5.5km SE from the town of Holyhead. The ultramafic bodies occur as a broad NE-SW trending zone (*Maltman, 1973*) but best exposed are three bodies that stretch across Holy Island to the neighbouring districts of the mainland of Anglesey. Together, they cover an area of *c.* 1.8km^2.

Lithological description (Maltman, 1978; Sutherland, 1982)

The Anglesey-Holy Island ultramafic rocks are mostly serpentinites derived from dunite and harzburgite. The rocks in the area are thoroughly serpentinised, the sole exception being remnant clinopyroxene in the few lherzolitic and wehrlitic parts. Serpentinites have undergone widespread natural carbonisation. All variations exist between ophicalcites, in which serpentine has been completely replaced by dolomite, weakly affected serpentinites with both calcite and dolomite and specimens lacking in carbonate. Other ultramafic rocks are represented by pyroxenites (orthopyroxenites and clinopyroxenites) and websterite.

There are few smaller (*c.* 0.7km^2) and less well exposed ultramafic bodies in the inland part of Anglesey, *c.* 5km south from the town of Amlwch, referred in the literature to as picrites. Due to its small size and the rock composition these are not considered further.

Degree of alteration classification: 4 & 5

SG: 2.54 tonnes/m^3 and 2.75 tonnes/m^3, up to 2.99 tonnes/m^3 for those containing clinopyroxene.

Mineral composition (Maltman, 1978)

Both lizardite and antigorite were found within the profoundly serpentinised ultramafic bodies. None shows any trace of olivine. Few rocks showed bronze-green clinopyroxene that is referred in the literature to as diopside containing about 20% of pigeonite component.

Comments and description of access etc.

The Anglesey-Holy Island ultramafic bodies are situated in close vicinity to the coast (Cymyran Bay in the Irish Sea) and the port of Holyhead. The NW-SE trending A55 road, together with a few minor A and B roads, links the islands with the mainland of Britain.

Overall amount of resource, suitability rating,

With the theoretical 35m depth of quarry, the bodies of Anglesey-Holy Island could supply *c.* 100Mt of potentially highly suitable rock. The profound serpentinisation and probable high degree of uniformity could potentially simplify the technological process of the pre-treatment. The location, with respect to the access to the sea and the main road, is very good.

Anglesey-Holy Island has a suitability rating of **A/B**.

SCOTLAND ISLE OF RUM

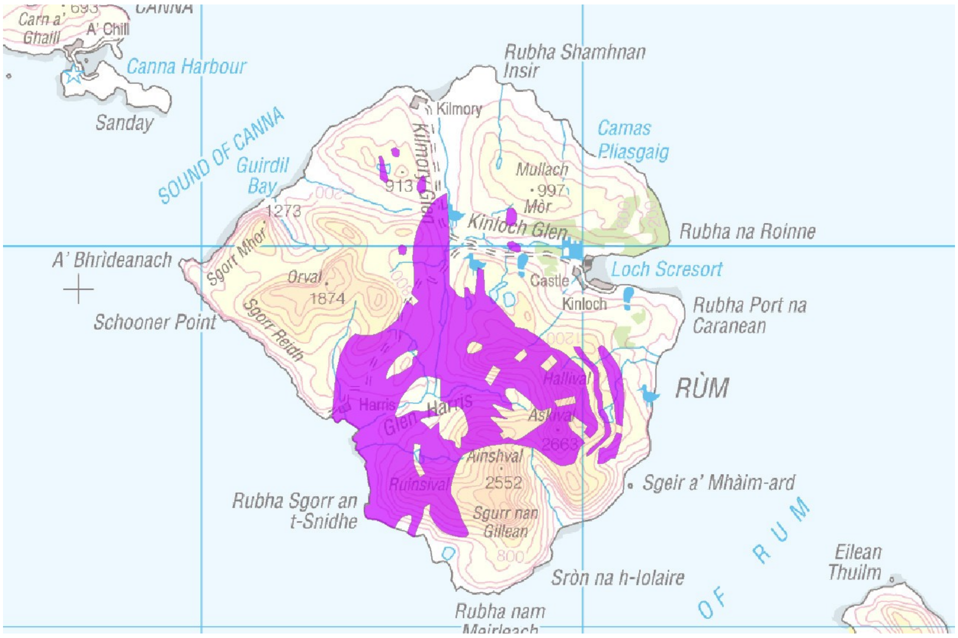


Figure 107 The location of the Rum ultramafic bodies, grid squares 10km. [Based on OS topography, © Crown copyright]

The ultramafic rocks present on the Isle of Rum [NM 339 963] are located within the southwestern part of the island. These display a characteristic compositional layering and occupy a roughly circular area of *c.* 22km^2.

Lithological description (Wadsworth 1994)

The Rum Central Complex is dominated by layered peridotites (olivine cumulates) and troctolites (plagioclase-olivine cumulates). These form three geographically and stratigraphically distinct sequences. The Eastern Layered Series consists of 15 or 16 cyclic units of peridotite (varying in thickness between 19 and 70m; Emeleus & Gyopari 1992) that are overlain by troctolite. The Western Layered Series comprises a thick peridotite member lying on top of gabbroic cumulates, while the Central Series (CS) is dominated by relatively feldspathic peridotites.

Degree of alteration classification: 6*

SG: no known published data, thus 3.0 tonnes/m^3 is assumed

Mineral composition (Emeleus & Gyopardi 1992 & Wadsworth 1960)

The Isle of Rum ultramafic rocks essentially comprise varying amounts of magnesian olivine, diopsidic pyroxene, Cr-spinel and calcic plagioclase. The composition of the olivine varies from $Fo_{82}Fa_{18}$ to $Fo_{86}Fa_{14}$, the clinopyroxene from $Ca_{44}Mg_{49}Fe_{7}$ to $Ca_{45}Mg_{45}Fe_{10}$ and the plagioclase from An_{78} to An_{84-85}.

Comments and description of access etc.

The mountainous terrain of the Isle of Rum, with the jagged peaks of Askival and Hallival in the east and the rounded hills of Orval and Ard Nev in the west, makes access extremely difficult. The road network is very poorly developed with only a few minor gravel roads being present in the eastern part of the island around Kinloch.

Overall amount of resource, suitability rating, with reasons

The entire layered complex of the Isle of Rum could potentially provide *c.* 2,325Mt of rock (assuming a quarry depth of 35m). The observed compositional variation, with feldspar present in many of the rocks and with feldspar-rich rocks intimately interlayered with ultramafic rocks, makes the rock body more demanding in terms of both quarrying and the thermo-chemical pre-treatment process. Despite its coastal location, the mountainous terrain together with the paucity of roads renders this area largely inaccessible. Furthermore, the Isle of Rum is one of Scotland’s national nature reserves.

Isle of Rum has a suitability rating of **B**

SCOTLAND GLEN NOCHTY

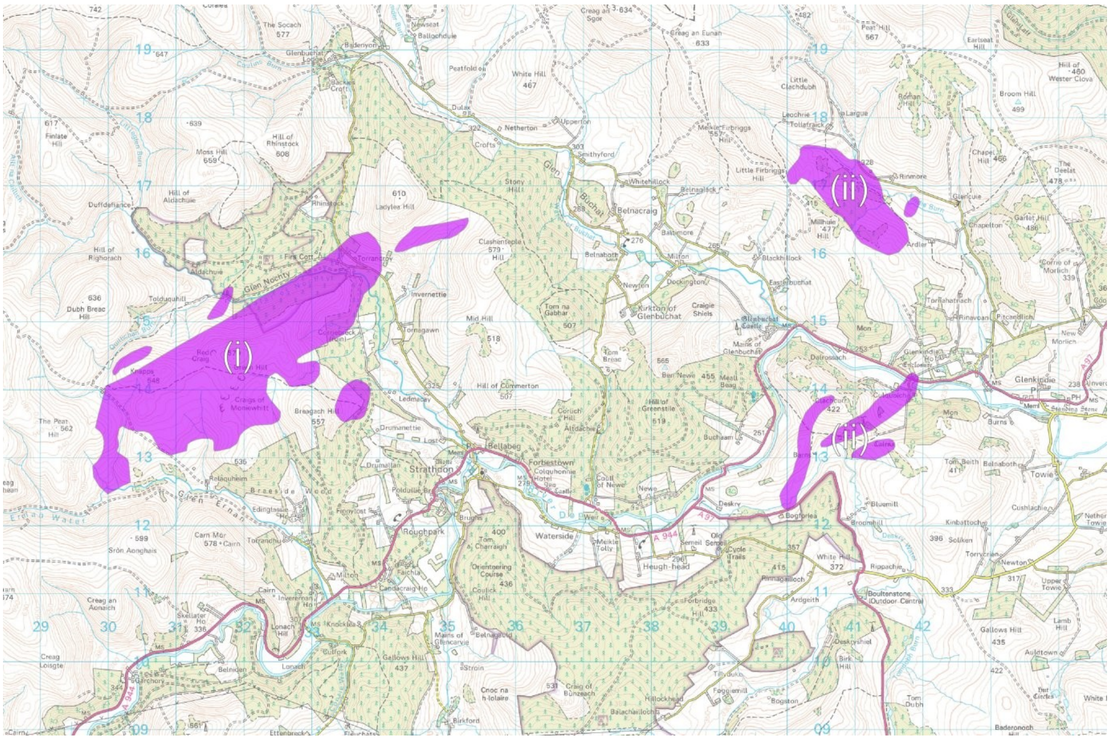


Figure 108 The location of the Glen Noghty ultramafic bodies, grid squares 1km. [Based on OS topography, © Crown copyright]

The *c.* 475 Ma Morven-Cabrach 'Newer Gabbro' intrusion includes ultramafic rocks along its northwestern shoulder. These rocks, herein referred to as the Morven-Cabrach (Glen Nochty) ultramafic rocks and designated (i) in the map above, have an elongate, NE–SW trending outcrop. Together, they cover an area of *c.* 6km^2. The nearest settlement of any size to the Morven-Cabrach (Glen Nochty) ultramafic rocks is Ballater, lying *c.* 19km to the SSE.

Lithological description (Styles 1994)

Now serpentinites, the Morven-Cabrach (Glen Nochty) ultramafic rocks were predominantly porphyroclastic harzburgites. An exception to this occurs in the southwestern corner of the mapped area, where a small development (*c.* 0.3km^2) of former olivine-clinopyroxenite is found.

Degree of alteration classification: 5

SG: no known published data, thus 2.65 tonnes/m^3 estimated

Mineral composition (Styles 1994)

Relict olivine borne by the former harzburgites is very magnesian, with a composition of Fo_{91-94}. In slight contrast, the olivine-clinopyroxenite olivine has a composition of Fo_{85}.

Orthopyroxenes from the harzburgites have Mg# of 91–93, while tremolite found in both the harzburgites and the olivine-clinopyroxenite yields Mg# of 91–95.

Comments and description of access etc.

The Glen Nochty ultramafic rocks occur within elevated, remote terrain in western Aberdeenshire. The A944 and an unclassified road provide general access to the area, but at present much of the ground underlain by ultramafic rocks is inaccessible except on foot.

Overall amount of resource, suitability rating, with reasons

The Glen Nochty ultramafic rocks, as mapped, could supply upwards of 500Mt of serpentine-rich rock. In addition, only heathland and (to a lesser extent) forestry would be lost if this potential resource were to be exploited. Unfortunately, there are no major CO_2 emitters nearby and logistical problems may preclude quarrying in this area.

Morven-Cabrach (Glen Nochty) has a suitability rating of **B**.

SCOTLAND SOUTH BOGANCLOGH

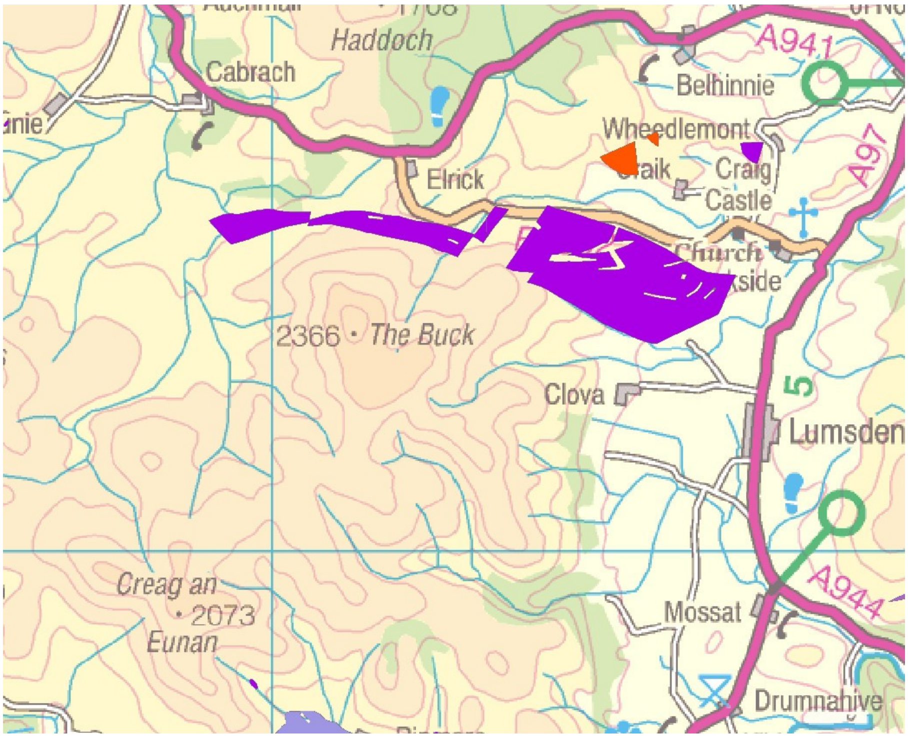


Figure 109 The location of the south Boganclogh ultramafic bodies, grid squares 10km. [Based on OS topography, © Crown copyright]

There is an almost continuous WNW–ESE trending belt of ultramafic rocks that extends along the sheared southern margin of the Insch pluton's Boganclogh sector from [NJ 393 247] to [NJ 470 237]. This 200–1,200m wide belt, along with isolated masses of ultramafic rock centred on Hill of Creagdearg [NJ 452 260], Red Craig [NJ 457 263] and Cnoc Cailliche [NJ 473 261], are herein referred to as the South Boganclogh ultramafic rocks. Mapping and geophysical investigations suggest that the main belt of ultramafic rocks occupies an area of *c.* 4.9km^2, while the secondary bodies together cover *c.* 0.25km^2. The bodies are close to the village of Lumsden but the nearest settlements of any size to the South Boganclogh ultramafics are Rhynie (*c.* 6km to the NE), Huntly (*c.* 17km to the NE) and Alford (*c.* 16km to the NE).

Lithological description (Styles 1994; Gould 1997)

With the exception of a small area of clinopyroxenite/olivine-clinopyroxenite (wehrlite according to Gould 1997), the South Boganclogh ultramafics are either dunites or harzburgites. The modal proportion of orthopyroxene rises from very little in the dunites to around 20% in the harzburgites. The rocks, in general, are very strongly serpentinized and fresh olivine cores are rare. There are, however, exceptions to this for example the rocks exposed on Red Craig and on Hill of Creagdearg (shown in red on the map above). In both of these areas, the dunites (± harzburgite) are only slightly serpentinised.

Degree of alteration classification: 3 & 4

SG: no known published data, thus 2.65 tonnes/m^3 estimated

Mineral composition (Styles 1994; Gould 1997)

Olivine borne by the fresh dunite exposed on both Red Craig and Hill of Creagdearg has a composition of Fo_{92}. This is virtually identical to the composition of the olivine in the more altered dunites and harzburgites. The harzburgite orthopyroxene gives an Mg# of 92. Clinopyroxene within the clinopyroxenites yields Mg# of 89–95, while the co-existing olivine has a composition of Fo_{89} (i.e. slightly more Fe-rich than in the dunites/harzburgites).

Comments and description of access etc.

The South Boganclogh ultramafic bodies are found within elevated, fairly remote terrain in west-central Aberdeenshire. General access to the area is provided by the A97 and B9002, but (at present) only narrow, unmetalled tracks penetrate the ground actually underlain by ultramafic rocks.

Overall amount of resource, suitability rating

Even if the Hill of Creagdearg, Red Craig and Cnoc Cailliche outcrops are excluded, the South Boganclogh ultramafics (as mapped) could supply over 450Mt of serpentine-rich rock. In addition, only heathland and poor quality grazing would be lost if this potential resource were to be exploited. Unfortunately, access to the South Boganclogh area is poor and there are no major CO_2 emitters nearby.

South Boganclogh has a suitability rating of **B**.

SCOTLAND Isle of Skye

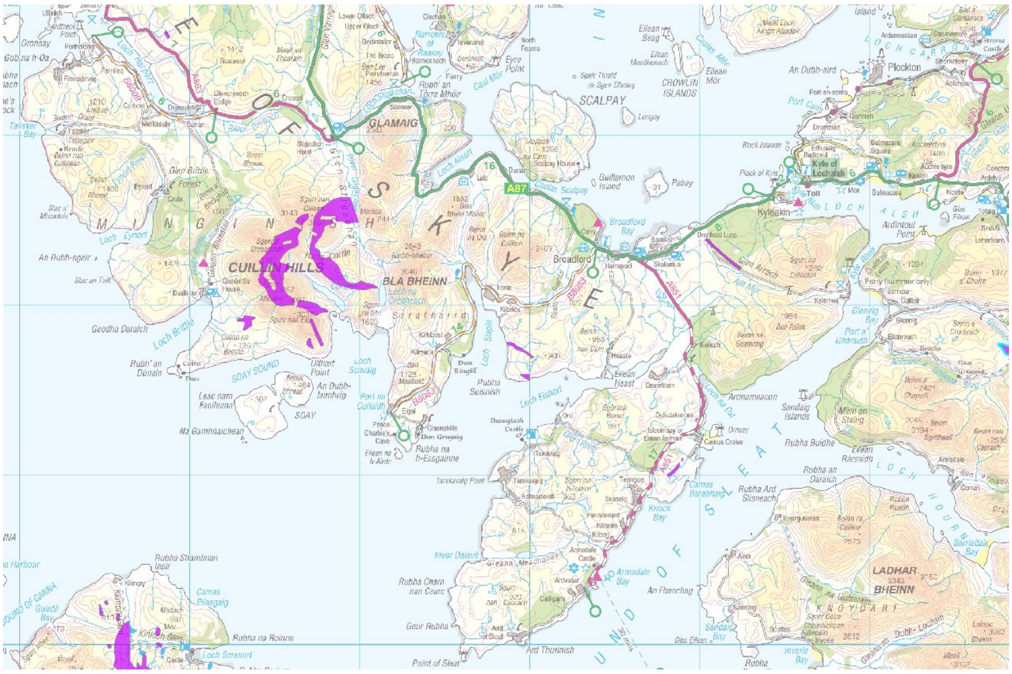


Figure 110 The location of the Skye ultramafic bodies, grid squares 10km. [Based on OS topography, © Crown copyright]

The ultramafic rocks of the Isle of Skye are situated in the central part of the island, within the heart of the Cuillin Hills. They form an arcuate belt between the head of Loch Scavaig and the northern end of the River Coruisk, and cover an area of *c*. 2.8km^2.

Lithological description (Sutherland, 1982 & Weedon, 1965)

The ultramafic and mafic rocks of the Isle of Skye are layered. They are largely olivine-rich adcumulates (dunite and peridotite) in the lower part of the succession (zone I), becoming olivine- and feldspar-rich adcumulates (feldspathic peridotites and allivalites) higher up (zone II).

In the north of the island, *c*. 11km from the town of Portree, there is a smaller (*c*. 0.6km^2) body of ultramafic rock, referred to in the literature as a picrite. Due to its limited size and composition, this body will be discussed no further.

Degree of alteration classification: 6 & 1*

SG: no known published data, thus 3 tonnes/m^3 is assumed

Mineral composition (Weedon, 1965)

Olivine dominates the mineralogy of the Isle of Skye ultramafic rocks. This occurs along with varying proportions of plagioclase, clinopyroxene and spinel. The olivine is highly magnesian, ranging in composition from Fo$_{87}$ in the dunites/peridotites (zone I) to Fo$_{83.5}$ in the allivalites and feldspathic-peridotites (zone II). Feldspar has a composition of An_{85} in zone I and An_{88-74} in zone II.

Comments and description of access etc.

The Isle of Skye is renowned for its mountainous terrain. As a direct consequence of this, road access to many parts of the island – including the area within which the ultramafic rocks occur – is limited. Advantageous, however, is the coastal location of these rocks.

Overall amount of resource, suitability rating

Assuming a quarrying depth of 35m, the Isle of Skye ultramafics could provide almost 300Mt of potentially suitable rock. The association of the ultramafic rock with more mafic lithologies may, however, create problems in terms of rock separation prior to thermo-chemical pre-treatment.

The Isle of Skye rocks have a suitability rating of **B**.

SCOTLAND GLEN URQUHART

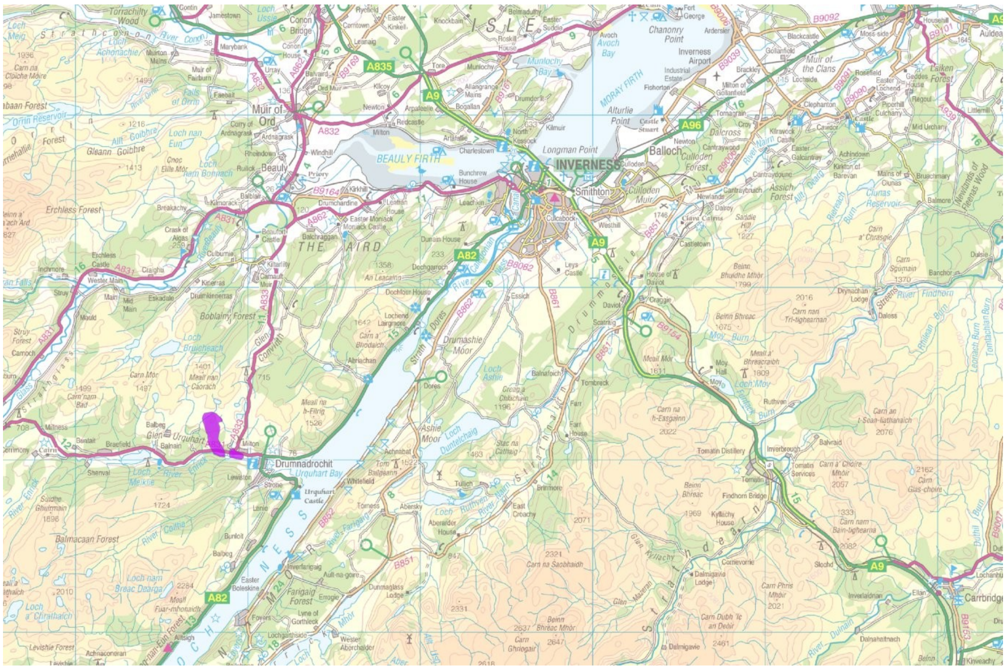


Figure 111 The location of the Glen Urquhart ultramafic bodies, grid squares 10km. [Based on OS topography, © Crown copyright]

The ultramafic rocks of Glen Urquhart Intrusion are situated *c.* 3km from the northwestern shore of Loch Ness in its middle part, in the vicinity of the town of Drumnadrochit. It is a pod-shaped body, up to 1km wide, which covers an area of *c.* 1.9km^2.

Lithological description (Francis, 1956)

The rocks of the Glen Urquhart Intrusion are serpentinites with relict olivine in the mesh centres.

Degree of alteration classification: 5 & 10

SG: no known published data, thus 2.65 tonnes/m^3 is assumed

Mineral composition (Francis, 1956)

Magnesian olivine must have formed the bulk of rock before serpentinisation; it is now present as a relict in mesh cores. Chlorite is more abundant than olivine; talc and tremolite are also present but in minute amounts. Both antigorite and chrysotile are present. Enstatite, or in three cases relicts of enstatite, is present within the cores of bastite. Carbonate-magnesite is common in the marginal bodies, where it occurs in veins and in the groundmass. Tremolite and actinolite were also found.

In the serpentinite that was not affected by subsequent hydrothermal alteration the olivine and enstatite are present as relicts.

Comments and description of access etc.

The serpentinites of the Glen Urquhart Intrusion are located *c.* 20km SW from Inverness. The road access to the site of interest is fairly good and could be provided by a combination of A and B roads.

Overall amount of resource, suitability rating

Given theoretical 35m depth of quarry the serpentinite body of Glen Urquhart could provide *c.* 182mT of rocks that show a fair compositional uniformity and therefore could potentially become a suitable material.

The Glen Urquhart mass has a suitability rating of **B**.

SCOTLAND MORVEN-CABRACH - KINDIE BURN

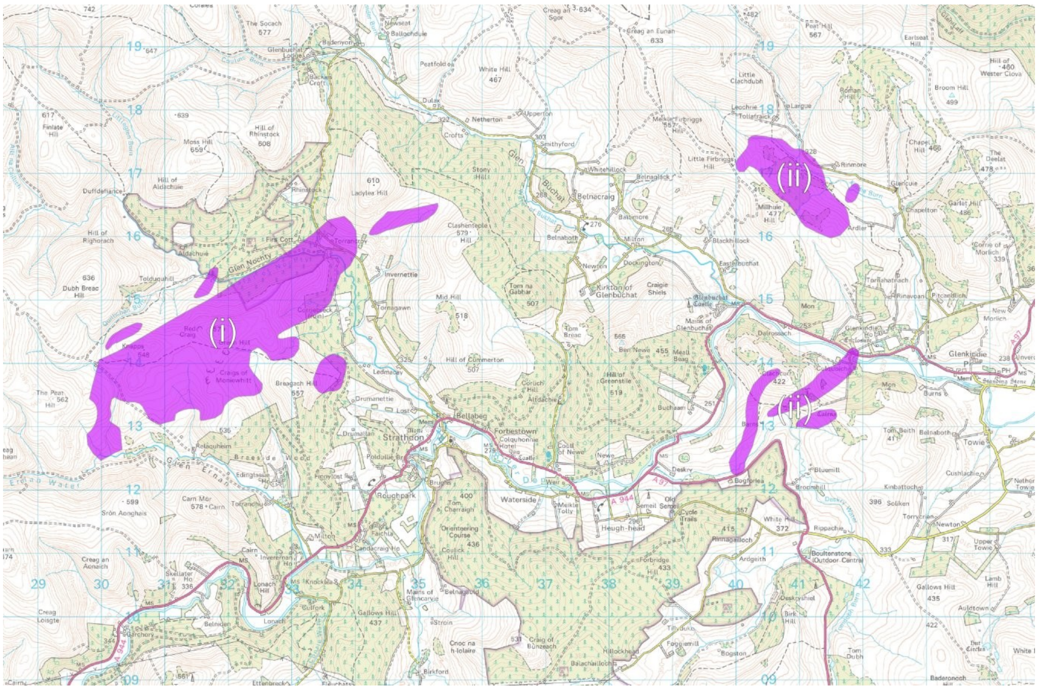


Figure 112 The location of the Kindie ultramafic bodies, grid squares 1km. [Based on OS topography, © Crown copyright]

Several fairly small bodies of ultramafic rock are found immediately east of the *c.* 475 Ma Morven-Cabrach 'Newer Gabbro' intrusion (designated (ii) in the map above). These bodies, lying both to the north and south of the River Don, are herein termed the Morven-Cabrach (Kindie Burn) ultramafics. The largest of the bodies, situated *c.* 2.5km NW of Glenkindie House [NJ 423 145], covers an area of *c.* 1.3km^2. The remaining bodies are of comparatively limited extent, together covering an area of only *c.* 0.5km^2 (and most of this is accounted for by the two elongate/sinuous bodies occurring immediately south of the River Don). The nearest sizeable settlements are Alford (located *c.* 16km to the E) and Ballater (located *c.* 20km to the SSW).

Lithological description (Styles 1994)

The largest of the Morven-Cabrach (Kindie Burn) ultramafic bodies is composed of serpentinised harzburgite (olivine and orthopyroxene modal abundances of 80% and 20%, respectively, are estimated). Evidence provided by a solitary relatively unaltered sample indicates that the original rock was coarse-grained with orthopyroxene crystals of up to 5mm in size set within a finer groundmass of olivine. Little is known about the smaller bodies of Morven-Cabrach (Kindie Burn) ultramafic rock beyond the fact that they are composed of either serpentinite (the roughly ovoid bodies) or altered clinopyroxenite (the elongate/sinuous bodies).

Degree of alteration classification: 5

SG: no known published data, thus 2.65 tonnes/m^3 estimated

Mineral composition (Styles 1994)

Relict olivine borne by the principal body of serpentinised harzburgite has a composition of Fo_{91}. The orthopyroxene gives an Mg# of 91, while the sparse tremolite yields a maximum Mg# of 95.

Comments and description of access etc.

The Morven-Cabrach (Kindie Burn) ultramafic bodies are found within hilly, fairly remote terrain in western Aberdeenshire. General access to the area is provided by the A97 and unclassified roads, but only unmetalled tracks penetrate the ground actually underlain by ultramafic rocks.

Overall amount of resource, suitability rating, with reasons

Based on the mapped extent of the largest body, the Morven-Cabrach (Kindie Burn) ultramafics could supply in excess of 125Mt of serpentine-rich rock. Only marginal farmland, heathland and (to a lesser extent) forestry would be lost if this potential resource were to be exploited, but there are no major CO_2 emitters nearby.

Morven-Cabrach (Kindie Burn) has a suitability rating of **B**.

SCOTLAND UPPER DEVERON, ULTRAMAFIC BODIES

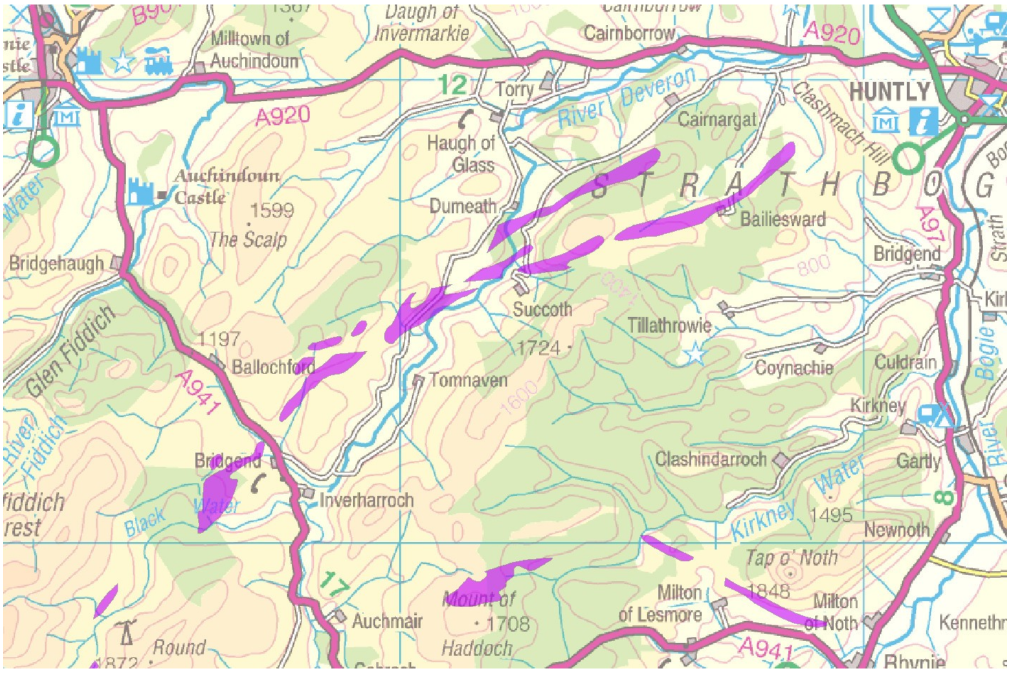


Figure 113 The location of the Upper Deveron ultramafic bodies, grid squares 10km. [Based on OS topography, © Crown copyright]

The ultramafic body, herein referred to as the Blackwater intrusion, is located *c.* 18km SW of Huntly. It is a small, somewhat irregular, NE–SW trending mass that covers an area of *c.* 0.8km^2. To the E and NE of the Blackwater intrusion lie several elongate, NE–SW trending masses of ultramafic rock. These particular ultramafic rocks belong to either the 'Kelman Hill meta-ultramafites' (an intra-Dalradian sequence of metamorphosed volcanic rocks) or the 'Succoth–Brown Hill bodies' shown on the map above. Several small intrusions of Succoth–Brown Hill type also occur to the N and NW of Huntly outside the map area. The 'Kelman Hill meta-ultramafites' and the 'Succoth–Brown Hill bodies' occupy areas of *c.* 2.8km^2 and *c.* 3.3km^2, respectively.

Lithological description (Styles 1994, 1999; Gunn et al. 1996; MacDonald et al. 2005)

The Blackwater intrusion is composed of a foliated, serpentinized wehrlite that shares much in common with the Succoth–Brown Hill type ultramafic rock. Remnants of large grains of olivine, reaching 2–3mm in size, reside in a variably foliated, serpentine-rich matrix. Interstitial tremolite, that probably replaced clinopyroxene, forms 5–10% of the rock. Succoth–Brown Hill type ultramafic rock itself comprises varying proportions of clinopyroxene and olivine, such that dunites, wehrlites and clinopyroxenites result. These rocks are commonly heavily serpentinized. The 'Kelman Hill meta-ultramafites', meanwhile, have mineralogies dominated by amphiboles (a direct result of their having undergone amphibolite-facies metamorphism). These rocks exist in either massive or fragmental forms. The former consist almost entirely of felted intergrowths of magnesian clinoamphibole, along with chlorite and sparse grains of chromian magnetite. The latter contain flattened fragments of varying type, which reach several centimetres in size and constitute between 60 and 80% of the rock. The matrix to these fragments is highly sheared, streaky and chlorite-rich.

Degree of alteration classification: 5 (strongly serpentinised rocks), 9, 10 or 13 (relatively fresh pyroxenites).

SG: no known published data, thus values of 2.65 tonnes/m^3 and 2.85 tonnes/m^3 are assumed respectively for strongly serpentinised rocks and relatively fresh pyroxenites.

Mineral composition (Styles 1994, 1999; Gunn et al. 1996)

Relict olivine from the Blackwater intrusion has a composition of Fo_{87}, while the tremolite yields Mg# of 95. Broadly similar olivine compositions are shown by the Succoth–Brown Hill rocks ($Fo_{92–88}$), although more Fe-rich compositions are found locally (Fo_{80}). Succoth–Brown Hill tremolite gives Mg# of around 90, very similar to the values yielded by the clinopyroxene which it replaces.

Comments and description of access etc.

The Blackwater, Kelman Hill and Succoth–Brown Hill ultramafic rocks occur mainly in sparsely populated, hilly, often forested terrain in western Aberdeenshire. General access to the area in question is provided by A, B and unclassified roads, but much of the ground actually underlain by ultramafic rock is inaccessible except on foot.

Overall amount of resource, suitability rating

The Blackwater intrusion and Succoth–Brown Hill bodies could together provide in the region of 400Mt of serpentine-bearing rock (based on as assumed quarrying depth of 35m). Although population displacement would be negligible if these potential resources were to be exploited, compositional variability, logistical problems and an absence of nearby CO_2 emitters somewhat lessen their attractiveness. The ‘Kelman Hill meta-ultramafites’, due to their amphibole-dominated mineralogies, are currently regarded as unsuitable targets.

The Blackwater intrusion and Succoth–Brown Hill bodies have a suitability rating of **B/C**.

SCOTLAND OLDMELDRUM

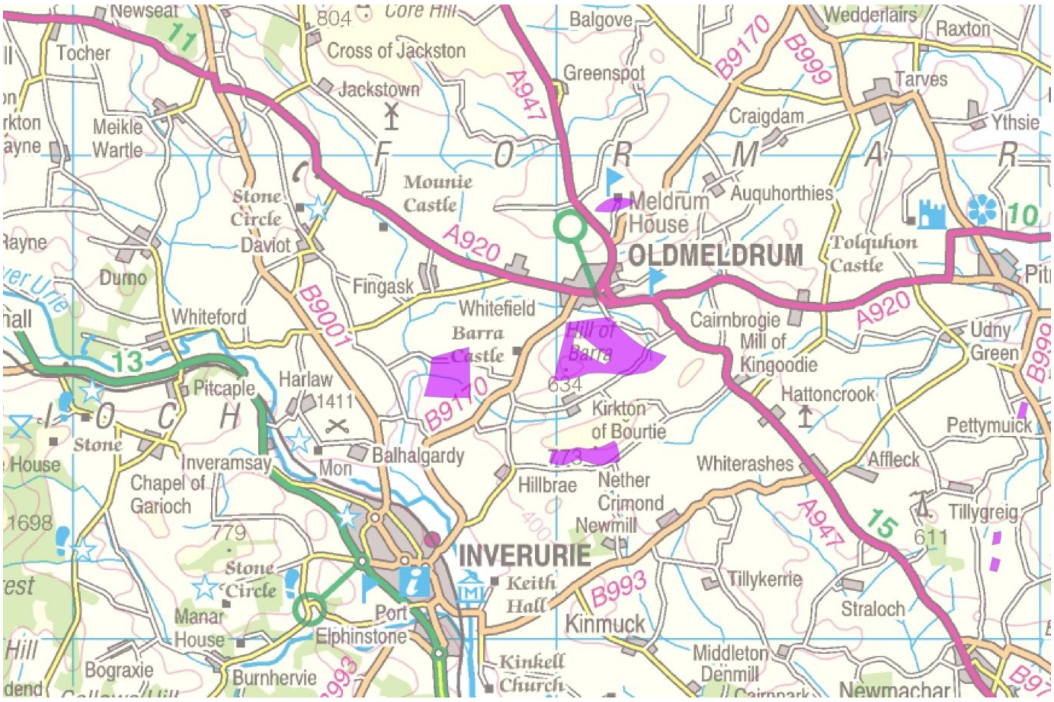


Figure 114 The location of the Oldmeldrum ultramafic bodies, grid squares 10km. [Based on OS topography, © Crown copyright]

The Oldmeldrum ultramafic bodies are found within a 4km radius of the town of Oldmeldrum (itself located 25km to the NW of Aberdeen). These tectonically-bounded bodies, which lie at the eastern end of the *c.* 475 Ma Insch 'Newer Gabbro' pluton, together occupy an area of *c.* 2.6km^2. The majority of this 2.6km^2 is accounted for by the two largely rectilinear bodies that sit immediately south and southwest of Oldmeldrum.

Lithological description (Gould 1997)

Mapped as either 'serpentinite and tremolite schist' or 'ultramafic rock', the Oldmeldrum ultramafic rocks are dark, coarse-grained rocks composed of 80–95 % olivine (hence dunites or peridotites). Variable amounts of chromite, plagioclase, clinopyroxene and, more rarely, orthopyroxene are present. The pyroxenes form large oikocrysts. Most of the olivine is serpentinised, while the associated minerals (especially plagioclase) have frequently suffered partial alteration. With increasing abundance of plagioclase, the dunites and peridotites grade into troctolites.

Degree of alteration classification: 4 & 5

SG: no known published data, thus 2.85 tonnes/m^3 assumed

Mineral composition (taken from Gould 1997 and references therein)

The olivine in the dunite has a composition of $Fo_{83–87}$. In the associated troctolite, it is slightly less magnesian, having a composition of $Fo_{80–83}$.

Comments and description of access etc.

The Oldmeldrum ultramafic bodies occur within undulating to hilly terrain accessed by A, B and unclassified roads. The Aberdeen–Inverness railway line lies approximately 5km to the southwest of the area, and is accessible at Inverurie.

Overall amount of resource, suitability rating

Collectively, the Oldmeldrum bodies could potentially supply around 260Mt of ultramafic rock. Further investigations, however, would be required to assess the extent and suitability of the ultramafic rock developments in this area (exposure is notably poor to the south of Oldmeldrum). Road access is reasonable, and ‘export’ by rail is feasible.

Oldmeldrum has a suitability rating of **C/B**.

SCOTLAND SOUTH INSCH

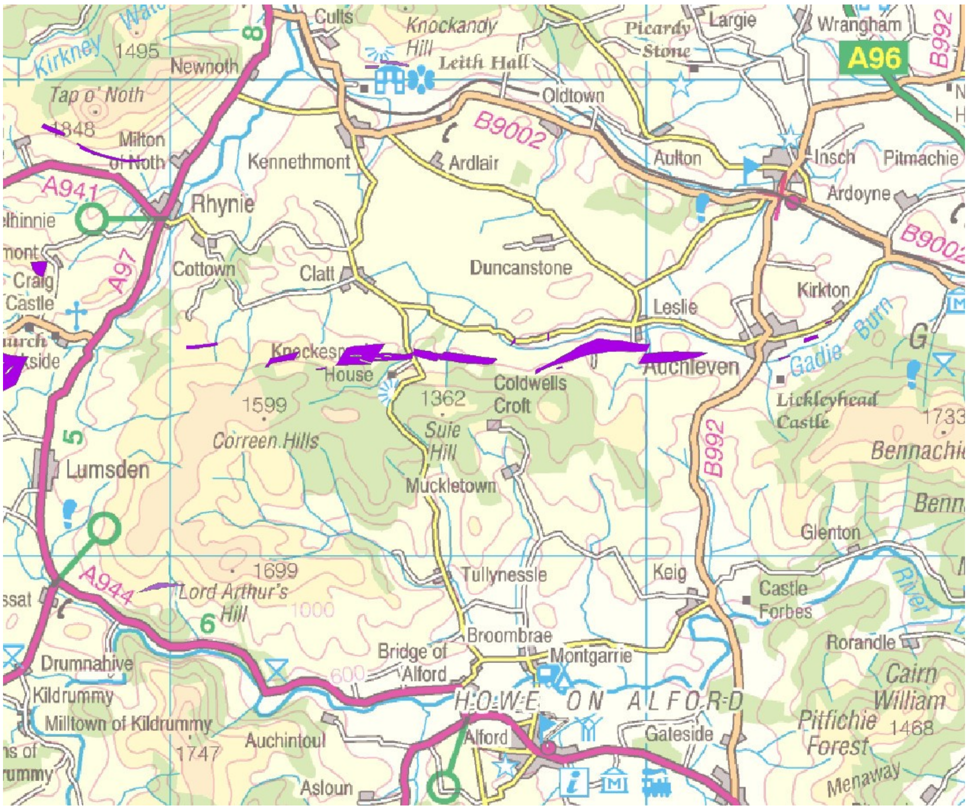


Figure 115 The location of the south Insch ultramafic bodies, grid squares 10km. [Based on OS topography, © Crown copyright]

The South Insch ultramafic bodies form a narrow, discontinuous strip that runs between Auchleven [NJ 624 244] in the east and Cairn More [NJ 504 250] in the west; the nearest settlement of any size is the small town of Insch, situated *c.* 7km to the northeast. These particular ultramafic bodies – both strongly sheared and affected by faulting – lie along the tectonic southern margin of the *c.* 475 Ma Insch 'Newer Gabbro' pluton. Mapping and geophysical investigations suggest that the South Insch ultramafics occupy an area of *c.* 1.5km^2, but their true extent remains unknown.

Lithological description (Gould 1997; Styles 1994)

Now serpentinites, some of which are conspicuously foliated, the South Insch ultramafic rocks were originally dunites or harzburgites containing up to 40% orthopyroxene. Thin section studies have revealed considerable textural variation. In some areas, the rocks are clearly olivine adcumulates characterized by a polygonal olivine texture (120° triple junctions are commonly observed). Orthopyroxene is present, occurring as small interstitial crystals with a modal abundance of 5–15%, while chromite forms 0.1–0.2mm euhedra either enclosed within the cumulus olivine crystals or lying along grain boundaries. At other localities, large (up to 8mm) pseudomorphs after orthopyroxene reside in a matrix of serpentine-replaced olivine (1–2mm in size). Still elsewhere, the rocks have a ghost augen texture consistent with high temperature shearing. Veins and patches of talc are locally present, which suggests some minor metasomatic alteration by siliceous fluids.

Degree of alteration classification: 5

SG: no known published data, thus 2.65 tonnes/m^3 assumed

Mineral composition (taken from Gould 1997 and references therein)

No chemical analyses of the South Insch bodies, or of minerals from them, are available.

Comments and description of access etc.

In general, the South Insch ultramafic bodies are found on moderately inclined, north-facing slopes along the northern flank of the Correen Hills. These slopes are partially forested. The area is accessed by a network of B/unclassified/minor roads and tracks, but these are narrow and winding. The Aberdeen–Inverness railway line lies 4–13km NE/ENE of the most sizeable of the ultramafic bodies, and is potentially accessible at number of points.

Overall amount of resource, suitability rating

As mapped, the South Insch ultramafic bodies could together supply around 140Mt of serpentine-rich rock. Establishing the overall nature, extent and hence resource potential of these ultramafic bodies would, however, necessitate further investigations. Road access to the area in question is currently poor, and the relatively nearby presence of the Aberdeen–Inverness railway line does not mitigate the resultant ‘export’ problem. Only farms, farmland, and forestry would be lost as a result of the exploitation of the South Insch ultramafic rocks.

South Insch has a suitability rating of **C/B**.

ENGLAND POLYPHANT

Figure 116 The location of the Polyphant intrusion, grid square 100km. [Based on OS topography, © Crown copyright]

The ultramafic body of Polyphant is located in the eastern part of Cornwall, *c.* 8km SW of the town Launceston. It is a small, NW-SE trending, lensoidal body with a total area of 1.2km^2.

Lithological description (Chandler, 1984)

Ultramafic rocks of the Polyphant Complex are well exposed in New Quarry, [SX 262 8221]. The rocks are dominated by peridotite that occurs in association with minor amounts of gabbro and dolerite. The peridotite is variably altered from fresh material containing serpentinised olivine, clinopyroxene, brown hornblende and biotite to an assemblage of serpentine, chlorite and carbonate minerals. The most pervasive alteration is associated with flat-lying shear zones that cut the body. The thickness of the Polyphant Complex is 32m.

Mineral composition (Power, Scott, 1995)

The olivine has been completely serpentinised.

Degree of alteration classification: 4 & 5

SG: no known published data, thus 2.65 tonnes/m^3 estimated

Comments and description of access etc.

The road access to the Polyphant Complex is fairly good. The access is provided by a combination of the SW-NE trending A30 and subordinate A and B roads.

Overall amount of resource, suitability rating, with reasons

The Polyphant body could potentially supply ≤110.2mT of rocks (max depth of the complex is 32m, *Chandler, 1984*). The small size of the body together with the complexity of alteration of peridotite makes the Polyphant mass of low desirability as a source material for the mineral carbonation process.

Polyphant peridotite has a suitability rating of **C**

SCOTLAND COYLES OF MUICK

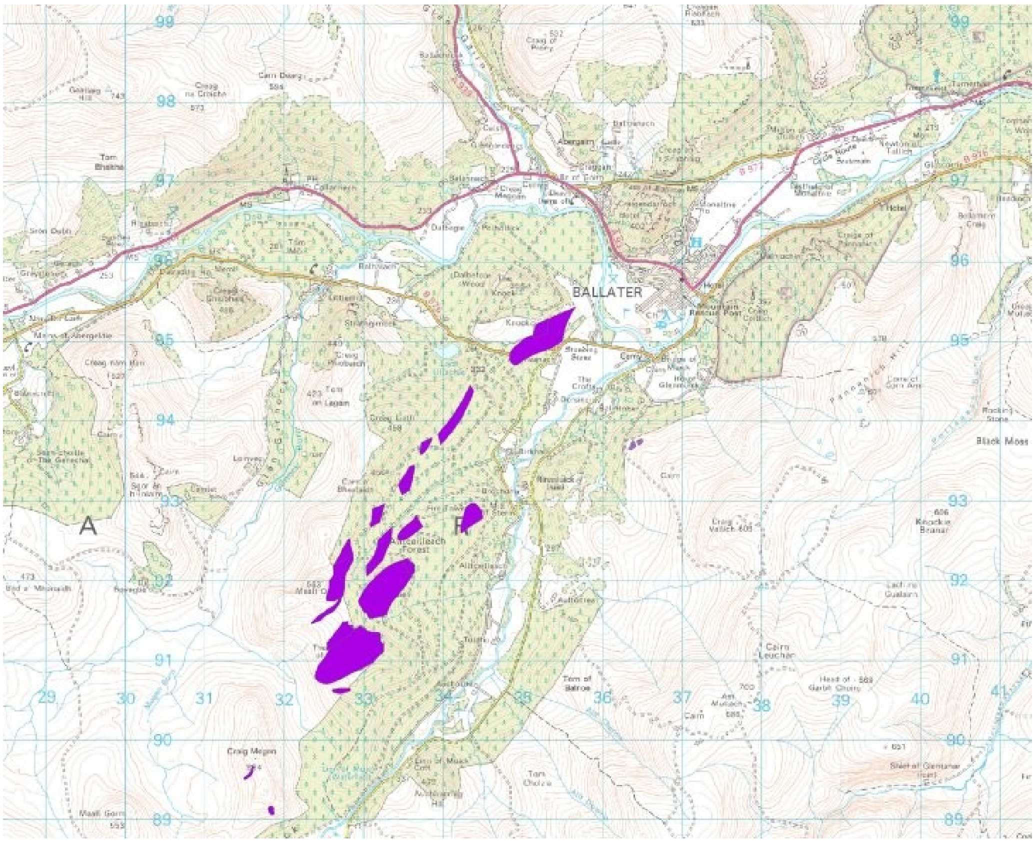


Figure 117 The location of the Coyles of Muick ultramafic bodies, grid squares 1km. [Based on OS topography, © Crown copyright]

Several small bodies of ultramafic rock, which may be linked at depth, extend for around 5km southwestward from the village of Ballater in western Aberdeenshire. These bodies – herein termed the Coyles of Muick ultramafic rocks – have a mapped extent of *c.* 1.4km^2. The elongate, NE–SW trending outcrop pattern of the Coyles of Muick ultramafics almost certainly reflects the presence in this area of the Coyles of Muick Shear Zone.

Lithological description (Styles 1994)

Petrographic examination of a number of samples from the area in question indicates that the Coyles of Muick ultramafic rocks were mainly coarse-grained olivine-clinopyroxenites composed largely of olivine and clinopyroxene along with minor opaque minerals. No clinopyroxene remains in any of the Coyles of Muick samples, this particular mineral phase having been mimetically replaced by tremolite during what is interpreted as a high-temperature hydration process. Some samples are relatively fresh (only around 10% serpentinised), but in others no traces of the original mineralogy remain (due to a combination of deformation and pervasive serpentinisation).

Degree of alteration classification: 9

SG: no known published data, thus 2.85 tonnes/m^3 assumed

Mineral composition (Styles 1994)

Olivine borne by the Coyles of Muick ultramafic rocks is generally Mg-rich, with a composition of around Fo_{88}. The amphiboles, meanwhile, are dominantly low-alumina tremolites, and yield Mg# of around 94. The chlorite and serpentine analyzed from these rocks typically possess more magnesian compositions than the high-temperature phases they replace (amphibole and olivine, respectively).

Comments and description of access etc.

The Coyles of Muick ultramafic rocks lie along the steep, east-facing, forested, western slopes of Glen Muick. General access to this area is provided by the A93, B976 and an unclassified road, but only Forestry Commission tracks penetrate the ground actually underlain by ultramafic rocks.

Overall amount of resource, suitability rating

As mapped, the Coyles of Muick ultramafics could supply around 140Mt of serpentine-bearing rock. The degree of serpentinisation is variable, however, with the result that these bodies have debatable value in this context. Despite the fact that only forestry would be lost if this potential resource were to be exploited, quarrying in this area presents considerable logistical problems. Furthermore, there are no major CO_2 emitters nearby and considerable transport distances would have to be anticipated.

Coyles of Muick has a suitability rating of **C**.

SCOTLAND NORTH BOGANCLOGH (MOUNT OF HADDOCH)

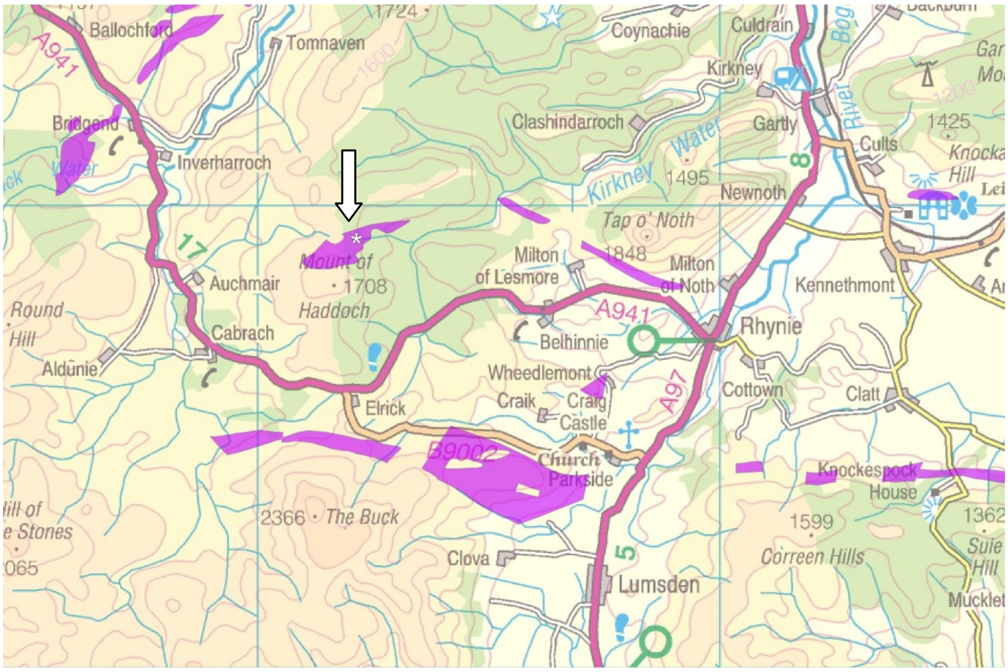


Figure 118 The location of the north Baganclogh ultramafic bodies, grid squares 10km. [Based on OS topography, © Crown copyright]

Ultramafic rocks are found locally along the northern margin of the Insch pluton's Boganclogh sector. The largest body, occupying an area of just under 1km^2, occurs to the north of Mount of Haddoch around [NJ 420 290] (marked with an arrow in the map above). The nearest settlements of any size to the Mount of Haddoch body are Rhynie (*c.* 8km to the ESE) and Huntly (*c.* 15km to the NE).

Lithological description (Styles 1994; Gould 1997)

The Mount of Haddoch ultramafic body is composed of strongly serpentinized harzburgite. Secondary recrystallization is greater than in the South Boganclogh harzburgites, and some carbonate veins are present.

Degree of alteration classification: 5

SG: no known published data, thus 2.65 tonnes/m^3 assumed

Mineral composition

No mineral composition data are available for the Mount of Haddoch ultramafic body.

Comments and description of access etc.

The Mount of Haddoch body is found within elevated, fairly remote terrain in west-central Aberdeenshire. General access to the area is provided by the A97 and A941, but only unmetalled tracks penetrate the ground actually underlain by ultramafic rocks. Much of this area is currently forested.

*Overall amount of resource, suitability rating**, with reasons***

As mapped, the Mount of Haddoch ultramafic body could supply *c.* 90Mt of serpentine-rich rock. Only heathland and forestry would be lost if this potential resource were to be exploited, but access to the Mount of Haddoch area is poor and there are no major CO_2 emitters nearby.

North Boganclogh (Mount of Haddoch) has a suitability rating of **C**.

Appendix 3

SECONDARY WASTE RESOURCES FOR CCSM IN THE UK

About 80,000 tonnes of incinerator sewage sludge ash (ISSA) are generated every year in the UK and commonly disposed to landfill (Petavratzi and Wilson, 2007). Currently about 70% of the 130,000 tonnes of paper sludge incineration ash (PS) produced every year goes to end uses, such as brick and cement manufacturers. The remaining 30% (42,000 tonnes) is sent to landfill and would be available for CCSM (Environment Agency, 2010).

Small volumes of paper ash are currently available in the UK due to the new combined heat & power plant at Shotton Paper mill. Together with the Aylesford Newsprint plant, this incinerates all the paper sludge produced in Britain. Shotton alone produces approximately 60,000 tonnes of ash per annum (Dunster, 2007). Paper sludge ash can contribute to sequestrate about 1% of the annual emissions in a typical paper making plant. For example, the paper plant at Aylesford Newsprint emits 0.5 Mt of CO_2 per year, and the ash produced from the incineration of the paper sludge has the potential to capture about 0.04 Mt CO_2/yr.

About 62,000 tons per year of biomass ash are available in the UK. All sixteen major UK power plants are now co-firing a proportion of biomass, at an average level of 3% (energy basis) making use of a range of fuels including wood (virgin and recycled), olive cake, palm kernel expeller and energy crops (Biomass Energy Centre, 2010). However, the overall volume produced every year of these secondary resources would be able to sequestrate only 0.3%/year of the targeted CO_2 emissions.

QUARRY WASTE AS POTENTIAL RESOURCE

Section 2.2.1 on resource definition of rocks showed that ultramafic rocks are the only rock type suitable for CCSM. There are currently no quarries of any size producing ultramafic rocks and therefore none of the quarry waste and fines should be considered as a resource for CCSM.

SECONDAY RESOURCES POTENTIAL

Minor waste resources are shown in Table 31 and have a theoretical potential to capture an additional 0.3% of the annual CO_2 target. It should be taken into considerations that very low amounts of paper sludge and biomass ash are currently available in the UK (high volumes in other countries, e.g. paper sludge in Brazil or Finland) and low ratio 'waste' to CO_2 are shown by ISSA. However, the future volumes available of some resources such as sewage sludge ash and biomass ash may significantly increase due to high fraction of sewage sludge sent to incineration (about 1Mt of sewage sludge sent to landfill may be incinerated), and production of high amounts of biomass ash through co-firing, pyrolysis and gasification.

The total tonnage available of the secondary waste resources was estimated to be about 2Mt with a variation of 30%. In addition, the efficiency of the resource has been shown by experiments to be variable even in this case, with the ratio $Rx_{\%}/RCO_2$ ranging from 22 for BA and to below 5% for ISSA and biomass ash.

Resource	yield Mt	RCO_2	Rx%	Rx/RCO_2	theoretical CO_2 uptake, Mt	theoretical target CO_2, %
ISSA	1.2	6.7	20.0	3.0	0.2	0.1
Paper sludge ash	0.4	2.0	44.0	22.0	0.2	0.1
Biomass ash	0.4	2.0	5.0	2.5	0.2	0.1
Total (±30%)	2.3				0.6	**0.3**

Table 31 Secondary waste resources for carbonation in the UK from 1990 to 2010. [Copyright University of Nottingham]

CHEMICAL COMPOSITION OF INORGANIC WASTE RESOURCES

A summary of the chemical composition and theoretical CO_2 uptake of the CCSM resources and potential resources is shown in Table 32. The experimental CO_2 uptake, defined as the % by weigh gained after the carbonation, were obtained from previous studies: Li et al, 2007 (3 bar, 75% humidity, 100% CO_2 atmosphere), Gunning et al, 2009 (10% moisture in waste, 100% CO_2 atmosphere, 24hrs, 2 bar), Gunning et al, 2010 (2 bar 100% CO_2 atmosphere, 72hrs, saturated sodium chloride solution to maintain the humidity).

The table clearly shows the high variability of the same material that directly depends on the starting material (e.g. coal, iron ore). Particularly, the variation of the reactive calcium and magnesium oxides can be associated with the efficiency of the carbonation process.

	Chemical composition								Theoretical CO_2
	CaO	MgO	Fe_2O_3	SiO_2	Cl	SO_3	Na_2O	K_2O	uptake, %
Blastfurnace Slag	15-20	8	0.5	36		1.4			25
Steel slag	15-20	3	71	0.8		8	0.3	0.1	25
Cement Kiln Dust	40-50	1.5	2.9	16.4		5-22	0.4	2-4	30
Biomass and wood ash	24-46	8-9	1-1.3	5.17		0.63-3	0.5	14-21	50
Recycled concrete aggregate	15-20	2-3							50
Inceneritor sewage sludge ash	9-37	3	5.6	40		0.3	0.7	2.3	15
Incinerator Bottom Ash	35-50	5	1	5-30	19	5	3	2	25
Pulverized-Fuel Ash and FBA	5-30	1	14	56		4	0.5	3	5
Air pollution control residue	50-60	8	0.5-1.5	10	1.8			6	60
Paper sludge incineration ash	50-70	2-5	1-3	10-25		1-7	1	0.2	50

Table 32 chemical compositions of the carbonation resources and potential resources in the UK and their theoretical CO_2 uptake [FHWA, 2008; Gunning et al, 2010; WRAP b, 2010, Bociocchi et al, 2009]

CALCULATIONS

Recycled Concrete Aggregate (RCA)

The composition of the Construction & Demolition (C&D) waste used to assume the fraction or RCA available for CCSM is shown in Table 33. About 55% of C&D waste in the UK is made of concrete and masonry wastes (Collins, 1997). In particular, 40% of demolition waste is made of concrete (Oikonomoru, 2005). Also, a typical prior art masonry cement contains approximately 50% Portland cement, 42% high grade limestone and approximately 8% of other components, including an air entraining agent (Maul and Robertson, 2001). From the above data, 0% of 100Mt of the C&D waste was considered the current theoretical fraction suitable to source calcium oxide for the CCSM (100% of RCA is currently reused). Instead, the RCA fraction (46Mt) was considered as future potential resource assuming that CCSM will be an intermediate stage toward a final environmental friendly reuse, due to future economical advantages.

Construction waste	**%**
Concrete, bricks, aggregate	7.4
Metals	6.0
Excess mortar/concrete	2.6
Timber and products	1.7
Plastic products	1.9
Plasterboard	0.6
Paper	0.4
Vegetation	0.2
Soil	0.2
Total Construction waste	21.3
Demolition waste	
Concrete	25.5
Masonry	15.3
Paper and plastic	10.9
Asphalt	9.6
Wood	2.1
Total demolition waste	63.8
Road planning	14.9
TOTAL	100.0

Table 33 Quantities of waste from various sources in England [Lawson et al., 2001]

The future potential amount of RCA waste available for CCSM was assessed to be between 5 and 10Mt/year. The low value was calculated considering 20% of concrete and excess mortar from construction waste being cement and 20% of concrete and 15% of masonry from demolition waste being cement. Instead, the high value was calculated considering 50% of concrete and excess mortar from construction waste being cement, and 50% of demolition concrete and 20% of demolition masonry being cement. A theoretical and experimental CO_2 uptake of 50% and 15% were considered for the calculations, respectively. Overall, the C&D waste potentially available in a lifespan of 20 years was estimated to be 128Mt (±50Mt). The efficiency considered was 50% for a total possible CO_2 uptake of 64Mt (Gunning et al, 2010; Kashef-Haghighi and Ghoshal, 2010).

Pulverised Fuel Ash (PFA)

The assumption of a constant 6.61Mt of PFA and Bottom Fuel Ash (BFA) production during a lifespan of 20 years (1990-2010) and a variable fraction sent to landfills or stockpiled (50% to landfill from 1996 to 1999, 60% to landfill in 2000, 0% available from 2001 to 2005, 3% available in 2006, 10% from 2007 to 2009) were taken into account (UK Quality Ash Association, 2010). The total PFA and BFA available for a lifespan of 20 years were estimated to be about 40Mt. In addition, a theoretical and experimental efficiency of 5% was used for the calculations for a total possible CO_2 uptake of 2Mt (Gunning et al, 2010). The high variable chemical composition of the PFA is shown in Table 34 and it directly depends to the original coal burned in the power station.

Component	**Bituminous**	**Sub-Bituminous**	**Lignite**
SiO_2	20-60	40-60	15-45
Al_2O_3	5-35	20-30	10-25
Fe_2O_3	10-40	4-10	4-15
CaO	1-12	5-30	15-40
MgO	0-5	1-6	3-10
SO_3	0-4	0-2	0-10

Table 34 Normal range of chemical composition for fly ash produced from different coal types (data in wt%) [FHWA, 2008]

Table 35 indicates that big emitters would not significantly benefit from the use of their wastes in terms of CO_2 reduction and large amount of silicate rocks would be required. For this reason, a costal location is imperative for the economics of CCSM in large scale.

power plants	CO2 emissions, Mt/y	PFA potential, CO2 Mt/y	potential, %
Drax	22.8	0.013	0.06
Cottam	10	0.007	0.07
Kingsnorth	9	0.007	0.08
Ferrybridge C	9	0.007	0.08
Fiddlers Ferry	8.4	0.007	0.08
Aberthaw B	7.3	0.005	0.07
Didcot A	7.2	0.007	0.10
Cockenzie	4.4	0.004	0.09
Ironbridge	3.3	0.003	0.09

Table 35 Potential CO_2 emission reduction in a selection of power plants. [Copyright University of Nottingham]

Stainless Steel (SS) and Blast furnace Slag (BFS)

Currently, no SS and BFS are available for carbonation technology. However, the fraction of blast furnace slag currently used to produce low-end aggregate (0.77Mt/year) and also 1.18Mt/year of steel slag were included in the average values to calculate the future potential resource for CCSM in a lifespan of 20 years, taking into account that the production of steel and blast furnace slag increased about 30% from 1990 to 2009 (Iron and Steel Statistics Bureau, 2010). The total amount available was evaluated in 15 and 24Mt for BFS and Steel slag, respectively. A 33% theoretical and 25% experimental CO_2 uptake was considered for the calculations for a potential CO_2 sequestration of 5.5 and 5Mt for BFS and SS, respectively.

The quantification of the steel slag ash available from 1990 to 2010 was extrapolated from the tonnage of steel produced in the same period. The chemical composition of the steel slag is shown in Table 36, while the CO_2 sequestration potential of the steel slag produced in two of the most important steel works is shown in Table 37.

Constituent	Composition (%)
CaO	40 - 52
SiO_2	10 - 19
FeO	10 - 40
MgO	5 - 10
Al_2O_3	1 - 3
P_2O_5	0.5 - 1
S	< 0.1
Metallic Fe	0.5 - 10

Table 36 Range of compounds present in steel slag from a typical BOF [FHWA, 2008]

steel works	CO2 emissions, Mt/y	SS potential, CO2 Mt/y	potential, %
Corus, Port Talbot	6.2	0.1	1.6
Corus, Scunthorpe	7.4	0.1	1.4

Table 37 Potential CO_2 emission reduction in a selection of steel works. [Copyright University of Nottingham]

Incinerator Bottom Ash (IBA) and air pollution control (APC) residue

The total amount available was evaluated in 0.73Mt/year including the 0.4Mt for aggregate use for a total of 14.6Mt considering a lifespan period of 20 years (DEFRA b, 2009) A 25% theoretical CO_2 uptake was taken into account for the calculations for a total sequestration of 3.65Mt of CO_2 (Li et al, 2007, Gunning et al, 2010). The amount of IBA available in the 20 years lifespan was calculated considering the MSW production from 1997 to 2007.

The total amount of air pollution control (APC) residue available in a lifespan of 20 years was estimated in 2Mt, considering 70,000 tonnes/yr and 128,000 tonnes/yr for the period between 1990 and 2000 and 2001-2010, respectively (Baciocchi et al 2009). The variation of air pollution control residue is reported in Figure 119.

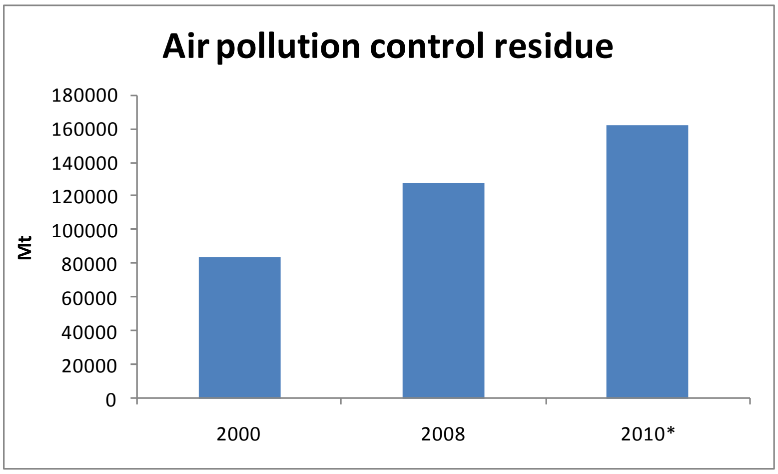


Figure 119 Variation of air pollution control residue production from 2000 to 2010 [Baciocchi et al, 2009]. * forecast.

Cement Kiln Dust (CKD)

The amount of CKD available for CCSM between 1990 and 2010 was calculated considering 290000 tonnes produced from 1990 to 2000 and 45,000 tonnes from 2001 to 2010 (Mineral Products Association, 2009) for a total amount available of 3.35Mt in 20 years. The efficiency considered was 30% for a total possible CO_2 uptake of 1Mt (Gunning et al, 2010).

Table 38 indicates the fraction of carbon dioxide that might be sequestered with the CKD produced in a selected cement works.

Cement works	CO2 emissions, Mt/y	CKD potential, CO2 Mt/y	potential, %
Dunbar	1.07	0.006	0.6
Hope	0.66	0.004	0.6
Cauldon	0.33	0.002	0.6
Aberthaw	0.63	0.004	0.6
Westbury	1.10	0.002	0.2
Northfleet	0.33	0.002	0.7
Cookstown	0.58	0.003	0.5
South Ferriby	1.07	0.008	0.7
Rugby	0.30	0.002	0.6
Barrington	0.94	0.006	0.6
Ketton	0.62	0.003	0.5
Padeswood	0.60	0.003	0.6
Ribblesdale	0.25	0.001	0.6

Table 38 Potential CO_2 emission reduction in a selection of cement works. [Copyright University of Nottingham]

Secondary resources

The total Incinerated Sewage Sludge Ash (ISSA) available was evaluated in 0.08Mt/year for a total of 1.24Mt/20 years considering 0.08Mt produced from 2006 to 2010 and 0.056Mt produced from 1990 to 2005. A 15% theoretical CO_2 uptake was taken into account for the calculations for a total sequestration potential of 0.19Mt of CO_2. The total paper sludge ash available from 1990 to 2010 was estimated in 0.38Mt considering 0 tonne from 1990 to 2000 and 42,000 tonnes from 2001 to 2010. A 50% theoretical CO_2 uptake was taken into account for the calculations for a total CO_2 uptake of 0.19Mt in 20 years. A total of 0.37Mt of biomass and wood ash was estimated to be available between 1990 and 2010, assuming that 0 tonnes were produced from 1990 to 2000, 20,000t from 2001 to 2006, and 62,000t from 2007 to 2010. A 50% theoretical CO_2 uptake was taken into account for the calculations (Gunning et al, 2010), for a total CO_2 uptake of 0.19Mt. The annual variation of sewage sludge sent to incineration is shown in Figure 120.

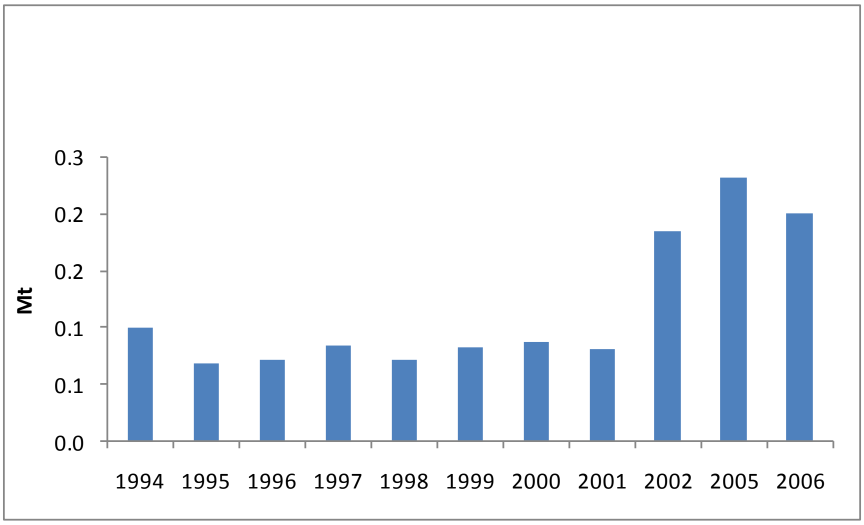


Figure 120 Variation of sewage sludge to incineration from 1994 to 2006 [DEFRA c, 2006]

WASTE RESOURCES IN THE UK

	Location			Estimated Tot Quantity [Mt per 20 years]		Variation [%]		Theoretical	CO2 uptake (Mt)
	Source	Longitude	Latitude	Average	(from 1990 to 2010)	±		uptake	
incineration bottom ash					14.6	0	24	25%	3.7
incineration bottom ash	Edmonton, London	-0.0416	51.6127		2.2				0.55
incineration bottom ash	SELCHP, London	-0.0464	51.4843		1.8				0.46
incineration bottom ash	Tysesley , Birmingham	-1.8348	52.4611		1.5				0.38
incineration bottom ash	Stockton-on-Tees, Cleveland	-1.2777	54.5945		1.1				0.27
incineration bottom ash	Coventry	-1.4925	52.3961		1.1				0.26
incineration bottom ash	Stoke on trent	-2.1881	52.9905		0.9				0.22
incineration bottom ash	Marchwood	-1.4452	50.9006		0.7				0.18
incineration bottom ash	Portsmouth	-1.0540	50.8230		0.7				0.18
incineration bottom ash	Nottingham	-1.1381	52.9467		0.7				0.16
incineration bottom ash	Sheffield	-1.4457	53.3869		1.0				0.24
incineration bottom ash	Dundee	-2.9004	56.4850		0.5				0.13
incineration bottom ash	Wolverhampton	-2.1235	52.5969		0.5				0.11
incineration bottom ash	Dudley	-2.0341	52.5159		0.4				0.10
incineration bottom ash	Chineham	-1.0646	51.2871		0.4				0.10
incineration bottom ash	Kirklees	-1.7739	53.6569		0.6				0.15
incineration bottom ash	Douglas (Isle of Man)	-4.5389	54.1849		0.3				0.07
incineration bottom ash	North East Lincolnshire	-0.1639	53.5998		0.2				0.06
incineration bottom ash	Shetland	-1.1643	60.1704		0.1				0.03
incineration bottom ash	Isles of Scilly	-6.3020	49.9198		0.01				0.00
incineration bottom ash	Allington	0.4949	51.2913		1.9				0.47

Table 39 Incinerator bottom ash resource distribution in the UK. [Copyright University of Nottingham]

	Location			Estimated Tot Quantity [Mt per 20 years]		Variation [%]		Theoretical	CO2 uptake (Mt)
	Source	Longitude	Latitude	Average	(from 1990 to 2010)	±		uptake	
Pulverized fuel ash					39.7	0	24	5%	2.0
Pulverized fuel ash	Aberthaw B	-3.4237	51.4126	2.0					0.10
Pulverized fuel ash	Cockenzie	-2.9802	55.9601	1.6					0.08
Pulverized fuel ash	Cottam	-0.8448	53.2905	2.7					0.13
Pulverized fuel ash	Didcot A	-1.2611	51.6060	2.8					0.14
Pulverized fuel ash	Drax	-1.0402	53.7433	5.3					0.27
Pulverized fuel ash	Eggborough	-1.1154	53.6775	2.7					0.13
Pulverized fuel ash	Ferrybridge C	-1.2720	53.7112	2.7					0.13
Pulverized fuel ash	Fiddlers Ferry	-2.6703	53.3770	2.7					0.13
Pulverized fuel ash	Ironbridge	-2.4969	52.6391	1.3					0.07
Pulverized fuel ash	Kingsnorth	0.4824	51.4615	2.7					0.13
Pulverized fuel ash	Longannet	-3.7064	56.0698	3.1					0.16
Pulverized fuel ash	Lynemouth	-1.5435	55.1886	0.6					0.03
Pulverized fuel ash	Ratcliffe	-1.2336	52.8570	2.7					0.14
Pulverized fuel ash	Rugeley	-1.9298	52.7353	1.3					0.07
Pulverized fuel ash	Tilbury B	0.4057	51.4670	1.4					0.07
Pulverized fuel ash	West Burton	-0.8854	53.3657	2.7					0.13
Pulverized fuel ash	Wilton	-1.2379	54.5730	0.1					0.01
Pulverized fuel ash	Uskmouth	-2.9153	51.5525	0.6					0.03
Pulverized fuel ash	Kilroot	-5.7673	54.7692	0.7					0.04

Table 40 UK pulverised fuel ash share. [Copyright University of Nottingham]

	Location			Estimated Tot Quantity [Mt per 20 years]		Variation [Mt]		Theoretical	CO2 uptake (Mt)
	Source	Longitude	Latitude	Average	(from 1990 to 2010)	±		uptake	
Cement kiln dust					3.4	0	24	30%	1.0
Cement kiln dust	Dunbar	-2.5707	55.9760	0.3					0.08
Cement kiln dust	Hope	-1.7432	53.3483	0.4					0.12
Cement kiln dust	Cauldon	-1.8792	53.0203	0.3					0.08
Cement kiln dust	Aberthaw	-3.3922	51.4007	0.1					0.04
Cement kiln dust	Westbury	-2.1855	51.2603	0.2					0.07
Cement kiln dust	Northfleet	0.3266	51.5172	0.1					0.04
Cement kiln dust	Cookstown	-6.7451	54.6459	0.1					0.04
Cement kiln dust	South Ferriby	-0.5063	53.6745	0.2					0.06
Cement kiln dust	Rugby	-1.2617	52.3732	0.5					0.15
Cement kiln dust	Barrington	0.0390	52.1314	0.1					0.03
Cement kiln dust	Ketton	-0.5517	52.6315	0.4					0.11
Cement kiln dust	Padeswood	-3.0714	53.1541	0.2					0.07
Cement kiln dust	Ribblesdale	-2.9489	53.7251	0.2					0.07
Cement kiln dust	Buxton	-1.9130	53.2589	0.1					0.03

Table 41 Cement kiln dust distribution in the United Kingdom. [Copyright University of Nottingham]

		Location			Estimated Tot Quantity [Mt per 20 years]	Variation [%]	Theoretica	CO2 uptake (Mt)
		Source	Longitude	Latitude	Average (from 1990 to 2010)	±	uptake	
Industrial	pollution control residue				14.6	0	65%	1.3
Industrial	APC	Edmonton, London	-0.0416	51.6127	0.3			0.19
Industrial	APC	SELCHP, London	-0.0464	51.4843	0.2			0.16
Industrial	APC	Tysesley , Birmingham	-1.8348	52.4611	0.2			0.14
Industrial	APC	ockton-on-Tees, Clevelar	-1.2777	54.5945	0.1			0.09
Industrial	APC	Coventry	-1.4925	52.3961	0.1			0.09
Industrial	APC	Stoke on trent	-2.1881	52.9905	0.1			0.08
Industrial	APC	Marchwood	-1.4452	50.9006	0.1			0.06
Industrial	APC	Portsmouth	-1.0540	50.8230	0.1			0.06
Industrial	APC	Nottingham	-1.1381	52.9467	0.1			0.06
Industrial	APC	Sheffield	-1.4457	53.3869	0.1			0.09
Industrial	APC	Dundee	-2.9004	56.4850	0.1			0.05
Industrial	APC	Wolverhampton	-2.1235	52.5969	0.1			0.04
Industrial	APC	Dudley	-2.0341	52.5159	0.1			0.03
Industrial	APC	Chineham	-1.0646	51.2871	0.1			0.03
Industrial	APC	Kirklees	-1.7739	53.6569	0.1			0.05
Industrial	APC	Douglas (Isle of Man)	-4.5389	54.1849	0.0			0.02
Industrial	APC	North East Lincolnshire	-0.1639	53.5998	0.0			0.02
Industrial	APC	Shetland	-1.1643	60.1704	0.0			0.01
Industrial	APC	Isles of Scilly	-6.3020	49.9198	0.00			0.00
Industrial	APC	Allington	0.4949	51.2913	0.3			0.17

Table 42 Air pollution control residue in the UK. [Copyright University of Nottingham]

		Location			Estimated Tot Quantity [Mt per 20 years]		Variation	[%]	Theoretical	CO2 uptake (Mt)
		Source	Longitude	Latitude	Average	(from 1990 to 2010)	±		uptake	
General	Recycled concrete aggregate					128	23	24	50%	64.0
General	Recycled concrete aggregate	East Midlands (Derbyshire)	-1.4522	52.8680		5.1	23	2.0		2.55
General	Recycled concrete aggregate	East Midlands (Leicestershire)	-1.1027	52.7121		4.5	23	1.8		2.23
General	Recycled concrete aggregate	East Midlands (Nottinghamshire)	-1.1981	53.1673		2.7	23	1.1		1.34
General	Recycled concrete aggregate	East Midlands (Northamptonshire)	-0.9793	52.2301		3.2	23	1.3		1.59
General	Recycled concrete aggregate	South East (Buckinghamshire)	-0.6374	52.0304		1.3	23	0.5		0.64
General	Recycled concrete aggregate	East of England (Bedfordshire)	-0.3929	52.1305		5.1	23	2.0		2.55
General	Recycled concrete aggregate	North West (Cheshire)	-2.71156	53.3000		10.5	23	4.2		5.24
General	Recycled concrete aggregate	North West (Greater Manchester)	-2.3869	53.4416		7.9	23	3.2		3.97
General	Recycled concrete aggregate	West Midlands (Staffordshire)	-2.0542	52.9530		7.1	23	2.8		3.54
General	Recycled concrete aggregate	West Midlands (Metropolitan District)	-1.7128	52.5142		5.1	23	2.0		2.55
General	Recycled concrete aggregate	East of England (Suffolk)	1.2706	52.0253		3.7	23	1.5		1.87

Table 43 Recycled concrete aggregate in the UK, part 1. [Copyright University of Nottingham]

		Location			Estimated Tot Quantity [Mt per 20 years]		Variation [%]		Theoretical	CO2 uptake (Mt)
		Source	Longitude	Latitude	Average	(from 1990 to 2010)	±		uptake	
General	Recycled concrete aggregate					128	23	24	50%	64.0
General	Recycled concrete aggregate	East of England (Hertfordshire)	-0.0789	51.7960		7.7	23	3.1		3.83
General	Recycled concrete aggregate	South East (Kent)	0.7316	51.3407		3.8	23	1.5		1.91
General	Recycled concrete aggregate	South East (Hoo Island)	0.5512	51.4203		3.8	23	1.5		1.91
General	Recycled concrete aggregate	South East (Surray)	-0.2674	51.2451		5.7	23	2.3		2.87
General	Recycled concrete aggregate	South East (Hampshire)	-1.4465	50.9817		3.2	23	1.3		1.59
General	Recycled concrete aggregate	Yorkshire	-1.7366	54.4052		10.2	23	4.1		5.10
General	Recycled concrete aggregate	South Yorkshire	-1.2801	53.4540		5.7	23	2.3		2.87
General	Recycled concrete aggregate	London	0.1911	51.5333		13.3	23	5.3		6.63
General	Recycled concrete aggregate	South West (Devon)	-3.5957	50.6136		7.2	23	2.9		3.58
General	Recycled concrete aggregate	South West (Dorset)	-2.0130	50.7815		3.8	23	1.5		1.91
General	Recycled concrete aggregate	North East	-1.7052	54.9630		5.1	23	2.0		2.55

Table 44 Recycled concrete aggregate in the UK, 2/2. [Copyright University of Nottingham]

Material		Location							
Material group	Material type	Source	Longitude	Latitude					
					Estimated Tot Quantity [Mt per 20 years] Average	(from 1990 to 2010)	Variation [%] ±	Theoretical uptake	CO2 uptake (Mt)
Metal slag	blastfurnaceslag					15.3	0	33%	5.0
Metal slag	blastfurnaceslag	Corus, Port Talbot	-3.7809	51.5963		4.1			1.35
Metal slag	blastfurnaceslag	Corus, Scunthorpe	-0.6246	53.5783		4.1			1.35
Metal slag	blastfurnaceslag	Corus, Rotherham	-1.1212	54.6208		4.1			1.35
Metal slag	blastfurnaceslag	Corus, Teesside	-1.3250	53.4466		0.4			0.15
Metal slag	blastfurnaceslag	Cesla steel, Cardiff	-3.1588	51.4731		1.7			0.58
Metal slag	blastfurnaceslag	rgemasters International Ltd, Sheffie	-1.4212	53.4051		0.4			0.15
Metal slag	blastfurnaceslag	Thamesteel Ltd, Sheerness	0.7463	51.4311		0.4			0.15
		Location							
		Source	Longitude	Latitude	Estimated Tot Quantity [Mt per 20 years] Average	(from 1990 to 2010)	Variation [%] ±	Theoretical uptake	CO2 uptake (Mt)
Metal slag	steel slag					23.6	0	33%	7.7
Metal slag	steel slag	Corus, Port Talbot	-3.7809	51.5963		6.3			2.08
Metal slag	steel slag	Corus, Scunthorpe	-0.6246	53.5783		6.3			2.08
Metal slag	steel slag	Corus, Rotherham	-1.1212	54.6208		6.3			2.08
Metal slag	steel slag	Corus, Teesside	-1.3250	53.4466		0.7			0.23
Metal slag	steel slag	Cesla steel, Cardiff	-3.1588	51.4731		2.7			0.89
Metal slag	steel slag	rgemasters International Ltd, Sheffie	-1.4212	53.4051		0.7			0.23
Metal slag	steel slag	Thamesteel Ltd, Sheerness	0.7463	51.4311		0.7			0.23

Table 45 Blast furnace and steel slag in the UK. [Copyright University of Nottingham]

					Estimated Tot Quantity [Mt per 20 years] Average (from 1990 to 2010)	Variation [%] ±	Theoretical uptake	CO2 uptake (Mt)
Process waste	Incinerator sewage sludge ash				1.2	0	15%	0.2
Process waste	ISSA	Crossness, London	0.1016	51.5252	0.17			0.03
Process waste	ISSA	Beckton, London	0.0602	51.5158	0.29			0.04
Process waste	ISSA	Widnes, Northwest	-2.7328	53.3621	0.32			0.05
Process waste	ISSA	Coleshill, Warwickshire	-1.7054	52.4974	0.13			0.02
Process waste	ISSA	Roundhill, West Midlands	-2.1230	52.5491	0.05			0.01
Process waste	ISSA	Knostrop Treatment Works, Leeds	-1.5491	53.7996	0.09			0.01
Process waste	ISSA	Brighhouse, West Yorkshire	-1.7826	53.7029	0.08			0.01
Process waste	ISSA	Sheffield, South Yorkshire	-1.4647	53.3831	0.05			0.01
Process waste	ISSA	Bradford, West Yorkshire	-1.7524	53.7938	0.06			0.01

Table 46 Incinerator sewage sludge ash in the UK. [Copyright University of Nottingham]

		Location			Estimated Tot Quantity [Mt per 20 years] Average (from 1990 to 2010)	Variation [%] ±	Theoretical uptake	CO2 uptake (Mt)
		Source	Longitude	Latitude				
Process waste	Paper sludge				0.4	0	50%	0.2
Process waste	Paper sludge	Aylesford Newsprint Ltd	0.4478	51.3075	0.19			0.09
Process waste	Paper sludge	St Regis Paper Co Ltd	0.7410	51.3395	0.04			0.02
Process waste	Paper sludge	UPM	-3.0361	53.2380	0.11			0.06

Table 47 Paper sludge ash available in the UK. [Copyright University of Nottingham]

		Location			Estimated Tot Quantity [Mt per 20 years]	Variation [%]	Theoretical	CO2 uptake (Mt)
		Source	Longitude	Latitude	Average (from 1990 to 2010)	±	uptake	
General	Biomass ash				0.4	0	50%	0.2
Industrial	Biomass ash	Aberthaw B	-3.4237	51.4126	0.019			0.01
Industrial	Biomass ash	Cockenzie	-2.9802	55.9601	0.015			0.01
Industrial	Biomass ash	Cottam	-0.8448	53.2905	0.025			0.01
Industrial	Biomass ash	Didcot A	-1.2611	51.6060	0.026			0.01
Industrial	Biomass ash	Drax	-1.0402	53.7433	0.042			0.02
Industrial	Biomass ash	Eggborough	-1.1154	53.6775	0.025			0.01
Industrial	Biomass ash	Ferrybridge C	-1.2720	53.7112	0.025			0.01
Industrial	Biomass ash	Fiddlers Ferry	-2.6703	53.3770	0.025			0.01
Industrial	Biomass ash	Ironbridge	-2.4969	52.6391	0.012			0.01
Industrial	Biomass ash	Kingsnorth	0.4824	51.4615	0.025			0.01
Industrial	Biomass ash	Longannet	-3.7064	56.0698	0.029			0.01
Industrial	Biomass ash	Lynemouth	-1.5435	55.1886	0.005			0.00
Industrial	Biomass ash	Ratcliffe	-1.2336	52.8570	0.025			0.01
Industrial	Biomass ash	Rugeley	-1.9298	52.7353	0.013			0.01
Industrial	Biomass ash	Tilbury B	0.4057	51.4670	0.013			0.01
Industrial	Biomass ash	West Burton	-0.8854	53.3657	0.025			0.01
Industrial	Biomass ash	Wilton	-1.2379	54.5730	0.001			0.00
Industrial	Biomass ash	Uskmouth	-2.9153	51.5525	0.005			0.00
Industrial	Biomass ash	Kilroot	-5.7673	54.7692	0.007			0.00
Industrial	Biomass ash	Cullompton, Devon	-3.2406	50.9153	0.004			0.00
Industrial	Biomass ash	Shotton, Deeside, Flintshire	-3.0102	53.2178	0.004			0.00

Table 48 Biomass ash distribution in the UK. [Copyright University of Nottingham]

Table 49 CO_2 emissions from UK industrial point sources [NAEI]

SECTOR	Plant Name	CO_2 emissions (Mt)
Power	Drax Power Station	22.76
Power	Cottam Power Station	10.03
Power	Ferrybridge 'C' Power Station	8.97
Power	Kingsnorth Power Station	8.92
Power	West Burton Power Station	8.9
Power	Fiddlers Ferry Power Station	8.4
Power	Ratcliffe on Soar Power Station	7.81
Power	Eggborough Power Station	7.65
Iron&Steel	Scunthorpe Steel Works	7.4
Power	Aberthaw B Power Station	7.34
Power	Didcot A Power Station	7.18
Iron&Steel	Port Talbot Steel Works	6.15
Power	Longannet Power Station	5.96
Iron&Steel	Teesside/Lackenby Steel Works	5.83
Power	Teeside Power Sation	4.99
Power	Tilbury Power Station	4.9
Power	Cockenzie Power Station	4.43
Power	Rugeley Power Stations	4.06
Power	Peterhead Power Station	3.66
Refineries	Grangemouth Refinery and petrochemicals complex	3.44
Power	Ironbridge Power Station	3.29
Power	Connah's Quay Power Station	3.16
Power	Saltend CCHP	3.11
Non-iron metals	Lynemouth Smelter	2.96
Refineries	Stanlow Manufacturing Complex	2.93
Power	Barking Power Station	2.78
Non-iron metals	Lynemouth	2.75
Refineries	BP Grangemouth Refinery	2.72
Power	Kilroot Power Station	2.64
Power	Didcot B Power Station	2.32
Refineries	Fawley Refinery	2.3
Power	South Humber Bank Power Station	2.3

Power	Immingham CHP LLP	2.14
Power	Ballylumford Power Station	2.13
Refineries	South Killingholme, Humber Refinery	2.01
Power	Sutton Bridge Power Station	1.98
Power	Seabank Power Station	1.96
Refineries	Coryton Refinery	1.86
Refineries	Lindsey Oil Refinery	1.82
Power	Rocksavage Power Station	1.8
Power	Barry, Npower Cogen LTD	1.74
Power	Spalding Power Station	1.74
Power	Keadby Power Station	1.74
Iron&Steel	Morfa Coke Oven Plant	1.6
Power	Medway Power Station	1.33
Refineries	Sage (Scottish area Gas Evacuation) Gas Terminal	1.3
Power	Damhead Creek Power Station	1.3
Refineries	Pembroke Refinery	1.24
Power	Coryton Power Station	1.2
Power	Baglan Bay Works	1.14
Chemicals	Grangemouth BP Chemicals	1.12
Refineries	Milford Haven Refinery	1.11
Power	Little Barford Power Station	1.11
Cement	Northfleet Cement Works	1.1
Cement	Hope Cement Works	1.07
Cement	New Rugby Cement Works	1.07
Power	Coolkeeragh Power Station	0.98
Ammonia	Severnside Fertilzer Works	0.96
Cement	Ketton Cement Works	0.94
Power	Great Yarmouth Power Station	0.88
Power	Fifoots Point (Uskmouth) Power Station	0.87
Power	Derwent Power Station	0.83
Power	Wilton Power Station	0.83
Power	Shoreham Power Station	0.79
Oil&Gas Processing	Barrow Terminal	0.77
Ethylene	Fife Ethylene Plant, Beverkae House	0.74
Power	Brunner Mond Winnington CHP	0.73

Power	Rye House Power Station	0.73
Chemicals	Methanol Plant	0.71
Ammonia	Billingham Site	0.71
Power	Killingholme B Power Station	0.7
Cement	Cauldon Cement Works	0.66
Power	Grangemouth CHP	0.65
Chemicals	North Tees Site, Port Clarence	0.64
Power	Deeside Power Station	0.64
Cement	Dunbar Cement Works	0.63
Cement	Westbury Cement Works	0.63
Cement	Padeswood Cement Works	0.62
Power	Cottam Development Centre	0.61
Cement	Ribblesdale Cement Works	0.6
Cement	South Ferriby Cement Works	0.58
Cement	Tunstead Cement Works	0.58
Ammonia	Kemira Agro UK Ltd	0.56
Power	Fellside Heat and Power	0.56
Power	Killingholme A Power Station	0.56
Chemicals	BASF plc, Seal Sands	0.51
Paper and pulp	Aylesford Papermills Cogen Plant	0.5
Power	Shotton CHP Power station	0.49
Power	Enfield Power Station	0.48
Power	Fawley Refinery	0.46
Refineries	Billingham P Refinery	0.46
Cement	Whitwell Quarry	0.44
Chemicals	BP Petrochemicals	0.42
Refineries	North Tees Refinery	0.4
Refineries	Kinneil Terminal	0.39
Oil&Gas Processing	Hound Point	0.39
Power	Peterborough Power Station	0.37
Power	King's Lynn Power Station	0.36
Power	Kemsley CHP	0.35
Other	Wissington Sugar Factory	0.34
Power	Corby Power Station	0.34
Cement	Derrylin Cement Works	0.34

Cement	Shap Cement Works	0.34
Refineries	St Fergus Gas plant	0.33
Refineries	BOC Ltd, North Tees Works	0.33
Cement	Aberthaw Cement Works	0.33
Cement	Cookstown Cement Works	0.33
Power	Grain Power Station	0.32
Cement	Melton Ross Quarries	0.32
Power	Roosecote Power Station	0.31
Power	Steven's Croft Power Station	0.3
Cement	Barrington Cement Works	0.29
Chemicals	ExxonMobil Chemical Ltd, Cadland Road	0.28
Oil&Gas Processing	Theddlethorpe Gas Terminal	0.27
Other	Station Road, Norbord Ltd	0.26
Paper and pulp	Auchmuty Rothes and Crocker Mills	0.26
Chemicals	Grangemouth Refinery	0.26
Power	Sullom Voe Power Station	0.26
Other	Acordis UK Ltd , Grimsby Site	0.25
Power	Tyseley Energy from Waste Plant	0.25
Refineries	Flotta Main Terminal	0.24
Chemicals	Ineos Chlor, Runcorn Site	0.24
Power	Barry Power Station	0.24
Power	AES Barry CHP Plant	0.24
Other	Bury St. Edmunds Sugar	0.24
Power	Flotta Offshore Oil and Gas	0.24
Power	Stoke Incineration Plant	0.23
Power	Smurfit Townsend Hook CHP plant	0.23
Power	Teeside energy from Waste Plant	0.23
Non-iron metals	Penrhos Works	0.22
Chemicals	Seal Sands	0.22
Cement	Hindlow Cement Works	0.22
Power	Erith CHP	0.21
Power	Ellesmere Port, Npower Cogen Ltd (previously Innogy)	0.21
Oil&Gas Processing	Bacton Gas Terminal	0.21
Power	Littlebrook D Power Station	0.21

Power	Workington CHP Plant	0.21
Power	Salt Union Ltd	0.21
Chemicals	Drakemyre, Dalry CHP DSM Nutritional Products (UK) Ltd	0.2
Power	Grimsby Power Station CHP	0.2
Power	Glanford Brigg Generating Station	0.19
Refineries	Seal Sands refinery	0.19
Power	Fife NGL Plant	0.18
Oil&Gas Processing	Singleton Wellsite	0.18
Other	Ancillary Components	0.17
Other	Bacton Tullow	0.17
Power	Hythe CHP	0.17
Power	Thames (Sugar) Refinery	0.17
Power	Conoco Phillips Seal Sands CHP	0.17
Other	Redfearn Glass Ltd	0.16
Chemicals	Cassel Works	0.16
Refineries	St Fergus North Sea Gas Terminal	0.16
Other	Glasshouse Loan	0.15
Power	Cantley Sugar Factory	0.15
Chemicals	VC3 Runcorn Plant	0.15
Power	Edmonton Solid Waste Incineration Plant	0.15
Power	Wolverhampton Waste to Energy Plant	0.15
Cement	Thrislington Cement Works	0.15
Power	Coventry & Solihull Waste to Energy Plant	0.15
Power	Port of Liverpool CHP	0.14
Other	Whittlesey Brick Works	0.14
Power	Sandbach CHP (Operated by Hays Chemical Distribution Ltd)	0.14
Paper and pulp	Inverurie Mills	0.13
Other	Cerestar UK Ltd, Trafford Park	0.13
Iron&Steel	Rotherham Steel Works	0.13
Power	Blackburn Mill CCGT	0.13
Other	Granox Ltd	0.13
Other	Amylum UK Ltd	0.12
Paper and pulp	Caledonian Paper	0.12
Chemicals	Sevalco Ltd	0.12

Refineries	Sullom Voe	0.12
Power	Dudley Waste to Energy Plant	0.12
Power	MIC Chemical Works	0.12
Chemicals	Smithkline Beecham plc, Shewalton Road	0.11
Chemicals	Saltend Chemicals	0.11
Power	Kevlar Cogen Plant, Maydown	0.11
Power	Fawley Power Station	0.11
Power	SELCHP Waste to Energy facility, Landmann Way	0.11
Oil&Gas Processing	Avonbridge Compressor	0.11
Power	Kirriemuir Compressor Station	0.1
Power	Greengairs Landfill Site	0.1
Power	Westfield Biomass Plant	0.1
Power	Stallingborough Power Station	0.1
Non-iron metals	Urlay Nook	0.1
Power	Broughton Airbus	0.1
Oil&Gas Processing	Bacton Interconnector	0.1
Power	Cleanaway Ltd	0.1
Cement	Batts Combe Quarry Cement Works	0.1
Oil&Gas Processing	Isle of Grain LNG installation	0.1
Other	Kronospan Ltd	0.1

Appendix 4

MECHANICAL MINERAL PROCESSING REVIEW: INDUSTRIAL EQUIPMENT

The field of mineral processing has also been given other titles such as *mineral dressing*, *mineral extraction*, *mineral beneficiation*, and *mineral engineering*. Generally, mineral processing begins when an ore is delivered from a mine, to a processing facility. At this point, the ore is called *run-of-mine material* because there has been no treatment performed on it.

The process of size reduction is called c*omminution*. Comminution in the mineral processing plant is carried out in a sequential manner using *crushers* and *screens* followed by *grinding mills* and *classifiers*. The comminution process is shown in Figure 35 and detailed description of various large-scale equipment and cost can be found in Appendix 5.

The two most common *primary crushers* used for coarse run-of-mine material are the *jaw* and the *gyratory crushers*. These primary crushers break rock through compressive forces created by a hard moving surface forcing and squeezing the rocks towards a hard stationary surface. The most common type of *secondary crusher* is the *cone crusher*. In addition, *roll crushes* are seeing a significant increase in use due to advances in their design and the improved liberation of minerals in the crushed product.

The *primary grinding* stage of the comminution process is usually conducted in cylindrical *tumbling mills* where the particle size is reduced through a combination of impact and abrasion. The primary differences between these mills are in the ratio of diameter to the length of the cylinder and the type of grinding media employed. Grinding media can be steel rods, steel balls, hard pebbles or the ore itself.

Autogenous (AG) and *Semi-Autogenous (SAG)* milling has seen increased use in recent years, especially in large mineral processing operations. AG mills employ ore as the grinding media, while semi-autogenous grinding involves the addition of steel grinding balls.

The products from AG or SAG mills typically feed *secondary grinding mills* with particles that range in size from 5cm down to below 100 microns (0.1mm). The final particle size is determined by downstream processing requirements. Grinding is carried out as a wet process with water content of 50% - 70% by weight. *Rod mills* can take coarse rocks ~5cm and utilizes steel rods as grinding media, while *ball mills* take feed material ~ 2.5cm and employ steel balls. *Pebble mills* are similar to ball mills except that the grinding media is closely sized rocks or pebbles.

There are two distinct methods for separation of particles based on size: *screening* follows the crushing process, while *classification* is performed during grinding process. Screening is generally utilized for coarse feed above 0.5mm. Classification is usually carried out at particle sizes that are considered to be too fine for sorting efficiently by screening methods. *Grizzlies, trommels and vibrating or shaking screens* are used for rough screening of coarse materials. There are various types of horizontally inclined screens such as the reciprocating, oscillating, vibratory or shaking screening. Many of these types of screens have multiple decks so different particle size products can be obtained from a single feed. The vibratory screen is probably the most common screening device found in mineral processing applications.

Various type of equipment can be used for mineral powder *classification* after or during grinding process. *Sedimentation* and *Hydraulic Classifiers* (also called free settling classifiers) are essentially large pools, ponds or conical bottomed tanks with a free settling zone. The *spiral and rake* classifiers are also used as mechanical classifiers. *Hydrocyclones (cyclones)* have become one of the most important and widely used classifiers in the mineral processing industry. They are most commonly used to return coarse material back to the ball or rod mill for further grinding. The main advantages of cyclones are that they have large capacities relative to their size and can separate at finer sizes than most other screening and classification equipment. In the last 20 years, advancements in the design and operation of *centrifugal gravity concentrators* have made them an attractive method for gravity concentration of minerals. *Jigging* is one of the oldest methods for concentrating minerals based on differences in the density of the particles. In terms of daily tonnages of ore that are treated globally, *froth flotation* is the single most important mineral recovery process. This is driven by its ability to selectively separate minerals. *Shaking tables* are often used downstream of other gravity concentration equipment such as jigs and centrifugal gravity concentrators for final cleaning prior to refining of product.

The cost of mineral processing equipment is a function of the processing capacity and formulas for cost estimation for various equipments described above are summarized in Table 50 below.

Equipment	**Capacity (W, A, Q)**	**Cost estimation formula**
Cone crusher	20-300 t/h	C (K$) = $1.55W^{1.25}$
Gyratory crusher	25-200 t/h	C (K$) = $8.0W^{0.60}$
Jaw crusher	10-200 t/h	C (K$) = $6.3W^{0.57}$
Hammer mill	2-200 t/h	C (K$) = $2.44W^{0.78}$
Ball mill	1-30 t/h	C (K$) = $50.0W^{0.69}$
Vibrating screen separators	0.5-35sqft	C (K$) = $3.1A^{0.59}$
Disc separators, 316 SS	15-150 gpm	C(K$) = $8.0Q^{0.52}$
Centrifuge separators	see Table 51 below	C (K$) = a + b W

Table 50 Cost Estimation of Standard Mineral Processing Equipment. [Walas S. M., 1988]

	Inorganic Process **10 < W t/h < 90**		**Organic Process** **5 < W t/h < 40**	
Material	a	b	a	b
Carbon steel	42	1.63	-	-
SS 316	65	3.50	98	5.06
Monel	70	5.50	114	7.14
Nickel	84.4	6.56	143	9.43
Hastelloy	-	-	300	10.0

Table 51 Cost Estimation of Centrifuge Separators. [Walas S. M., 1988]

Appendix 5

POST-PROCESSING TECHNOLOGIES REQUIRED TO OBTAIN FINAL PRODUCTS

The typical products of CCSM are in form of slurry or dry mixture powder or single product powders and are usually moved in the plant using centrifugal pumps and pipelines (about 3kWh/tonne). This section illustrates the technologies that can be involved in the post-processing of the CCSM products:

- sorting particle size
- gravity concentration
- magnetic separation
- mechanical dewatering
- drying
- agglomeration

All or part of these processes can be involved in the CCSM products post-processing based on the final utilise that is required. The energy requirement and the tonnages that can be treated are reported where data were found. Drying might not be required in the dry CCSM processes.

Size separation

The separation of particles by their size is a typical practice in mineral processing to suit the material for specific applications. The devices that are used to for size separation are divided in two big categories: screens and classifiers. Typically, classifiers such as non-mechanical classifiers, mechanical classifiers, cyclones and pneumatic classifiers are used for particle size < 100μm with air cyclones and pneumatic classifiers suitable for particle size about 5μm. These last groups of size separators can be used to separate microsilica and precipitated carbonates.

The classification takes advantages of the following particle properties (Fuerstenau M.C et al, 2003):

- Small particles fall more slowly in fluid than large particles
- Centrifugal forces are more effective on big particles than small particles (e.g. cyclones)
- Small particles behave like a suspended medium or fluid

A mechanical classifier presents parts (spirals and racks) that agitate the material in a tank moving the underflow out from the separation area. Spirals are less costly to maintain than racks. Parameters that affect the separation capacity are degree and end flare, number of spiral flights, point of feed entry, tank slope and spiral (rake) speed, feed rate and feed size. For example, a slope (in/ft) of 3 in the tank is required for particle size about 40μm while a slope 4 is preferred for particles around 800μm (Fuerstenau M.C et al, 2003).

Hydrocyclones (HC) use the centrifugal force to separate particles in a fluid (e.g. slurry) and present reasonable maintenance costs and separation capacity. The slurry is feed for gravity or pumped into a feeding pipe flowing at a tangent to a cylindrical feed chamber under pressure that possesses an angle of 20° in large cyclones. The small particles leave the chamber in the overflow pipe through the vortex while the coarse particles travel by gravity in a spiral leaving from the underflow pipe. In a vortex the centrifugal force is low close to the wall and higher in the air cone so that the small particles are kept there and the coarser follow the spiral downward close to the walls. In mineral processing, the slurry classified with HC contains 55-65% of solids. The performance of a HC is influenced by cyclone diameter, vortex finder diameter and length, cylindrical section length, feed size distribution and feed % solids, slurry type, specific gravity and viscosity (Fuerstenau M.C et al, 2003). This technique can be employed in the separation of the aqueous phase CCSM products. For example, Hydrocyclones require about 36kWh/tonne to separate plastics in a concrete recycling facility (Bilitewski et al, 1996).

A pneumatic classifier is a technique that uses a combination of gravity, aerodynamic drag, and centrifugal force and collision force to separate particles with different size. It is effective in separate particles between 0.1 and 1,000µm using air or other gases. Air cyclones, expansion chambers, vane classifiers, inertial classifiers, tank through-flow classifiers are all pneumatic classifiers (Fuerstenau M.C et al, 2003). The pneumatic classifier can be used in the dry CCSM technologies to separate the carbonates from the silica sand in dry forms.

Separation technologies

Gravity and magnetic separation can be achieved by a long list of devices where the most used are jigs, screens and classifiers, agglomeration flotation, HI and LI wet magnets. However, not all of these techniques can be employed in CCSM because they require coarse particles to be efficient.

The investigated CCSM technologies can be divided into two main groups considering the particle size needed: 37-100µm and 100-300µm. The concentration technology can be divided into two groups based on the CCSM particle size distribution. Wet classifiers, spirals, cones, wet sluices, Li/HI wet magnets, froth flotation, and HI dry magnets can be used for the group with coarser particles (100-300µm) and Hydrocyclones, tilting frames, centrifugal concentration, froth flotation, and matrix magnets can be employed for the CCSM technologies that involve small particles (37-100µm)

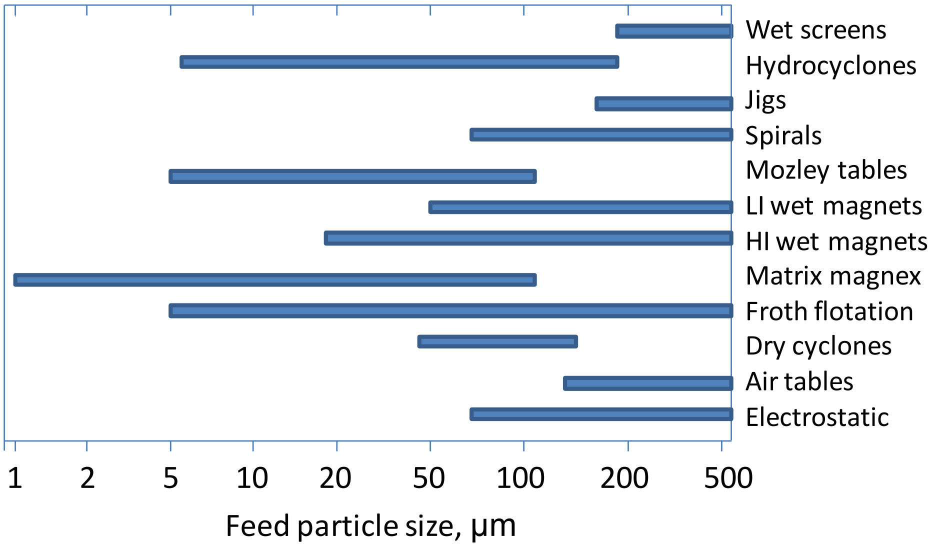


Figure 121 Range of application of conventional mineral processing techniques [Wills et al, 2007]

For multi-precipitation processes, Shiller's work (2006) suggests the possibility to separate the CCSM precipitation products (precipitation happens in three different vessels) from the reaction residue by counter-current decantation. Only separation of contaminants will be required in these multi-product technologies.

GRAVITY CONCENTRATION

Different materials can be separated by gravity concentration technique. This set of techniques is less common than flotation but is gaining major attention due to the increasing costs of flotation reagents and the capacity to treat materials with particle size in the 50μm range. Gravity concentration works best when the difference in density among materials is large, and typically the efficiency increases with the increase of the particle size. In fact, slimes with particles below 10μm are usually diverted in the tailing by hydrocyclones. This allows recycling the large amount of water needed in the process as well. The final product of the gravity concentration is typically treated by magnetic separators to recover metal particles (Wills et al, 2006).

Pinched sluices and cones are inclined launder that can treat slurry between 50 and 65% and 55-70% solids, respectively. The difference is that in the cones, slurry flow is not influenced by sidewall effects as it is in the pinched sluices. The solid stratify when it descends the inclined launder and the different materials are separated by various means (e.g. slitters) during the discharge operations. The Reichert cone in a device designed to treat large volumes of slurry (65-90 tonnes/h) and it is made of a series of cone sections stacked vertically that not require movement and permit a concentration in sequent stages. The pulp moves down in the cone, and the heavier particles separate and are removed by an annular slot. The lighter particles flow over the slot. Its efficiency is low and the operations need to be repeated for a number of times to obtain a reasonable separation. In addition, they can treat materials as fine as 30μm but the efficiency is higher between 100 and 600μm. The cones are successfully employed in the mineral sand industry and for the recovery of magnetite, and gold and present higher operational capacity and lower costs than shaking tables and spirals (Wills et al, 2007).

Spirals are mainly used for the treatment of heavy mineral sand deposits that contain ilmenite, rutile and zircon. The feed pulp can range from 15 to 45% and the particle size can range between 3mm and 75μm. The pulp flow downward in the spiral and the different materials stratifies in consequence of the centrifugal force and due to the different setting rate of the materials. They can be used to separate silica from iron oxides in CCSM post-processing.

Centrifugal concentrators such as the Knelson, Falcon SB concentrators and the Mozley Multi-gravity-separator are other systems used in gravity concentration. Knelson concentrator is a batch centrifugal separator with a fluidised bed to capture the heavy minerals that are trapped in a series of rings, while the lighter minerals are flushed out. It can treat up to 150 tonnes/h of solid and small particles down to 10μm. This technique well applied for materials where the fraction to be separated is very small (<0.05 wt%) and it is used to recover platinum and gold. The Falcon SB concentrator can treat 400 tonnes/h and is used when the fraction to concentrate is < 1% (Wills et al, 2007). As spirals, they can be used to separate silica and iron oxides.

FLOTATION

Froth Flotation is the most important mineral processing technique and its cost is typically less than 1/3 of the grinding and crushing cost. It has been patented in 1906 and the ore is usually grinded to grain size between 50 and 100μm before the treatment (this suit well with CCSM products particle size). This technique is based on the different surface properties of the minerals and involves the solid, liquid and froth phases and it is based on three mechanisms: selective attachment to air bubbles, entrainment in the water that flues through the froth and finally, aggregation of particles in the froth (Wills et al, 2007). Electrostatic adsorption is due to dissolution of lattice ions or to hydrolysis of surface species dependent on pH of minerals in water. The pH at which the net charge of the surface is zero is namely point of zero charge that is at pH 2-12-10.8, for quartz, magnesia and calcite, respectively (Fuerstenau M.C et al, 2003).

The minerals can be divided into two main groups based on their surface characteristics: polar and non-polar. The non-polar minerals such as coal have surface that do not readily attach to the water dipoles and are naturally flotable. Instead, the polar minerals such as magnesite and calcite, with strong covalent or ionic surface react with water and can be rendering hydrophobic by addition of chemical agents (sulphidisation of the mineral surface in an alkaline medium). The surfactants are called collectors are added during the agitation stage namely conditioning period. Typical industrial flotation cells produced by Outokumpu and Wemco are able to treat 100,000 tones/day of ore.

In addition to the collector, other substances are added during flotation, namely frothers, regulators and depressants. Frothers are used to stabilise bubble formation in the pulp phase, regulators are used for increase/decrease the water repellent effect of the collector and finally, the depressant are used to increase the selectivity by rending the minerals that do not need to be froth hydrophilic. Commercial flotation is a continuous process where flotation cells are arranged in series forming a bank. This arrangement is needed because the separation is not very efficient, and to further separate, the grains of mineral remaining in the pulp are passed to the next cell, and so on until the last cells that contain middling particles, which are re-circulated to the head of the system. The pulp level is raised from cell to cell (Wills et al, 2007).

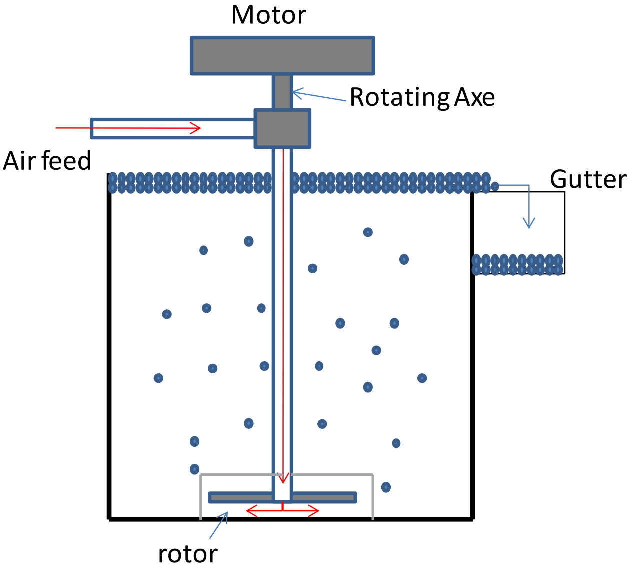


Figure 122 Flotation cell [Kaartinen et al, 2002]

Solubility of quartz is very limited and the anionic flotation is used due to the dissociation producing silicon cations. The flotation happens when the ionic metal is present and the pH is in the rage needed for hydrolysis. The xantate is used as anionic collector. Calcite flotation can be performed with oleate, laurate and short-chained carboxylates (e.g. lauric acid) as collectors. Anionic collectors are also used for magnesite and the principles of actions are adsorption in acid medium or chemisorption in basic medium (Fuerstenau M.C et al, 2003; Predali, 1969). A study highlight that the flotation of calcite from sulphide minerals can be achieved by using sodium oleate as a collector, and a mixture of thioglycollic acid and citric acid as a selective depressant between pH 9 and 11 (Liu Y et al, 2004). High purity magnesite concentrate can be obtained by reverse cationic flotation instead of the traditional direct anionic flotation used in Brazil that produces concentrate with 0.30% SiO_2 and a recovery fraction of 84%. The cationic flotation can achieve 0.17% SiO_2 and a weight recovery of 92% (Santana et al, 2001).

Flotation of pyrite and other ores was investigated in the range 0.1 to100kWh per tonne of dry ore and it was established that conditioning energy between 5 and 10kWh/tonne of dry ore enhances considerably the total recovery and flotation rate of the valuable minerals. Similar energy consumption (7kWh/tonne) is currently used in the Australian mining industry (Stassen, 1991; CRCORE, 2010).

MAGNETIC AND ELECTRICAL SEPARATION

Magnetic separation uses the different magnetic properties among minerals to separate the valuable magnetic-fraction from the non-magnetic minerals. Overall, the minerals can be divided in diamagnetics and paramagnetics, where the diamagnetics are repelled from magnetic fields and the paramagnetics (Ni, Co, PtMn, Ti metals) are instead attracted. The second group can be recovered by using high-intensity magnetic separators. Iron is a separate case, because presents very strong paramagnetism and for this reason they required low-intensity magnetic separators to be recovered (Wills et al, 2007).

High intensity separators work with a field intensity of 2T or higher. The processes can be dry or wet. Dry separation requires particle size > 75μm and is not widely used. The wet process allows running materials with small particle size in a continuous way. The most famous wet high intensity separator is the Jones separator that uses 4 tonnes of water each tonne of solid treated and consumes about 16kW per pole (2 poles required per unit) of electricity in the coil. This wet high intensity device is currently used to recover hematite and to remove impurities from asbestos and cassiterite. It is made of a frame with welded magnetic jokes and magnetic coils. Water at 5bar is used to wash out the magnetic particles that remain in the plate boxes.
The electrical energy consumption for low and high intensity magnetic separation respectively is 0.05 – 0.1 and 0.4 – 1kWh/tonne ore (Hardy-Smith, 1983).
Low-intensity magnetic separators are the drum separators that are typically used to concentrate fine iron ore. The counter-current type, where the slurry flows in the opposite direction of the drum rotation, is designed for fine materials with particles size below 250μm.

In same circumstances high-gradient magnetic separators are required to separate minerals with low magnetic susceptibility. To produce this high strength magnetic fields large amount of iron are required in the big separators (200 tonnes) enhancing the capital and installation costs. This type of separator is used to remove micro particles that contain iron from industrial kaolin and the commercial devices are able to trap up to 80 tonnes/h at magnetic fields of 2T. It might be used to remove iron particles from the CCSM carbonates to enhance their quality.

Electrical separation can be only used for dry materials and has low efficiency fro materials with small particle size < 75μm.

These techniques can be applied to the mineralisation products where high purity products want to be generated.

Mechanical Dewatering

Sludge drying is an energy intensive process and usually, the sludge is mechanically dewatered to decrease the drying costs. Dewatering can be carried out by vacuum filters, belt filter presses, centrifuges and membrane filter presses. Belt filters are the more energy efficient dewatering mean but vacuum filters are still popular. The sludge is drained under gravity before being pressed between two endless filtering belts and discharging a wet cake. Membrane filter presses are filter presses with an added membrane system. In the centrifugal dewatering the force developed by a spinning bowl is used to separate the solid from the liquid (Mujunder A.S, 2007). Several factors affect the selection of the technology/ies for the liquid-solid separation such as operating and capital costs, energy consumption, moisture content of solid product etc.

Usually, gravity sedimentation can remove 1/3 of the water in slurry and the rest of the water can be removed by the association of a thickener and a final dewatering stage (pressing or vacuum filter) to be economical (Fuerstenau M.C et al, 2003).

Most of the CCSM technologies use water during the process has occurred in the mineral processing where 90% of the tonnage is processed using water. The use of water requires separating the solid from the liquid. The costs of dewatering are related to the particle size with small particles giving higher costs. When the particles size is around 10μm the solids tent to form colloids and this is reflected in higher costs. In this latter case, sedimentation, centrifugation and filtration are not enough to separate the solid from the liquid fraction and a flocculant is added to promote flocculation of the solid. To have an idea of the cost increase it is estimated that the capital costs of a coal preparation plant can rise about 40% when the particle size is below 600µm. However, dewatering is much less costly than thermal drying and it is strongly suggested to include it into a processing plant that produces slurry to decrease the drying cost. For example, the energy required to dewater a magnetite concentrate from the beneficiation of taconite is only 6 kWh/tonne of water removed or electro-dewatering of water sludge is about 150-350 kWh/tonne, while the thermal drying typically requires around 800-1300 kWh/tonne of water removed as can be seen in Figure 123.

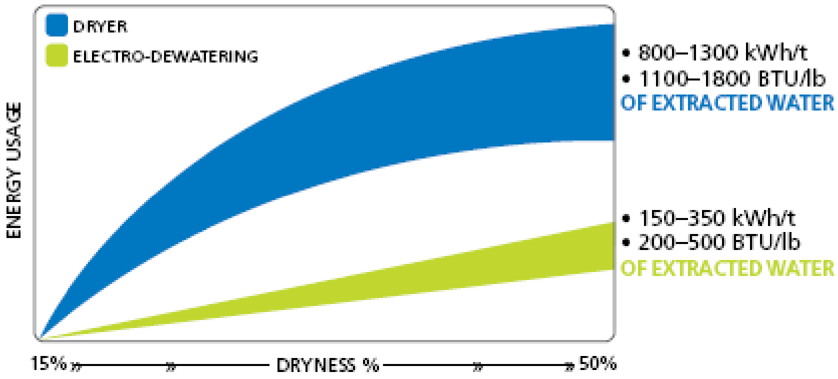


Figure 123 Comparison of drying and electro-dewatering [EIMCO, 2010]

In addition, dewatering allows reuse of water in the process obtaining a close water circuit. The main parameters that affect the efficiency of a solid-liquid separation technique are the particle size and shape, weight and volume % of solids, fluid viscosity and temperature, pH, specific gravity and chemical composition of the solid and quality requirements of the final products (Fuerstenau M.C et al, 2003). A slurry of relatively fine kaolin particles (80 wt% < 2µ) is dewatered in a membrane filter press with an energy consumption of 15kWh/tonne (Phillips, 2008). Also, in situ dewatering of kaolin tailing deposits can be obtained using only 1 kWh/tonne by electrokinetic dewatering, starting from a water content of 158-75%. This was achieved by using low voltage (0.11 V/cm) (Fourie et al, 2007).

Gravity sedimentation or thickening is the most used dewatering technique in mineral processing that involves good flocculation of small particles; it is cheap and can process large volume of materials. The sedimentation increases the concentration of the solid and produces a clear liquid. Different configurations are present such as traction thickener, cable thickener and caisson thickener. This technology is very economical and the operational energy required for a 60m unit is in the order of 10kW motor, so that capital costs are the main voice for a thickener.

Centrifugal separation can be included in the gravity separation technologies and can be performed by hydrocyclones or centrifuges. However, cyclones are better suitable for classification than thickening because their efficiency decrease consistently in presence of small particles (10µm will appear in the overflow). This concept well applies to the CCSM technology that use particle size ranging from 37 to 300µm. Centrifuges are more expensive and complex than thickeners but in the same time for flexible and with high clarifying power. The *solid bowl scroll centrifuge* is the most used in mineral processing due to the capacity to continuously discharge the material. The slurry is sent to a bowl where it is affected by a centrifugal force (generated by the revolving-screw conveyor), settling the particles on the inner surface of the bowl where it is discharged after being conveyed by the screw. Instead the water is removed by an overflow through another exit. Usually, the centrifuges present bowls with diameter between 15 and 150cm and can treat between 0.25 and 100 tonnes/h of solid (Wills et al, 2007).

For example, the Westfalia centrifuge separator in Figure 124 is widely used to produce ground calcium carbonate and PCC. In addition, nozzle-type separators are required for ultra-fine particles (PCC). This separator discharge concentrated suspensions continuously via nozzles that are installed on the periphery of the bowl. The product flows via the feed into the bowl, where it is separated into concentrate (underflow) and centrate (overflow) (Westfalia, 2010).

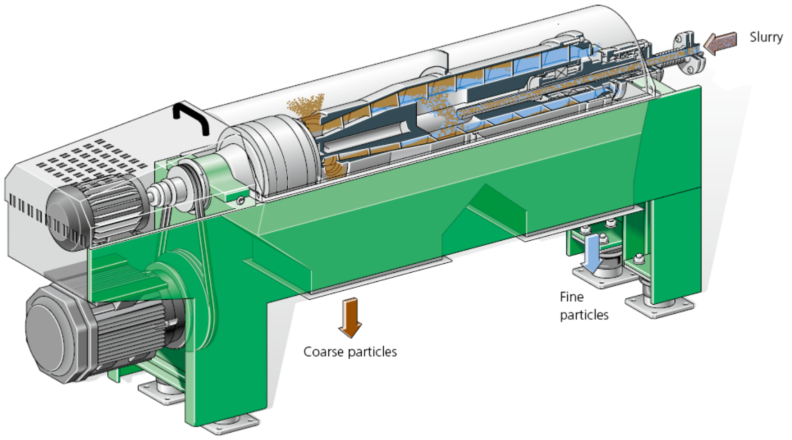


Figure 124 GEA Westfalia centrifuge separator can treat up to 350,000 L/h [Westfalia, 2010]

Filtration involves separation of a solid from a liquid by the use of porous media that only allow the passage of the liquid through them. The solid that is blocked by the porous mean create a filter cake. Parameters that affect the rate of filtration are: the pressure drop the feed to the other side of the filter, the surface area of the filter, the viscosity of the filtrate, the resistance of the filter cake, filter medium and initial layer of the cake. Different filter media can be employ such as cotton, wool, nylon, glass fibre etc but cotton is the most widely used due to its low cost and large availability. It can be successfully used for solids with particle size not smaller that 10µm. In mineral processing the cake filters (pressure, vacuum filters) are most used type due to the necessity to process large quantity of materials.

Pressure filters operates mainly in batch unit and can process up to 150 t/h of dry solid. The moisture remaining after the filtration is in the range of 7-12%. Vacuum filters are mainly used with continuous flow and the rotary-drum filter is the most used. It consists in a horizontal drum partially immerged in the filter trough where the slurry is fed. The drum is divided into compartment and is wrapped with filter medium. The drum rotates very slowly (0.2 rev min-1). The cake is discharged by a reverse air blast that lifts it and allows a knife to cut it. Another system that can be used in hydrometallurgical circuits where metals can be recovered after dissolution in acids or alkali is the horizontal belt filter (Wills et al, 2007).

After dewatering, a fraction of water (5-15%) has to be removed by drying if a dry final product is desired.

Thermal Drying

CCSM wet technologies require a final dewatering and drying step, while dry technologies do not need this post-processing in some cases. Table 52 shows the energy consumption of selected drying technologies and the most appropriate feedstock for each technology.

Most of the industrial products need to be dried before their final uses. Thermal removal of water from slurries is an important and highly energy intensive technique in mineral processing applications. Drying can be carried out at the raw material stage after the ore beneficiation / concentration or at the product-handling stage and usually is preceded by mechanical dewatering (e.g. filtration, centrifugation) to minimise the energy output. The handbook of industrial drying edited by Mujunder clearly illustrates the drying state of the art in mineral processing.

There are two different types of moisture: bound and unbound. The unbound moisture can be removed by evaporation and vaporisation. For evaporation the temperature is raised to the liquid's boiling point. In the vaporisation the drying is carried out by convection, passing hot air over the product (Mujunder A.S, 2007). The drying can be convective (direct) or conductive (indirect). In the first the heat is provided by a hot flow of air or other gases as in rotary, fluid-beds, flash or spray dryers. Instead, the conductive or indirect the heat is passed to the material by a heated surface and the moisture is removed by a flow of gas (carrier) as in the drum or puddle dryers. Conductive drying is appropriate for slurries.

Dryer type	Evaporation capacity kg H_2O/h m^3	Energy consumption kWh/t H_2O	Inlet hot-air °C	Residence time min	Dryer selection vs Feedstock
Tunnel dryer	/	1530-1700	100-200	10-60	Free-flowing solids
Rotary dryer	30-80	1280-2550	200-600	10-60	Cakes and powders
Fluid-bed dryer	/	1110/1670	100-600	10-60	Slurry, cakes, powders
Flash dryer	5-100	1250-2500	400-600	0-10 sec.	Cakes and powders
Spray dryer	1-30	1250-3190	200-450	10-30	Slurry
Drum dryer	6-20 (m^2)	889-1800	100-150	10-30	Slurry

Table 52 Comparison of different drying techniques [Mujunder A.S, 2007]

Typical dryers used in the mining and metallurgical sectors are the following:

- Hearth type
- Grate type
- Shaft dryers (tower and rotary dryers)

However, hearth and grate types are not adapted for slurries. A shaft dryer consists in "shower" the material that needs to be dried through a current of the drying medium. These types of dryer are called rotary or tower dryers when the drying medium flow is horizontal or vertical, respectively. Overall, it is important select the right drying system for each material or application and the selection should be done after pilot plant tests and prior experiences (Mujunder A.S, 2007).

The rotary dryers (direct and indirect type) represent the most used dryer's category in mining processing and their larger thermal performance is an evaporative capacity of 120kg/h/m^2 with an efficiency varying from 35 to 70%. Low capital and maintaining costs plus high reliability in long periods are the main advantages while difficult of sealing and non-uniform residence time are among the disadvantages. Rotary dryers are very versatile and economic for large tonnages drying of low cost materials. Waste-heat is not typically used in the mineral industry and it can improve the economics of the CCSM post-processing.

The direct rotary dryer requires between 1,200 and 2,200Btu/lb (1,410kWh/tonne of water removed), high temperature (< 980°C) and airflow, a loading of 8-12% in volume and 5-15 minutes. If the moisture content is > 1%, a parallel flow dryer is recommended and high residence time are expected for sticky or caking solids (25 minutes) (Mujunder A.S, 2007). The estimated cost of a steam-heated air rotary dryer including the auxiliary structures is of $320,000 for a dryer size 3m x 17m, an evaporation capacity of 861kg/h water and a discharge of 2.5 tonnes/h, for a carbon steel structure. If 304 stainless steel is used the cost is 50% higher.

Other important categories of dryers for CCSM post-processing would be spry drying, vacuum dryers, fluidised bed dryers, flash dryers, drum dryers, rotating shelf or disk dryers.

Spray drying is used to dry mineral flotation concentrates (pulp, sludge and precipitate) and it can be substitute for dewatering followed by drying in rotary dryers or kilns. The concentrates can be dried to < 0.5% water content in a single stage. This technology might well apply to CCSM products in forms of slurry. The main advantages are:

- the feed can be taken from the thickener underflow directly improving the handling of colloidal suspensions (e.g. silica gel) that are difficult to filter
- easy products handling (bone-dry type)
- better thermal efficiency compared to traditional processes and simple control and plant operation

The solids of the slurry (50 – 70%) are atomized into a cloud of droplets that contact the hot drying gases (500 – 1,000°C) giving excellent heat economy. The atomiser is the single most important part of the spry dryer and there is version suitable for abrasive slurries. The exit heat gas temperature is around 150 °C and the product temperature is much lower. Also, waste-heat can be used to reduce the heat consumption. After the material is dried, it is discharged from the bottom of the dryer into a conveyor. The costs of this technology are functions of the fuel, power and labour that are required. The typical energy consumption per tonne of bone-dry concentrate is of 378kWh/tonne of product. This technique might be used for silica and iron oxide slurries but lower temperatures are needed to dry mixed slurries or carbonate product streams. This can lower the heating economy (Mujunder A.S, 2007).

Fluidised bed dryers (FBD) can be used to dry non-sticky solids (CCSM dry products) and even slurries at temperature that ranges from 650 to 980°C for 5-25 minutes by a continuous upward flow of hot gas. FBD gives important advantages such as good solid mixing, high rates of heat and mass transfer, low maintaining costs, and easy material transport. This technique is energy-efficient, consuming only 967kWh/tonne water removed and is competitive with the more traditional rotary and tunnel dryers for particle size between 50 and 2,000μm. In addition, the capital and maintenance costs are low but the maximum feed size is ¾ in. It is commercially used for titanium dioxide, sand, zirconium silicate and coal and ceramics powders. Again, this technique might be employed in the CCSM processes that produces separated products while for mixed slurries or carbonates product stream it can only be used with temperature < 400°C, decreasing the energy efficiency of the process. Recently, FBD has been used to dry fine powders, cakes and slurries by using inert particles with high heat capacity. In this technique, the material slurry is sprayed into the FBD, coating the inert particles. After the material is dry it cracks and is removed by attrition from the inert particle surface and discharged.

Drum dryers are employed to dry slurries or pastes where the slurries are sprayed on the outer drum's surface or insert into it in a liquid form and the drums rotates very slowly allowing the material to dry in only one revolution. The adhering thin sheet of slurry is rapidly dried by conductive heat created by condensing steam inside the drum. Very wet slurry drying is enhanced by blowing hot air on the thin slurry layer. The final dried product is in form of powder. This technique is very flexible due to the possibility to control separately all the parameters involved in the drying operation.

Rotating shelf and disk dryers are used for material that tends to produce dust when dry and in case there is a solvent to be recovered. Therefore, they can be useful in mineralisation technologies that produce very fine powders and use solvents in the process. The operating temperatures that range from -18°C to 600°C represent an important advantage to dry the carbonates slurry produced by CCSM. The wet slurry is placed in a series of circular trays cut out in the centre that rotate slowly. Hot air is introduced from the side and removed from the roof. Commercially this type of dryers is used for bauxite, calcium carbonate and iron ore concentrate.

Flash dryers transport wet pulverised solids in an airstream and can just the surface due to the short residence time of several seconds. This technique allows the integration of a hammer mill for the reduction of particle size.

The current high cost of fuels indicates that direct-fired rotary dryers might be the cheapest technique and easiest to adapt if coal is burned instead a liquid/gaseous fuel. In addition, rotary drying is able to treat high tonnages compared to other techniques such as fluid bed and spray that however show higher efficiency. The recent studies indicate in superheated steam instead heated air as best drying medium that can eliminate the mass-transfer resistance typical of air-drying systems.

Microwave drying represents another system that could dramatically decrease the energy requirements but is still underutilised in the industrial drying due to low familiarity of engineers with this technique and because it needs major changes in the drying system compared to the traditional methods.

Agglomeration process

Agglomeration might be used to produce aggregates for the construction industry using mineralisation products as feedstock. Every kind of fine powders both dry and wet can be converted into larger products by growth/tumble agglomeration process. The most general application of agglomeration technology is size-enlargement of powders particles by granulation where granulate means particles with size ranging from 0.1 to 10mm (Pietsch W, 2005). The granulation process involves the use of a binder and forces or attrition that bring together the particles and when the binding forces are larger than natural separating forces the particles stick together forming a bigger granule than the original separated particles and so on (Figure 125).

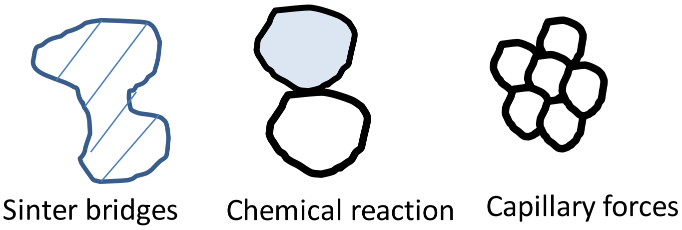


Figure 125 Different binding mechanisms [Pietsch, 2003]

Typically, tumble agglomeration is used to generate big granulates and this big granulates are then crushed to the wanted particle size (agglomeration post-processing). This is done to use the tumble with high efficiency and minimise the energy requirements.

To see a natural grown of agglomerates, particles below 100 and 200μm are needed. In particular, particles around 10μm aggregate naturally while larger particles require a binder. This means that tumble/growth technology require a crushing step to reduce the dimension of the particles in most of the cases. However, CCSM products can be directly aggregate/granulated by this technique escaping the size-reduction step and saving energy. Tumble/growth technique can be divided into:

- Devices that produce a movement of high density particulate solids

- Devices that produce a movement of solid particulates suspended into an appropriate liquid

This agglomeration technology can treat large tonnages of solids with small particle size and instantaneous bonding by a simple apparatus and low processing coats. Curing, is the most expensive process of agglomeration that it is often carried out by chemical or thermal-treatment,

High-density tumbling aggregators are rotating inclined pans, cones, drums and modified powder mixers where drums represent the simplest equipment and are used for large tonnages of solids.

The agglomeration-pelletisation of iron ore is a well-developed industrial process that treats million tonnes every year, where the energy required for mixing, balling, and induration ranges from 25 to 35kWh/tonne (Outotec, 2010). Mineralisation can provide the feedstock ready to be pelletised to the iron and steel industry.

Appendix 6

PATENTS RELATED TO CCSM TECHNOLOGIES ASSESSED IN THIS REPORT

Here a complete list is presented of all the patents found on mineral carbonation. The patents are listed chronologically from 2009 to 1993.

1) CAPTURE AND SEQUESTRATION OF CARBON DIOXIDE IN FLUE GASES

Publication number(s): WO2009139813 (A3); US2009202410 (A1).

Inventor(s): KAWATRA SURENDRA KOMAR; EISELE TIMOTHY C.; SIMMONS JOHN J.; Assignee(s): MICHIGAN TECHNOLOGICAL UNIVERSITY [US/US].

2) A PROCESS FOR PREPARING AN ACTIVATED MINERAL

Publication number(s): WO2009092718 (A1); WO2008142025 (A2) (A3); EP2158159 (A2); CA2687620 (A1); AU2008252987 (A1); CN101679060 (A).

Inventor(s): BOERRIGTER HAROLD; Assignee(s): SHELL INERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL].

3) CARBON DIOXIDE SEPARATION VIA PARTIAL PRESSURE SWING CYCLIC CHEMICAL REACTION

Publication number(s): US2009162268 (A1); EP2072111 (A2); US2010040520 (A1); JP2009149507 (A); CN101468790 (A); CA2646385 (A1).

Inventor(s): HUFTON JEFFREY RAYMOND; QUINN ROBERT; WHITE VINCENT; ALLAM RODNEY JOHN; Assignee(s): AIR PRODUCTS AND CHEMICALS INC [US] .

4) PROCESS FOR THE SEQUESTRATION OF CO_2 BY REACTION WITH ALKALINE SOLID WASTES

Publication number(s): WO2009077358 (A1); EP2070578 (A1).

Inventor(s): MONTES HERNANDEZ GERMAN; PEREZ LOPEZ RAFAEL; RENARD FRANCOIS; CHARLET LAURENT; NIETO JOSE MIGUEL; Assignee(s): UNIV. JOSEPH FOURIER [FR]; CENTRE NAT. RECH. SCIENT. [FR]; UNIV. HUELVA [ES].

5) INTEGRATED CHEMICAL PROCESS

Publication number(s): WO2008061305 (A1); US2009305378 (A1); MX2009005386 (A); KR20090102760 (A); EP2097164 (A1); CA2670299 (A1); AU2007324344 (A1).

Inventor(s): BRENT GEOFFREY FREDERICK; Assignee(s): ORICA EXPLOSIVES TECHNOLOGIE PTY LTD [-/AU].

6) SYSTEM, APPARATUS AND METHOD FOR CARBON DIOXIDE SEQUESTRATION

Publication number(s): WO2008101293 (A1); US2010021362 (A1); KR20090125109 (A); EP2134449 (A1); CA2678800 (A1); AU2009250983 (A1).

Inventor(s): HUNWICK RICHARD J; Assignee(s): HUNWICK RICHARD J.

7) A PROCESS FOR SEQUESTREATION OF CARBON DIOXIDE BY MINERAL CARBONATION

Publication number(s): WO2008142017 (A2) (A3); EP2158158 (A2); CA2687618 (A1); AU2008253068 (A1); US20070261947 (A1); CN101679059 (A).

Inventor(s): GEERLINGS JACOBUS JOHANNES CORNELIS; WESKER EVERT; BOERRIGTER HAROLD; Assignee(s): SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.

8) PROCESS FOR SEQUESTRATION OF CARBON DIOXIDE

Publication number(s): WO2007071633 (A1); US2009010827 (A1); EP1966092 (A1); CN101331084 (A).

Inventor(s): GEERLINGS JACOBUS JOHANNES CORNELIS; VAN MOSSEL GERARDUS ANTONIUS F.; IN T VEEN BERNARDUS CORNELIS M.; Assignee(s): SHELL INT RESEARCH [NL].

9) APPARATUS AND METHOD FOR SEQUESTERING FLUE GAS CO_2

Publication number(s): WO2007081561 (A2) (A3); US2008267838 (A1).

Inventor(s): REDDY KATTA J.; ARGYLE MORRIS D; Assignee(s): UNIVERSITY OF WYOMING [US/US].

10) METHOD FOR INDUSTRIAL MANUFACTURE OF PURE MgCO3 FROM AN OLIVINE CONTAINING SPECIES OF ROCK

Publication number(s): WO2007069902 (A1); US2008299024 (A1); RU2008119911 (A); NO20082270 (A); EP1951622 (A1); CN101356118 (A).

Inventor(s): GORSET ODDVAR; JOHANSEN HARALD; KIHLE JAN; MUNZ INGRID ANNE; RAAHEIM ARNE; Assignee(s): INSTITUTT FOR ENERGITEKNIKK [NO/NO].

11) PROCESS FOR PRODUCING CaCO3 OR MgCO3

Publication number(s): WO2006008242 (A1); CN1989073 (A); US2007202032 (A1).

Inventor(s): GEERLINGS JACOBUS J.C.; VAN MOSSEL GERARDUS ANTONIUS F.; IN T VEEN BERNADUS C.M.; Assignee(s): SHELL OIL COMPANY.

12) HEAT TREATMENT PROCESS OF SERPENTINE AS RAW MATERIAL FOR MINERAL CARBONATION BY REMOVING ADSORBED WATER MOLECULES, HYDROXYL GROUP AND ORGANIC FRACTION IN UNTREATED SERPENTINE

Publication number(s): KR2006110119-A.

Inventor(s): LEE JAE KEUN; KIM KI HYUNG; KIM DONG WHA; CHOI WEON KYUNG; CHO TAE HWAN; MOON SEUNG HYUN; HAN SANG SIK; KONG KI HOON; HWANG OK JUNG; KIM KYONG HOON; YOUN CHANG HWA; Assignee(s): KOREA ELECTRIC POWER CORPORATION.

13) METHOD FOR FIXING CARBON DIOXIDE

Publication number(s): JP 2005097072 (A).

Inventor(s): YOGO KATSUNORI; TOU EIKOU; YASHIMA TATEAKI.; Assignee(s): RESEARCH INSTITUTE OF INNOVATIVE TECHNOLOGY FOR THE EARTH.

14) METHOD FOR CARBON SEQUESTRATION IN THE FORM OF A MINERAL IN WHICH CARBON HAS A +3 DEGREE OF OXYDATION

Publication number(s): WO2005070521 (A1); FR2863911 (A1); US2008296146 (A1); RU2334547 (C2); PT1699545 (E); JP2007515283 (T).

Inventor(s): TOULHOAT HERVE; ROPITAL FRANCOIS; DUVAL SEBASTIEN; Assignee(s): INST FRANCAIS DU PETROLE [FR].

15) CARBON DIOXIDE SEQUESTRATION USING ALKALINE EARTH METAL-BEARING MINERALS

Publication number(s): US2005180910 (A1).

Inventor(s): PARK AH-HYUNG.; FAN LIANG-SHIH; Assignee(s): PARK AH-HYUNG; FAN LIANG-SHIH.

16) CARBON DIOXIDE CAPTURE AND MITIGATION OF CARBON DIOXIDE EMISSIONS

Publication number(s): WO2005108297 (A2) (A3); US2008031801 (A1); US2008138265 (AA); WO06009600 (A2) (A3).

Inventor(s): LACKNER KLAUS; GRIMES PATRICK; KREVOR SAMUEL; ZEMAN FRANK; Assignee(s): COLUMBIA UNIVERSITY; THE TRUSTEES OF COLUMBIA UNIVERSITY IN THE CITY OF NEW YORK.

17) PROCESS FOR REMOVAL AND CAPTURE OF CARBON DIOXIDE FROM FLUE GASES

Publication number(s): WO2004037391 (A1); US2004126293 (A1); JP2006503692 (T); DE60310594 (T2); CA2503096 (A1).

Inventor(s): GEERLINGS JACOBUS JOHANNES CORNELIS; WESKER EVERT; Assignee(s): SHELL INTERNATIONALE REASEARCH MAATSCHAPPIJ B.V.

18) CARBONATION OF METAL SILICATES FOR LONG-TERM CO_2 SEQUESTRATION

Publication number(s): WO2004094043 (A2) (A3); US2004213705 (A1); US2008112868 (A1); EP1617933 (A2); CA2523135 (A1).

Inventor(s): BLENCOE JAMES G.; PALMER DONALD A.; ANOVITZ LAWRENCE M.; BEARD JAMES S.; Assignee(s): UT BATTELLE LLC [US].

19) PROCESS FOR SEQUESTERING CARBON DIOXIDE AND SULFUR DIOXIDE

Publication number(s): WO2004098740 (A2) (A3); US2005002847 (A1); US7604787 (B2).

Inventor(s): MAROTO-VALER M. MERCEDES; ZHANG YINZHI; KUCHTA MATTHEW E.; ANDRESEN JOHN M.; FAUTH DAN J.; Assignee(s): PENN. STATE RES. FOUND [US].

20) SEQUESTRATION OF CARBON DIOXIDE

Publication number(s): US2004219090 (A1); US7132090 (B2).

Inventor(s): DZIEDZIC DANIEL; GROSS KENNETH B.; GORSKI ROBERT A.; JOHNSON JOHN T.; Assignee(s): GENERAL MOTORS CORPORATION.

21) PROCESS FOR MINERAL CARBONATION WITH CARBON DIOXIDE

Publication number(s): WO02085788 (A1); US2004131531 (A1); NO20034678 (A); JP2004525062 (T); DE60209492 (T2); CA2444576 (A1).

Inventor(s): GEERLINGS JACOBUS JOHANNES CORNELIS; MESTERS CAROLUS MATTHIAS ANNA; OOSTERBEEK HEIKO; Assignee(s): SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.

22) EXTRACTION OF SILICA AND MAGNESIUM COMPOUNDS FROM OLIVINE

Publication number(s): WO0248036 (A1); EP1373139 (A1); AU2554202 (A).

Inventor(s): HANSEN TORD; ZANDER BO; Assignee(s): SILICA TECH ANS [NO].

23) METHOD OF MANUFACTURING CARBONATION CURED COMPACT

Publication number(s): JP2002201085 (A).

Inventor(s): INAGAKI KENJI; ISU NORIBUMI; TERAMURA TOSHIFUMI; Assignee(s): CLION CO LTD; KENZAI GIJUTSU KENKYUSHO KK.

24) METHOD FOR EXTRACTING AND SEQUESTERING CARBON DIOXIDE

Publication number(s): US2001022952 (A1); US6890497 (B2); WO0010691 (A1); US7655193 (B1); AU5568099 (A).

Inventor(s): RAU GREGORY H.; CALDEIRA KENNETH G; Assignee(s): RAU GREGORY H.; CALDEIRA KENNETH G.; THE UNITED STATES OF AMERICA AS REPRESENTED BY THE UNITED STATES DEPARTMENT OF ENERGY.

25) CARBON DIOXIDE SEQUESTRATION BY COBALT (II) COMPLEXES

Publication number(s): WO0198313 (A1); GB2365428 (A); AU7424901 (A).

Inventor(s): FREEMAN JONATHAN DUNCAN; WALTON PAUL HOWARD; PERUTZ ROBIN NOEL.; Assignee(s): LATTICE INTELLECTUAL PROPERTY.

26) TREATMENT OF HYDRATED CALCIUM SILICATE AND TREATING APPARATUS

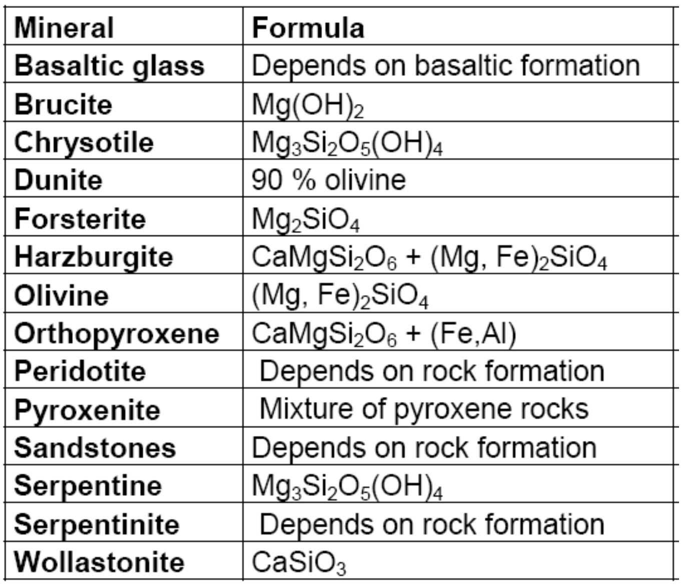
Publication number(s): JP6279017 (A).

Inventor(s): AKIYAMA TADASHI; NOMURA MASARU; Assignee(s): ASAHI CHEMICAL IND.

Appendix 7

SEVERAL MATERIALS AND CHEMICALS USED IN CCSM PROCESSING

Table 53 Mineral types that are being used for CCSM (various open literature 2008-2010)

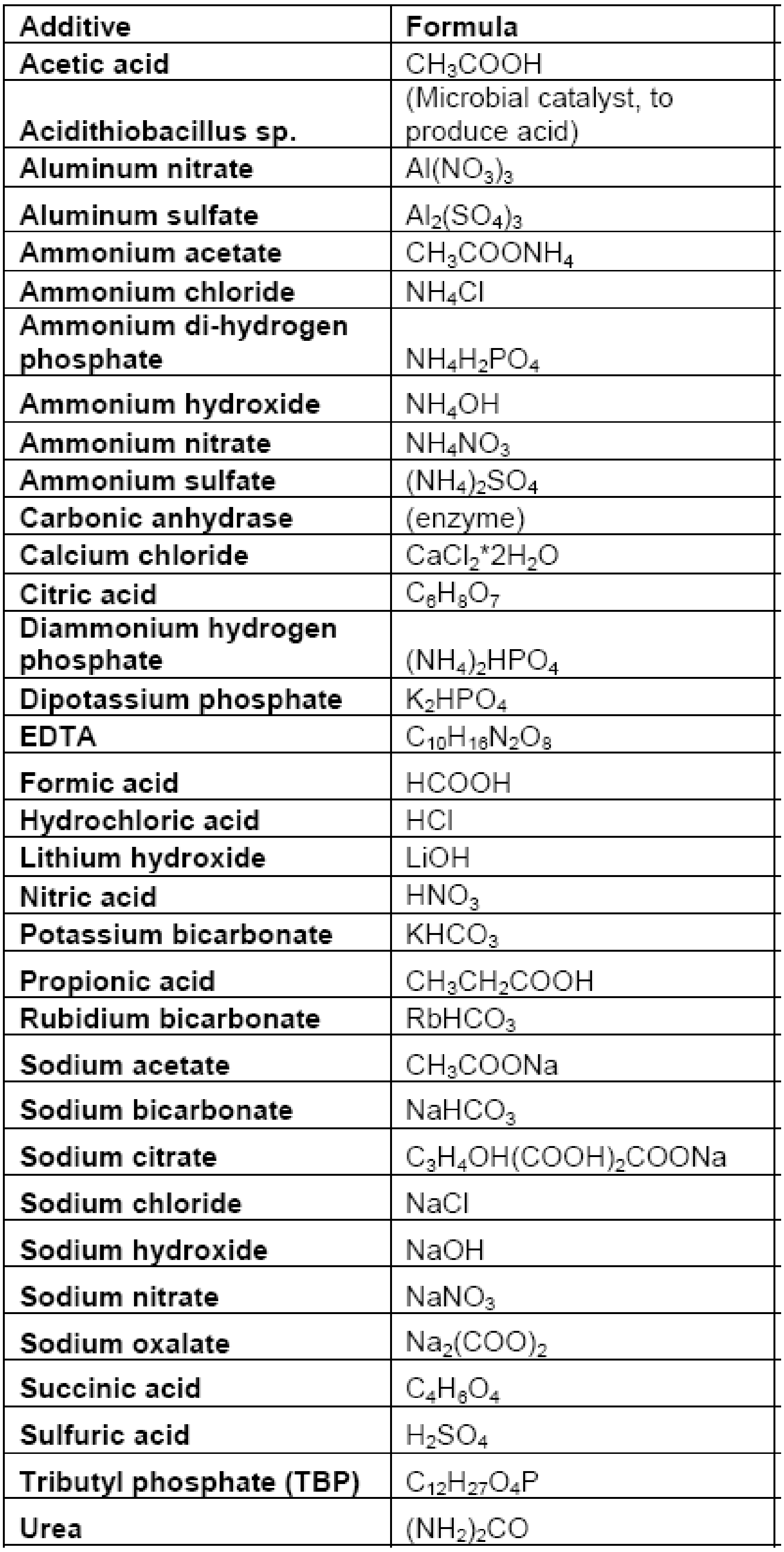


Mineral	**Formula**
Basaltic glass	Depends on basaltic formation
Brucite	$Mg(OH)_2$
Chrysotile	$Mg_3Si_2O_5(OH)_4$
Dunite	90 % olivine
Forsterite	Mg_2SiO_4
Harzburgite	$CaMgSi_2O_6 + (Mg, Fe)_2SiO_4$
Olivine	$(Mg, Fe)_2SiO_4$
Orthopyroxene	$CaMgSi_2O_6 + (Fe,Al)$
Peridotite	Depends on rock formation
Pyroxenite	Mixture of pyroxene rocks
Sandstones	Depends on rock formation
Serpentine	$Mg_3Si_2O_5(OH)_4$
Serpentinite	Depends on rock formation
Wollastonite	$CaSiO_3$

Table 54 Solid alkaline (industrial residue) materials that are being used for CCSM (various open literature 2008-2010)

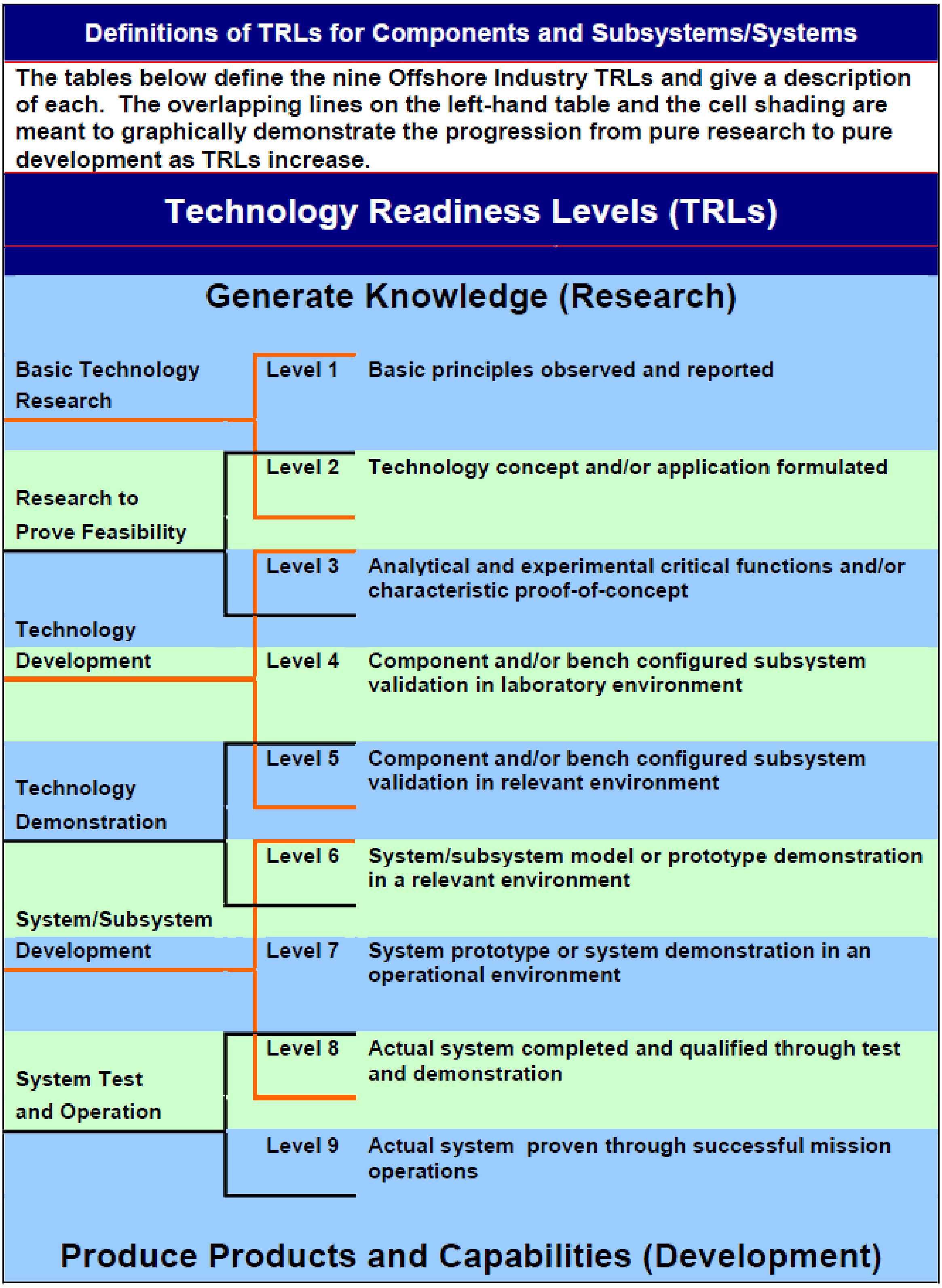
Residue
Air pollution control fly ash
Biomass ash
Blast furnace slag
Bottom ash
Cement wastes
Chrysotile milling and mining tailings
Coal combustion fly-ash
Lignite combustion fly ash
MSWI ash
Nirex reference vault backfill
Oil shale ashes
Paper mill waste
Paper wastewater incineration ash
Pressed lime-waste composites
Steelmaking slag

Table 55 Chemicals that are being used as additives for CCSM (various open literature 2008-2010)



Additive	Formula
Acetic acid	CH_3COOH
Acidithiobacillus sp.	(Microbial catalyst, to produce acid)
Aluminum nitrate	$Al(NO_3)_3$
Aluminum sulfate	$Al_2(SO_4)_3$
Ammonium acetate	CH_3COONH_4
Ammonium chloride	NH_4Cl
Ammonium di-hydrogen phosphate	$NH_4H_2PO_4$
Ammonium hydroxide	NH_4OH
Ammonium nitrate	NH_4NO_3
Ammonium sulfate	$(NH_4)_2SO_4$
Carbonic anhydrase	(enzyme)
Calcium chloride	$CaCl_2{*}2H_2O$
Citric acid	$C_6H_8O_7$
Diammonium hydrogen phosphate	$(NH_4)_2HPO_4$
Dipotassium phosphate	K_2HPO_4
EDTA	$C_{10}H_{16}N_2O_8$
Formic acid	$HCOOH$
Hydrochloric acid	HCl
Lithium hydroxide	$LiOH$
Nitric acid	HNO_3
Potassium bicarbonate	$KHCO_3$
Propionic acid	CH_3CH_2COOH
Rubidium bicarbonate	$RbHCO_3$
Sodium acetate	CH_3COONa
Sodium bicarbonate	$NaHCO_3$
Sodium citrate	$C_3H_4OH(COOH)_2COONa$
Sodium chloride	$NaCl$
Sodium hydroxide	$NaOH$
Sodium nitrate	$NaNO_3$
Sodium oxalate	$Na_2(COO)_2$
Succinic acid	$C_4H_6O_4$
Sulfuric acid	H_2SO_4
Tributyl phosphate (TBP)	$C_{12}H_{27}O_4P$
Urea	$(NH_2)_2CO$

Appendix 8 TRL Definitions



Definitions of TRLs for Components and Subsystems/Systems

The tables below define the nine Offshore Industry TRLs and give a description of each. The overlapping lines on the left-hand table and the cell shading are meant to graphically demonstrate the progression from pure research to pure development as TRLs increase.

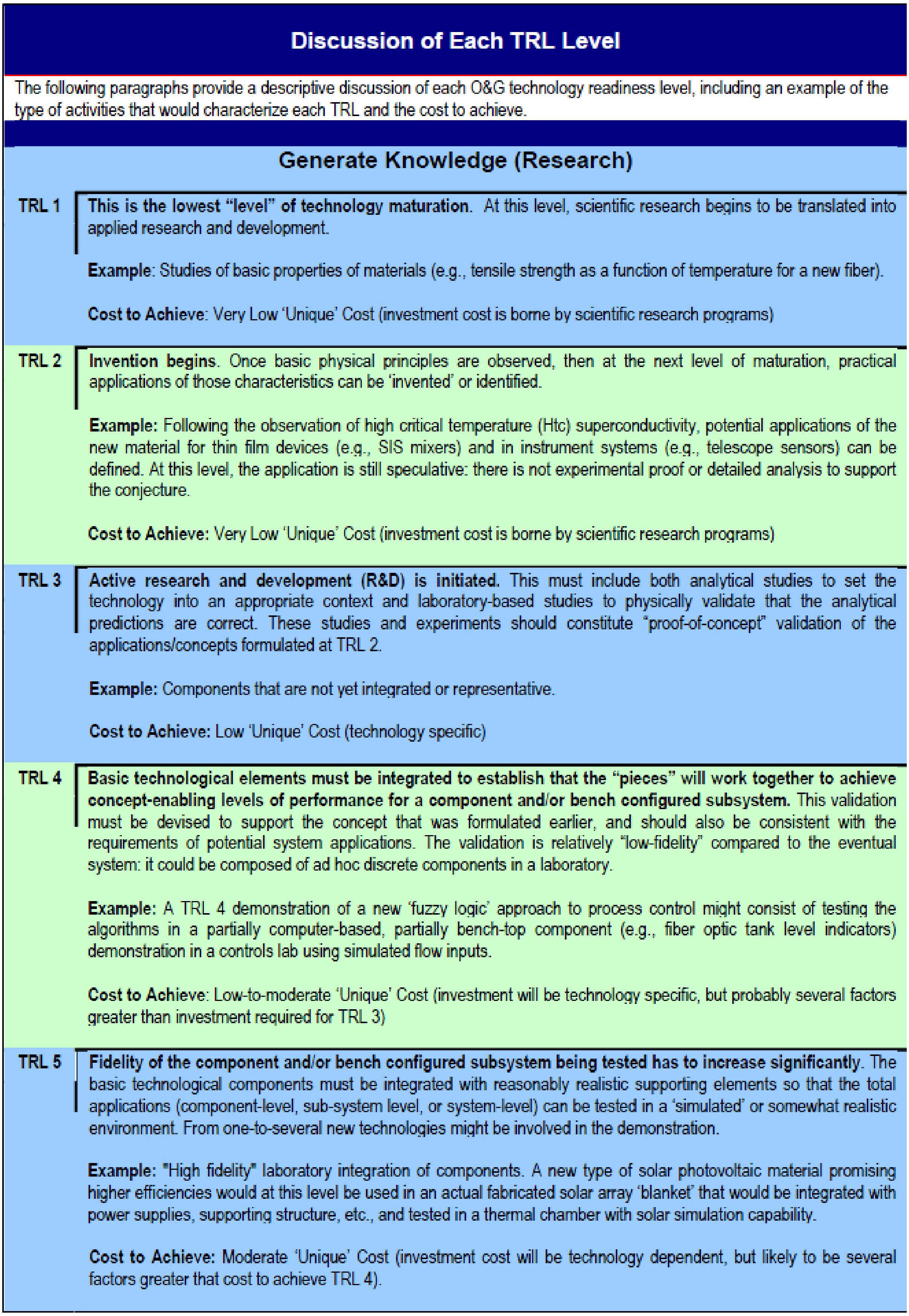
Technology Readiness Levels (TRLs)

Generate Knowledge (Research)

Basic Technology Research	Level 1	Basic principles observed and reported
Research to Prove Feasibility	Level 2	Technology concept and/or application formulated
	Level 3	Analytical and experimental critical functions and/or characteristic proof-of-concept
Technology Development	Level 4	Component and/or bench configured subsystem validation in laboratory environment
Technology Demonstration	Level 5	Component and/or bench configured subsystem validation in relevant environment
	Level 6	System/subsystem model or prototype demonstration in a relevant environment
System/Subsystem Development	Level 7	System prototype or system demonstration in an operational environment
System Test and Operation	Level 8	Actual system completed and qualified through test and demonstration
	Level 9	Actual system proven through successful mission operations

Produce Products and Capabilities (Development)

Table 56 Relative Technology Readiness Levels. [Copyright Offshore® Magazine, http://files.harc.edu/Projects/BlueWater/TRLDefinitions.pdf]



Discussion of Each TRL Level

The following paragraphs provide a descriptive discussion of each O&G technology readiness level, including an example of the type of activities that would characterize each TRL and the cost to achieve.

Generate Knowledge (Research)

TRL 1

This is the lowest "level" of technology maturation. At this level, scientific research begins to be translated into applied research and development.

Example: Studies of basic properties of materials (e.g., tensile strength as a function of temperature for a new fiber).

Cost to Achieve: Very Low 'Unique' Cost (investment cost is borne by scientific research programs)

TRL 2

Invention begins. Once basic physical principles are observed, then at the next level of maturation, practical applications of those characteristics can be 'invented' or identified.

Example: Following the observation of high critical temperature (Htc) superconductivity, potential applications of the new material for thin film devices (e.g., SIS mixers) and in instrument systems (e.g., telescope sensors) can be defined. At this level, the application is still speculative: there is not experimental proof or detailed analysis to support the conjecture.

Cost to Achieve: Very Low 'Unique' Cost (investment cost is borne by scientific research programs)

TRL 3

Active research and development (R&D) is initiated. This must include both analytical studies to set the technology into an appropriate context and laboratory-based studies to physically validate that the analytical predictions are correct. These studies and experiments should constitute "proof-of-concept" validation of the applications/concepts formulated at TRL 2.

Example: Components that are not yet integrated or representative.

Cost to Achieve: Low 'Unique' Cost (technology specific)

TRL 4

Basic technological elements must be integrated to establish that the "pieces" will work together to achieve concept-enabling levels of performance for a component and/or bench configured subsystem. This validation must be devised to support the concept that was formulated earlier, and should also be consistent with the requirements of potential system applications. The validation is relatively "low-fidelity" compared to the eventual system: it could be composed of ad hoc discrete components in a laboratory.

Example: A TRL 4 demonstration of a new 'fuzzy logic' approach to process control might consist of testing the algorithms in a partially computer-based, partially bench-top component (e.g., fiber optic tank level indicators) demonstration in a controls lab using simulated flow inputs.

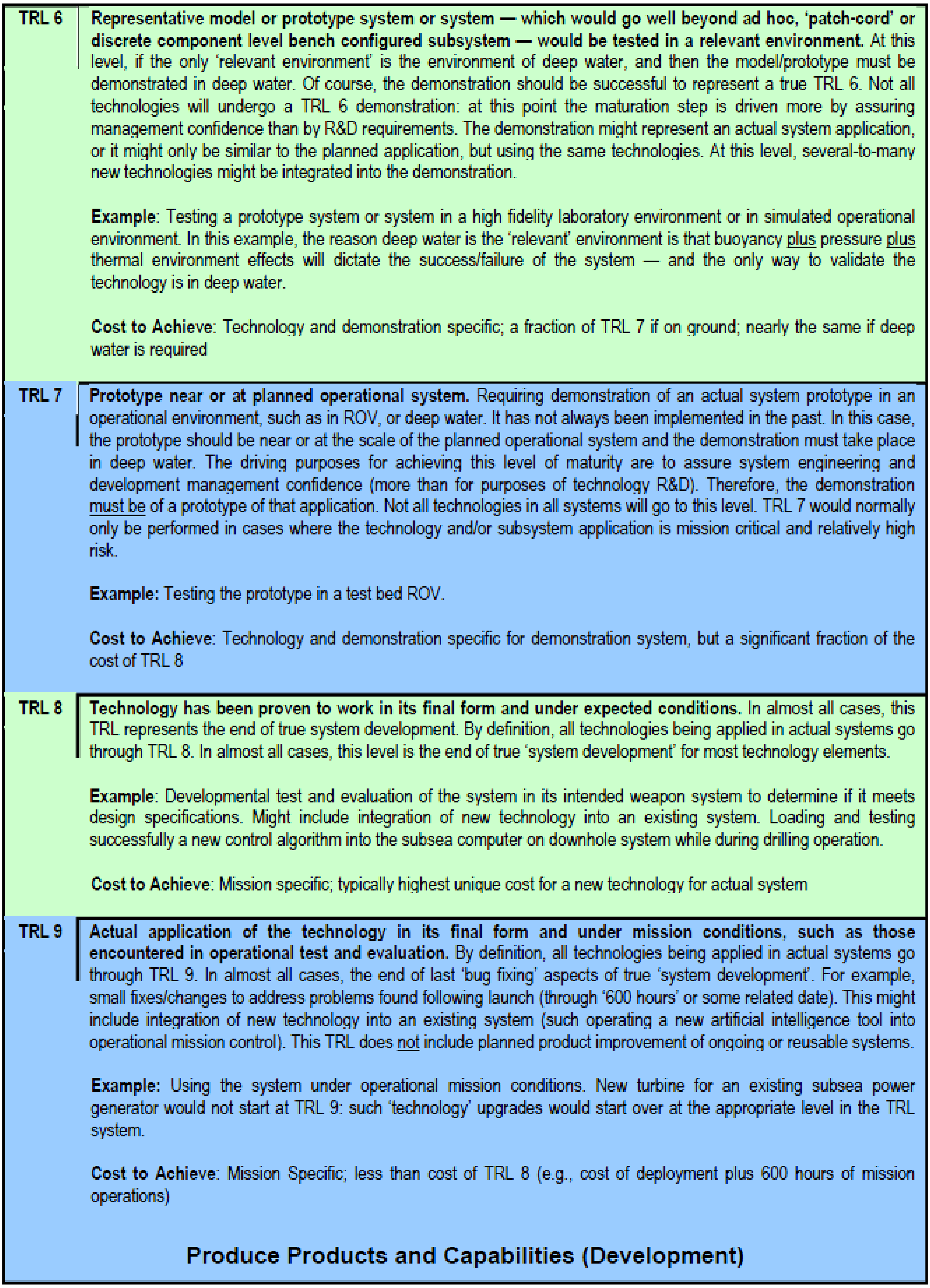
Cost to Achieve: Low-to-moderate 'Unique' Cost (investment will be technology specific, but probably several factors greater than investment required for TRL 3)

TRL 5

Fidelity of the component and/or bench configured subsystem being tested has to increase significantly. The basic technological components must be integrated with reasonably realistic supporting elements so that the total applications (component-level, sub-system level, or system-level) can be tested in a 'simulated' or somewhat realistic environment. From one-to-several new technologies might be involved in the demonstration.

Example: "High fidelity" laboratory integration of components. A new type of solar photovoltaic material promising higher efficiencies would at this level be used in an actual fabricated solar array 'blanket' that would be integrated with power supplies, supporting structure, etc., and tested in a thermal chamber with solar simulation capability.

Cost to Achieve: Moderate 'Unique' Cost (investment cost will be technology dependent, but likely to be several factors greater that cost to achieve TRL 4).



TRL 6	**Representative model or prototype system or system — which would go well beyond ad hoc, 'patch-cord' or discrete component level bench configured subsystem — would be tested in a relevant environment.** At this level, if the only 'relevant environment' is the environment of deep water, and then the model/prototype must be demonstrated in deep water. Of course, the demonstration should be successful to represent a true TRL 6. Not all technologies will undergo a TRL 6 demonstration: at this point the maturation step is driven more by assuring management confidence than by R&D requirements. The demonstration might represent an actual system application, or it might only be similar to the planned application, but using the same technologies. At this level, several-to-many new technologies might be integrated into the demonstration. **Example**: Testing a prototype system or system in a high fidelity laboratory environment or in simulated operational environment. In this example, the reason deep water is the 'relevant' environment is that buoyancy plus pressure plus thermal environment effects will dictate the success/failure of the system — and the only way to validate the technology is in deep water. **Cost to Achieve**: Technology and demonstration specific; a fraction of TRL 7 if on ground; nearly the same if deep water is required
TRL 7	**Prototype near or at planned operational system.** Requiring demonstration of an actual system prototype in an operational environment, such as in ROV, or deep water. It has not always been implemented in the past. In this case, the prototype should be near or at the scale of the planned operational system and the demonstration must take place in deep water. The driving purposes for achieving this level of maturity are to assure system engineering and development management confidence (more than for purposes of technology R&D). Therefore, the demonstration must be of a prototype of that application. Not all technologies in all systems will go to this level. TRL 7 would normally only be performed in cases where the technology and/or subsystem application is mission critical and relatively high risk. **Example:** Testing the prototype in a test bed ROV. **Cost to Achieve**: Technology and demonstration specific for demonstration system, but a significant fraction of the cost of TRL 8
TRL 8	**Technology has been proven to work in its final form and under expected conditions.** In almost all cases, this TRL represents the end of true system development. By definition, all technologies being applied in actual systems go through TRL 8. In almost all cases, this level is the end of true 'system development' for most technology elements. **Example**: Developmental test and evaluation of the system in its intended weapon system to determine if it meets design specifications. Might include integration of new technology into an existing system. Loading and testing successfully a new control algorithm into the subsea computer on downhole system while during drilling operation. **Cost to Achieve**: Mission specific; typically highest unique cost for a new technology for actual system
TRL 9	**Actual application of the technology in its final form and under mission conditions, such as those encountered in operational test and evaluation.** By definition, all technologies being applied in actual systems go through TRL 9. In almost all cases, the end of last 'bug fixing' aspects of true 'system development'. For example, small fixes/changes to address problems found following launch (through '600 hours' or some related date). This might include integration of new technology into an existing system (such operating a new artificial intelligence tool into operational mission control). This TRL does not include planned product improvement of ongoing or reusable systems. **Example:** Using the system under operational mission conditions. New turbine for an existing subsea power generator would not start at TRL 9: such 'technology' upgrades would start over at the appropriate level in the TRL system. **Cost to Achieve**: Mission Specific; less than cost of TRL 8 (e.g., cost of deployment plus 600 hours of mission operations)
	Produce Products and Capabilities (Development)

Table 57 Technology Readiness Levels – Detailed Definitions. [Copyright Offshore® Magazine, http://files.harc.edu/Projects/BlueWater/TRLDefinitions.pdf]

Appendix 9

CONVENTIONAL CALCITE APPLICATIONS

The focus of current analysis of CCSM process based on serpentines, therefore various conventional applications for calcite is discussed in the Appendix.

$CaCO_3$ is principally found as three anhydrate polymorphs: vaterite, aragonite and calcite, with markedly different physicochemical characteristics (Tai and Chen, 1998). Calcite has a rhombohedral crystal structure and is the thermodynamically stable phase at room temperature and atmospheric pressure. The growth equilibrium morphology of the form includes a multitude of variants (e.g. scalenohedral form). Aragonite is the high-temperature phase displaying a needle-like morphology and vaterite is the low-temperature phase often found as spherical aggregates (Domingo et al, 2006). CCSM carbonates might be useful to provide material for the construction sector. This aspect has been treated in a following section.

The hardened, densified calcium carbonate can have potential for re-use in engineering applications. The main user of calcium carbonate is the construction industry, where the options for use without release of CO_2 are either:

- Crushed granular aggregate of 40mm, 20mm, 10mm, and 4mm down to dust, e.g. granular base, concrete, asphalt, macadam, roofing layers, drainage, engineering rockfill/ballast
- Pulverised powder with a mean particle diameter passing the 300 micron sieve, e.g. void filler additive (asphalt, concrete), inert filler for CEM ii class ordinary Portland cement, self compacting concrete (SCC),

Obviously, the most common use of calcium carbonate for construction materials is as a feedstock for Portland cement production. According to EN197-1, 2000 cement is a hydraulic binder, i.e. a finely ground inorganic material which, when mixed with water, forms a paste which sets and hardens by means of hydration reactions and processes and which, after hardening, retains its strength and stability even under water. Ordinary Portland cement is, in its purest form, ≥ 95 powdered clinker plus gypsum powder, with an SSA of between 350 and $500 m^2/kg$. However, since this involves calcinations and therefore release of the sequestered CO_2 it is not considered a viable option for CCSM by-products.

CEMENT ADDITIVE AND AGGREGATES

It is of primary importance to define which mineral phases of magnesium/calcium carbonate are produced by CCSM and also, the LOI, sulphate and chlorine concentrations of the carbonated wastes, to assess their suitability as a potential cement additive or aggregates. In fact, the chemical composition of such aggregate and in general the re-use of industrial waste for cement production closely depends on presence of salts. In fact, elevated levels of sulphur and chloride can lead to the degradation of concrete. Sulphates, in the presence of water, can react with the hydrated tricalcium aluminate phase in hardened Portland cement forming expansive minerals (e.g. ettringite), which result in distortion and cracking, i.e. sulphate attack. Chloride ingress can corrode the steel reinforcing bars by removing the passive oxide layer (Mehta and Monteiro, 2006). However, levels of sulphur and chloride in the aggregate produced from waste so far were below the limits for Lightweight Expanded Clay Aggregate (LECA) that is a special type of clay that has been pelletised and fired in a rotary kiln at a very high temperature, and within the limits specified in British Standards. The carbonated aggregates were incorporated into concrete cubes that exhibited an acceptable mode of fracture, as specified in BS EN 12390 (Gunning et al, 2009).

CalciTech Ltd based in France has acquired a 1.5Mt waste carbide lime deposit in northern Spain to produce synthetic calcium carbonate (PCC) and export it to customers in the paper industry (Industrial Minerals, 2010). The technology involves high selective solubilisation of calcium oxide and/or calcium hydroxide and separation of the solid impurities before further carbonation. This speeds the process and finally PCC crystals of high purity are produced. Depending on the intended end use, the PCC may be concentrated and dispersed to a 72% solids slurry (for paper coatings) or it may be processed further via drying and milling (for use in polymer, food or pharmaceutical applications). The company claim that the synthetic calcium carbonate is of extreme chemical purity. The removal of virtually all non-calcium contaminants prior to carbonation not only allows use of impure raw materials, but also produces a calcium carbonate product that meets and exceeds all food and pharmaceutical purity requirements (CalciTech, 2010). This is a very important aspect for CCSM technology, because it indicates that similar waste materials can be successfully converted into high purity products

Calera Corporation developed the Calera Process that forms novel, detestable calcium and magnesium carbonate and bicarbonate minerals, by capturing carbon dioxide from flue gas and converting the gas to stable solid minerals. The novel process called Mineralization via Aqueous Precipitation (MAP), involves contacting gas from the power plant with natural waters producing carbonates with crystallographic not described or poorly known forms. These novel 'polymorphs' make it possible to produce high reactive cements and aggregate precursors. Many trace components will be captured from the flue gas as well, such as sulphur oxides and mercury and will be incorporated into the solid phase as insoluble sulphates and carbonates. After removal from the water and appropriate processing, the solids have value in a number of construction applications (Calera, 2010). It is important to highlight that the cement produced from silicate rocks and mineral waste carbonation instead of raw limestone has a carbon negative cycle, because the use of magnesium silicates eliminates the CO_2 emissions from raw limestone processing (Iizuka et al, 2004).

Combining CCSM together with agglomerates pelletising process allows waste to be re-used into a lightweight aggregate (Gunning et al., 2009). Lightweight aggregates are utilised in a diverse range of applications including lightweight structural concretes, low-density construction blocks, engineering fill, and horticultural growing mediums (Chandra et al, 2003). Agglomerating processes are used to increase the grain size of powders, by sticking particulates together with a liquid binder and mechanical agitation. The UK currently consumes around 280 million tonnes of aggregate annually, 25% of which is derived from secondary and recycled sources (WRAP, 2008) and virgin aggregates are subject to the Aggregate Levy, which is currently £2 per tonne and will increase to £2.10 since April 2011. As recycled aggregates are exempt from this tax and natural stone resources are becoming scarce, there is increasing interest in the use of alternative materials. This solution has been studied using the quarry fines either, that were used as aggregate together with industrial wastes (paper ash) as a binder, as shown in Figure 126.

Figure 126 Raw materials: (a) paper ash, (b) quarry fines, and (c) pelletised product [Gunning, 2009]

The formation of thaumasite and 'concrete cancer' can be exacerbated in presence of magnesium sulphate in the concrete. Therefore, the investigation of these aspects will require major attention to establish the potential of CCSM technology in produce cement additives and aggregates. Thaumasite ($Ca_3SiSO_4CO_3(OH)_6$ $12H_2O$) and ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}$ $26H_2O$) can occur during the attack on concrete by sulphate solutions.

Thaumasite reduces the C–S–H available in a cement paste decreasing the binding ability of the latter and leading to degradation of the concrete into a 'soft' mass. The formation of thaumasite occurs in presence of a magnesium or calcium carbonate-bearing aggregate (Loudon, 2003; Barnett et al, 2002). In particular, magnesium carbonate appears as the most aggressive in the occurrence of TSA due to reaction of formed magnesium sulphate with portlandite that produces high concentrations of calcium and sulphate ions in the outer layers of the mortar. In addition, TSA can be formed in absence of carbonates by reaction of atmospheric CO_2 with formation of bicarbonate ions (Collett et al, 2004).

Alkali Silica Reaction (ASR) also known as 'concrete cancer' is one of the main chemical reactions causing gradual but severe deterioration of hardened concrete structures. Certain types of siliceous aggregates can form a hygroscopic gel at the cement/aggregate interface causing micro-cracking throughout the hardened material. The attack of alkali hydroxide to aggregate particles composed of ASR-reactive minerals generates two layers of hydrated mature and immature alkali silicate. The mature layer reacts with Ca^{2+} ions to convert to calcium alkali silicate that occupies a lower volume. Also, the immature alkali silicate gradually reacts with Ca^{2+} ions covering the surface of the reactive minerals with calcium alkali silicate called 'reaction rims' that allow the penetration of alkaline solution but obstruct the outflow of the alkali silicate that accumulates giving an expansive pressure sufficient to crack the aggregate and the surrounding concrete (Ichikawa, 2009).

FURTHER CALCITE APPLICATIONS AND FUTURE POTENTIAL APPLICATIONS FOR MAGNESITE

In addition to its use as construction material, magnesite and calcite are also used in numerous industrial processes. Two forms commonly used are ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC). GCC is pulverised limestone that has a particles size ranging from a fraction of a micron to several microns (Myers, 2007).

The demand for powdered calcite and magnesite (less requested) is actually very important in various fields of industry: paper, paint, magnetic recording, textile, detergent, adhesive, plastic, cosmetic, food, etc. It is used as a coating pigment, filler, or extender. In the industrial applications, defined number of parameters plays a vital role in the determination of its effectiveness such as the particle size average and distribution, the morphology, the specific surface area, the polymorph or the chemical purity (Tai and Chen, 1998).

Carbonates as Drilling Agents

In geotechnical engineering, when drilling permeable rock formations (e.g. in crude oil extraction) calcium carbonate is often used as a bridging agent to block large void openings; hence the mean particle size usually has to be at least half the diameter of the void opening.

As this material is often derived from marble, a metamorphic and highly crystalline form of calcium carbonate, it does not break down in the high shear conditions encountered in drilling. Breakdown of weaker materials derived from other sources, leads to increased invasion of the producing formation (MI SWACO, 2010; JAY minerals, 2010; Excalibar minerals, 2010). Calcium carbonate used in fluid loss control situations requires a larger particle size than calcium carbonate fine. Calcium carbonate can also be added on a periodic basis for lost circulation and leak off to high permeability formations. It is particularly effective when drilling with high differential pressures caused by an overbalanced condition or when drilling depleted zones. Overall, appropriate selection of particle size distribution and mineral composition appear to be the key criteria for calcium and magnesium carbonates.

HIGH-END APPLICATIONS

Calcium carbonate, and to a lesser extent magnesium carbonate, are used as an additive or modifier in paper, paints, plastics, inks, adhesives and pharmaceuticals. In the manufacture of plastics, paper, and pharmaceuticals, it requires particles with more rigorously defined properties such as crystalline-only phases, and with a specific morphology and particle size distribution (Gorma et al, 2008). Calcitech is going to produce high quality PCC from carbide waste (see Section 4.5.1). This is a promising indication that low quality waste material can be converted into high quality products in an economical way. In addition, the typical PCC processing includes the mining, crushing, milling calcination and re-precipitation steps. The CCSM technology would provide to the PCC companies a precipitated material that does not require grinding and thermal treatment, producing a 90-99% pure ground calcium carbonate that would require be milling and purifying from iron oxide and silicate materials. In addition, no CO_2 emission would be associated with the PCC production enhancing the overall carbon dioxide sequestration efficiency. Therefore, the high-end applications will be driven by market forces if the CCSM products will have the correct level of purity and particle grading. However, a wide range of quality tests and a techno-economical investigation is required to evaluate the real potential of CCSM for PMC production.

Precipitated Calcium Carbonate (PCC)

The product of a synthetic calcium carbonate with specific morphology and particle size is namely precipitated calcium carbonate or PCC. It has a higher purity than natural or ground calcium carbonate (GCC) since impurities are removed in the production process. The current precipitated calcium carbonate (PCC) production uses mined, crushed calcium carbonate as raw materials and in 2007, the world's PCC consumption was approximately 13Mt. There are several various types of PCC grades, but the purity of PCC is usually over 99% with a density of 2,700kg/m^3. For filler pigments, 70% of the carbonate particles are smaller than 2μm and the specific surface area (BET) is about 10m^2/g. The particle size affects paper smoothness, gloss, and printing characteristics. The chemical and physical properties of a commercial precipitated calcium carbonate are shown in Table 58 and Table 59.

Important qualities of the raw material used for the PCC production are low manganese and iron content since these elements have a very negative influence on the brightness of the product. In particular, the iron content of PCC should be lower than approximately 0.1% for a commercial product (Teir et al, 2005). Precipitated calcium carbonate is commonly produced by a decarbonising process but unfortunately, PCC synthesized by this traditional method usually comprises a mixture of various crystalline polymorphs and the distribution of the particle sizes cannot be satisfactorily controlled.

Chemical Properties	%	USP XXII Limit
Assay as $CaCO_3$	98.4	98
Loss on drying	0.21	2
Magnesium and Alkali salts	0.22	1
Iron	0.013	0.05

Table 58 Chemical properties of a commercial PCC [Aristocratholding, 2010]

Properties	
Average Particle Size (D50)	< 1.5 µm
Specific Surface Area	≥ 22000 cm^2/g
Whiteness	> 95
pH Value	7-11
Total Solid Content (110°C for 2hrs)	48-52%
Viscosity (ASTM D4212)	9 ±3 sec.

Table 59 Physical properties of a commercial PCC [Aristocratholding, 2010]

PCC is precipitated in a very reproducible way as mono-disperse spherical particles with lower than 1μm as can be seen in Figure 127 (Gorma et al, 2008). Generation of PPC with high purity and specific particle size has the potential to open high value markets for calcium carbonate produced by inorganic waste materials by CCSM.

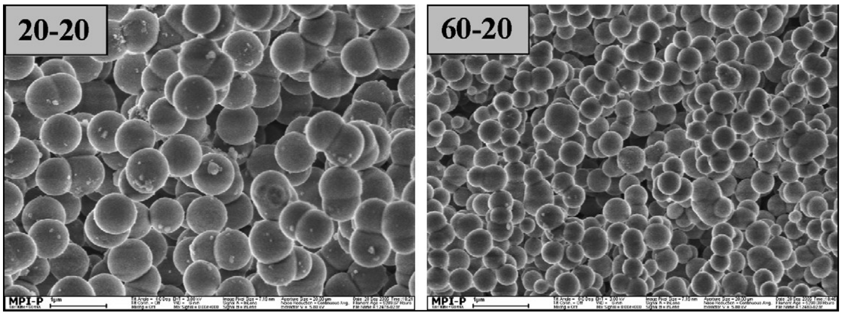


Figure 127 SEM micrographs of PCC synthesized [Gorma et al, 2008]

The use of high pressure, magnetic fields, or microwave irradiation method has been also used for shape control of calcium carbonate (Mathur, 2001; Chibowski et al, 2003; Rodríguez-Clemente et al, 1996; Domingo et al, 2006).

PCC with super-fine particle size is becoming attractive due to its excellent properties and increasing market demand. The traditional carbonation method produces PCC with spindle shape and particle size bigger than 2µm. Superfine calcium carbonate with controllable shape can be obtained by addition of chemicals and the adaptation of a suitable type of sparger on the carbonation process. CCSM might be able to produce a fraction of its product with characteristics comparable with those of GCC or PCC.

Pharmaceuticals

$CaCO_3$ and $MgCO_3$ are used as a base for tablets, antacid, and nutritional supplements. Calcium carbonate is the most commonly used liming agent for the amelioration of pH and metal ion toxicity in polluted waters (Exley et al, 1988). In addition, findings indicated a measure of protection against copper hepatotoxicity provided by the addition of calcium carbonate as a liming agent in the water (Vera et al, 1998).

Carbonates as fillers

Calcium carbonate and magnesium carbonates are traditionally used in plastics as a bulking agent to substitute the expensive polymers. The filling changes the properties of the polymer and a new material is generated by blending a polymer with inorganics. The properties of the resulting composite material are determined by the properties of the components such as type of polymer and filler, filler particle size, shape and modulus, concentration of filler in the polymer matrix and the kind of interaction between the filler and polymer particles (Gorma et al, 2008; Xantos, 2005).

Calcium carbonate has been increasingly used as a filler, since ca. 80% of the world paper production has been converted to an alkaline papermaking process (Domingo et al, 2006). In this process, particle shape and particle size distribution are two of the most important filler properties of $CaCO_3$ particles added during the manufacturing of paper. For instance, paper filled with rhombohedral calcite is more easily processed than paper filled with scalenohedral calcite, since the former is more easily drained leading to lower filler lost. Additionally, a narrow crystal size distribution is always preferred (Domingo et al, 2006).

Previous tests show that the $CaCO_3$ powder produced from steel slag presented inferior brightness to PCC, which gives it a significantly lower market value. The 2-step process consisted of dissolving the Ca by contacting the steel slag in water with an excess of CO_2. The Ca dissolved then as calcium bicarbonate, and in the next step, $CaCO_3$ was precipitated by boiling the solution (van Mossel, 2010).

The use of inorganic fillers in composite applications is increasing. Fillers can reduce the overall cost of composites by adding bulk, but can also improve performance or impart properties that might not otherwise be achieved by the reinforcement and resin ingredients alone. Fillers can improve mechanical properties including fire and smoke performance by reducing organic content in composite laminates. In addition, adding filler can reduce shrinkage, hence improving the dimensional control of moulded parts. Important properties, including water resistance, weathering, surface smoothness, stiffness, dimensional stability, and temperature resistance can all be improved through the proper use of fillers.

Calcium carbonate is widely used as inorganic filler. It is available at low cost in a variety of particle sizes and treatments from well-established regional suppliers, especially for composite applications. Most common grades of calcium carbonate filler are derived from limestone or marble and very common in automobile parts.

When used in composite laminates, inorganic fillers can account for 40 to 65% by weight. They perform a function such as enhanced inter-facial bonding through enhanced packing, which is analogous to the role of silica fume in concrete. In comparison to resins and reinforcements, fillers are the least expensive of the major ingredients. Fillers are also important in establishing the performance of the composite laminate because they:

- Reduce the shrinkage of the composites part.
- Influence the fire resistance of laminates.
- Lower compound cost by diluting resin that is more expensive and may reduce the amount of reinforcement required.

- Can influence the mechanical strengths of composites.
- Serve to transfer stresses between the primary structural components of the laminate (i.e., resin and reinforcement), thereby improving mechanical and physical performance.

The combination of small and medium filler particles helps control compound rheology at elevated temperatures and pressures, thereby helping to ensure that compression moulded parts are uniform. Low-density fillers are used extensively in the transportation industry. They offer the lowest cost of filled systems, without the increase in weight that can affect the performance of the final product. Calcium carbonates, including ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC), have replaced kaolin as the most common extender and filler used by the North American paper industry, according to consultant Kline & Co. Worldwide demand for GCC is growing fast, particularly in China where 18 Mt were used in 2008. In addition, $MgCO_3$ can be used as paper filler and further technical investigations are needed (Mineral Products, 2010; Kline & Co, 2010).

Calcium carbonate (91Mt global production)

The global market for Ground Calcium Carbonate (GCC) expanded from around 56Mt in 2004 to almost 72Mt in 2007, with an average annual growth rate of ~9%. The global demand is forecast to continue this level of growth reaching 87.4Mt in 2012. The plastics industry is the second largest user of GCC, after the paper industry, accounting for an estimated 14.4Mt/y of consumption in 2007. The production of GCC in China has grown from 5.2Mt in 2002 to 12Mt in 2007 (Global Information, 2008). The general shift from an acid-based to an alkaline process has transformed the use of fillers in papermaking creating an increased market for GCC and Precipitated Calcium Carbonate (PCC). China has emerged as the world's leading paper and board producer and its global share continues to grow. GCC is nowadays the main industrial mineral for paper production where some 19Mt was used in China alone in 2008. It can also be used as a filler, pre-coat, and topcoat (90% GCC and 10% Kaolin) coating pigment. The price of Kraft pulp in the USA is currently £560/tonne* and in China is about £576/tonne*. Chinese pre-coat GCC command the paper prices with £51-102/tonne while Chinese PCC as a filler costs about £51-58/tonne*. Comparing the pulp price to the Chinese PCC prices, it is clear the advantages for the producers to decrease the pulp loading and increase the mineral loadings. In 2007, the world's PCC consumption was approximately of 13Mt (Industrial Minerals, 2009 and 2010 a).

Commodity Prices

A summary of the prices for the mineralisation products is listed below (Industrial Mineral prices, b, 2010; US Geological Survey, 2010):

Silica sand, (2008):

- >92 brightness, FOB Durban £189/tonne* (<20µm, FCL'S bagged) (2010)
- glass sand, container, ex works £9-17* (<20µm, FCL'S bagged) (2010)
- ground sand for foundry molding and core had the highest value (£84/tonne*)
- ground sand for scouring cleansers (£77/tonne*)
- ground sand for ceramics (£61/tonne*)
- silica for swimming pool filters (£49/tonne*)
- silica for water filtration (£39/tonne*)
- ground sand used as fillers for paint, putty, and rubber (£38/tonne*)
- ground sand for fibre glass(£33/tonne*)
- sand for hydraulic fracturing (£31/tonne*)

GCC:

- Coated, fine grade, ex works, £80-103/tonne

PCC:

- Coated, fine grade, ex works, £350-550/tonne
- Uncoated, ex works, £320-480/tonne
- Chinese PCC as filler, £51-58/tonne*

Magnesite:

- Greek raw, max 3.5% SiO_2, £55-64/tonne**
- Chinese calcined magnesite (90-92% CaO) lump FOB £224-260/tonne*
- European calcined agricultural, CIF Europe, £172-183/tonne**
- Dead burned magnesia (refractory use)
- Chinese fused (refractory and electrical uses), FOB 96% MgO lump, £384-403/tonne*; 98% MgO lump, £410/tonne*

Iron Oxide pigment:

- US 2008 average producer price, £137/tonne*

High purity precipitated silica, iron oxide pigment; PCC and fused magnesite have high value, while raw magnesite and glass sand (high volumes required) show lower value.

Appendix 10 Scenarios and Economics

This section aims to provide an empirical analysis of new CCSM technologies by evaluating the existing economic assessments and suggesting appropriate directions for future effort in decreasing the early-stage costs of a technology. The section provides economic appraisals for the Caterpillar, Shell, University of Nottingham, and Åbo Akademi CCSM technologies in addition to more general economic summary of the other available data.

CAT CCSM USING SPRAY DRY ABSORBER (CATERPILLAR PROCESS)

Concept Selection

Caterpillar anticipates that future CO_2 regulations will impact foundries, heat treatment manufacturing facilities, other energy intensive operations, the sales of electrical power generators, and other industrial engine applications. Therefore, Caterpillar has set aggressive, sustainable development goals that include a 25% CO_2 emission reduction from operation and manufacturing facilities as well as 20% CO_2 emission reduction from power generation products (called Distributed Energy Resources, DER).

Various types of CCSM technologies were described in the literature and analyzed in previous chapters. CAT selected the direct flue gas treatment concept utilizing a combination of natural minerals and industrial wastes. The high-level process flow diagram for CAT CCS by Mineral Carbonation (CAT CCS MC) from flue gases of the industrial facility and/or DER was presented in Figure 63 previously. This concept could become attractive for CCS solution in DER applications as well as for energy intensive manufacturing processes for the following reasons:

- The process under development does not require a CO_2 separation step and can be specified as a single-step capture and conversion of CO_2 from flue gases. The single-step process has highest RTY (Raw Throughput Yield) in comparison with alternative multi-step processes.
- CCS MC allows utilizing of waste materials from Caterpillar industrial metallurgical processes such as steel slag. Various other alkaline waste streams (cement kiln dust, “red mud” etc.) can be utilized in combination with silicate minerals to reduce the environmental footprint of the manufacturing facility as well as to allow re-classification of hazardous industrial waste into non-hazardous by-product.
- CCS MC allows treating emissions at the point of origin (such as current energy intensive manufacturing facilities).
- CCS MC operations do not require any special operational permission (such as one for compressed liquid CO_2 pipelines).

TRL 1: Basic principles observed and reported.

The basic principles of CAT CCS MC technology were demonstrated through a series of laboratory scale experiments described in the following tests.

<u>Feedstock selection and pre-treatment.</u> In this study, the forsteritic olivine sand provided by Unimin Inc., Green Mountain, NC, USA (~75μm, $Mg_{1.8}Fe_{0.2}SiO_4$) was utilized. This sand is also employed for several other purposes at the CAT foundry at Mapleton, IL. In order to create the alkaline media for the efficient single-step CO_2 capture and conversion, waste streams were considered – steel slag, brines, cement kiln dust, fly ash, “red mud”, natural alkaline clays, etc. For the purpose of concept demonstration at the laboratory scale, CaO and NaOH were chosen as a substitute for any Ca or Na containing alkaline waste stream.

The chemical thermodynamic analysis of the system Mg_2SiO_4-CaO-H_2O using an on-line FACT™ tools showed that the following cation exchange reactions are thermodynamically favourable:

$$Mg_2SiO_4 + CaO + 2H_2O = CaSiO_3 + 2Mg(OH)_2$$

$$Mg_2SiO_4 + CaO + H_2O = (MgCa)SiO_4 + Mg(OH)_2$$

Temp	Mg2SiO4 (s)	Mg(OH)2 (s)	CaSiO3 (s)	Mg3Si2O5(OH)4 (s)	(CaMg)SiO4 (s)	MgO (s)	CaO (s)
25	0	2.18E+00	2.07E+00	4.84E-01	0	0	0
60	0	2.18E+00	2.07E+00	4.84E-01	0	0	0
110	0	2.18E+00	2.07E+00	4.84E-01	0	0	0
200	4.91E-01	1.04E+00	0	0	2.79E+00	0	0
300	4.91E-01	0	0	0	2.79E+00	7.19E-01	0
500	4.91E-01	0	0	0	2.79E+00	7.19E-01	0

Table 60 Mole fractions of various solid phases at different temperatures. (s) Designates solid state. [Copyright Caterpillar Inc.]

Therefore, several combinations of olivine:CaO:H_2O were tested; the ratio of olivine:CaO = 3:1 and Solid/Liquid = 1 were used for mineral pre-treatment. Further optimization could be done in a follow up TRL development stages in order to minimize the consumption of water and CaO. The mixture was ball milled at 50-70rpm for 8-24h and various characterization tests were performed. First, a portion of prepared slurry was thoroughly washed with water until a neutral pH was achieved; a filtrate was collected and dried (designated as “filtrate precipitate”).

The washed solid is designated as “residue”. SEM/EDX analysis showed that composition of starting olivine was Mg:Ca:Fe:Si:O = 1.9:0:0.20:1.1:6.7, while composition of the “residue” was close to 1.3-3.2-0.14-1.1-7.2 and composition of the “precipitate” was 0.03-2.53-0.0-0.09-7.32. XRD analysis of the “residue” showed the presence of brucite $Mg(OH)_2$, montichelilite $(MgCa)SiO_4$, and SiO_2 along with unreacted olivine. Wollastonite, predicted by FACT™ analysis above, was not detected by XRD. The “precipitate” from the filtrate was mostly composed of $Ca(OH)_2$ and $CaCO_3$ crystalline phases; the later one was formed during drying the $Ca(OH)_2$ containing aqueous filtrate in presence of atmospheric CO_2. It should be mentioned that some secondary peaks were present in XRD pattern of the “filtrate precipitate” that could not be assigned to the specific crystalline phases at this time. Overall it was concluded, that Mg<->Ca cation-exchange reaction does take place during olivine:CaO:H_2O milling, and the pre-treatment process can be described as mechano-chemical activation.

Carbonation performance tests. The performance of the prepared “activated” olivine samples were tested under CO_2, SO_2 and combined CO_2+SO_2 exposure using in-situ thermo gravimetric analysis method (TGA) at temperatures 70, 120, 200, 300, 400 and 500°C. As an example, Fig. 1 shows TGA weight change curves for as-received and activated olivine in pure CO_2 stream and in 14% CO_2/N_2 mixture. The initial weight loss is due to the moisture evaporation during heating in flowing N_2. Once the temperature set point is reached, pure CO_2 (or 14% CO_2/N_2 mixture) is introduced into the test chamber, and the gas environment is cycled every 10 min between N_2 and pure CO_2 (or 14% CO_2) while recording the sample weight.

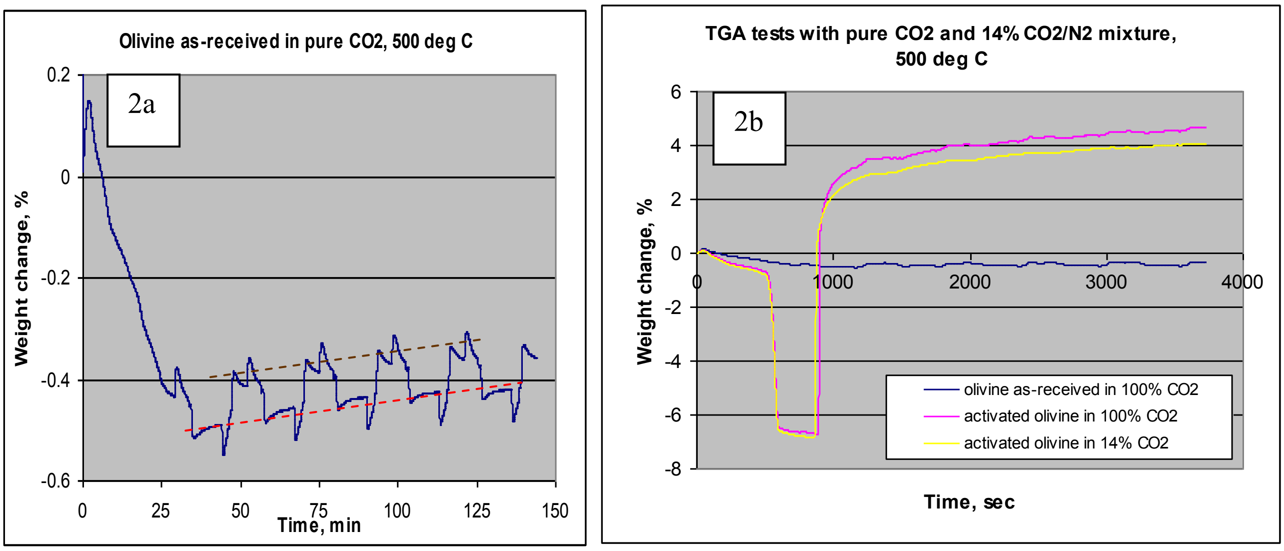


Figure 128 TGA data for olivine samples in 100% CO_2 and 14% CO_2 gas streams. [Copyright Caterpillar Inc.]

Based on the results obtained the following observations are made:

1. as-received olivine (Figure 128) exhibits two types of CO_2 storage – permanent (red dashed line) and temporary (brown dashed line); the latter one is demonstrated by weight increase under CO_2 cycle and sharp weight drop in N_2 cycle;
2. as-received olivine does not show any significant CO_2 capture performance (~0.1% permanent weight gain and ~0.2% temporary weight gain in CO_2 stream);
3. in the case of activated olivine (Figure 128), the switching from the 100% CO_2 stream to the diluted 14% CO_2 stream resulted in insignificant CO_2 performance decrease from ~12% weight gain to ~11% weight gain;
4. CO_2 capture and conversion onto activated olivine is very fast during first 10min of the gas-solid contact and then levels off (Figure 128); most probably, the chemical carbonation reaction is a rate limiting step at the beginning, while the layer diffusion becomes a rate limiting step as the carbonation product builds up on mineral particle surfaces.

Overall, it can be concluded that CO_2 separation from gas stream is not required and CO_2 capture can be performed from the diluted flue gas streams using activated olivine.

XRD analysis of the carbonation products showed the presence of unreacted olivine, unreacted $Ca(OH)_2$, $CaCO_3$ and SiO_2. Magnesium carbonates were not detected by XRD, although it should be mentioned that magnesite peaks do overlap with olivine peaks making magnesite detection difficult in presence of unreacted olivine. High resolution XRD will be performed in a follow up study to address this issue. In addition, the presence of amorphous carbonation products cannot be excluded, so other methods will have to be explored in a follow up TRL stage. Meanwhile, it should be mentioned that presence of silica could be explained only as a result of conversion of Mg silicate into Mg carbonates.

The chemical thermodynamic analysis was also performed to assess the possibility for SO_2/SO_3 (SOx) and combined CO_2 and SOx capture on silicate minerals. The following chemical reactions were found to be thermodynamically favourable:

$$Mg_2SiO_4 + SO_2 + O_2 = 2\ MgSO_4 + SiO_2 \qquad \Delta G = -33.9484\ kJ$$

$$Mg_2SiO_4 + SO_3 = 2\ MgSO_4 + SiO_2 \qquad \Delta G = -3323.39\ kJ$$

$$Mg_2SiO_4 + SO_3 + CO_2 = 0.6MgSO_4 + MgCO_3 + 0.4\ MgSiO_3 + 0.6\ SiO_2 \qquad \Delta G=-3130.86\ kJ$$

Figure 129 shows comparison of CO_2 (14% CO_2/N_2) and SO_2 (3,000ppm SO_2/air) capture on activated olivine at various temperatures between 70 and 500°C. The data showed that above 200°C there is a good linear correlation with the weight gain; and when the temperature was below 200°C, the weight gain levels off at ~3% in presence of CO_2, while no weight change is observed in presence of SO_2.

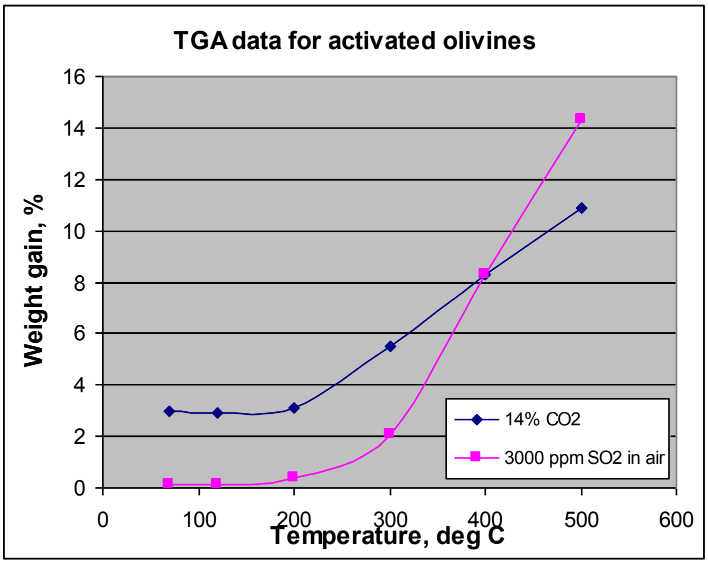


Figure 129 Weight gain for activated olivine at various temperatures. [Copyright Caterpillar Inc.]

Finally, Figure 130 shows an example of TGA data at 500°C for activated olivine sample exposed to the simulated flue gas composition (10% CO_2, 500ppm CO, 3,000ppm SO_2, 5% O_2). The heating up ramp was performed in N_2 flow and in simulated flue gas mixture.

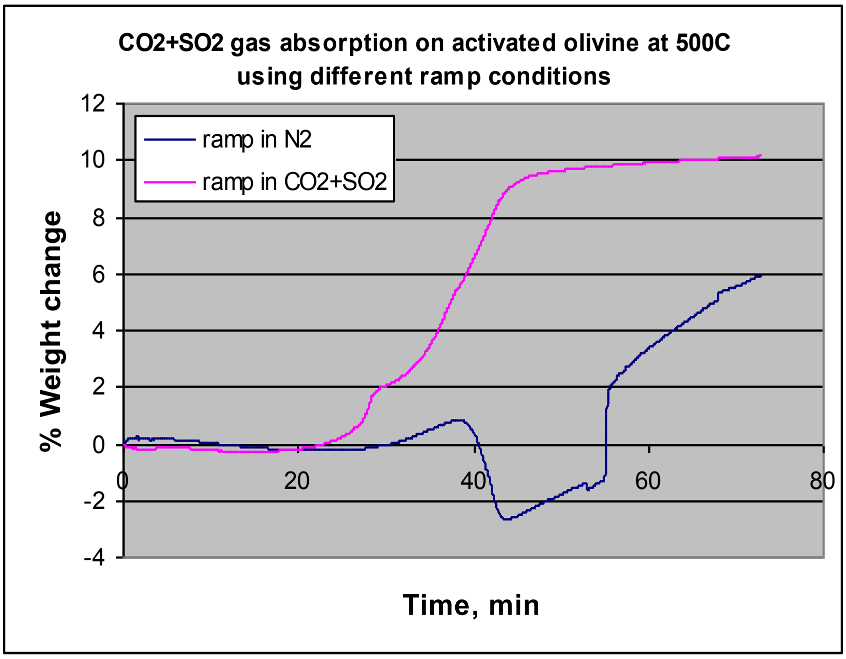


Figure 130 Example TGA Data. [Copyright Caterpillar Inc.]

The comparison of weight change curves recorded under different test conditions shows that:

(a) no weight change observed until ~25-30min test time (or T~250-300°C);

(b) when N_2 is used during the heating up step, the first the weight loss occurred due to moisture evaporation and then weight gain is observed due to the reaction with SO_2 and CO_2; the total weight gain is ~9%;

(c) when simulated flue gas is used during entire test duration, no weight loss step was observed and the total weight gain is almost the same ~10%;

(d) the weight gain levels off, probably, due to the diffusion layer becoming a rate-limiting step.

XRD analysis of the products showed the presence of unreacted olivine, $MgSO_4$, $MgSO_3$, $CaSO_4$, $CaSO_3$, $CaCO_3$, and SiO_2. The detection of magnesite, in the presence of unreacted olivine, was problematic. This will be addressed in a follow up TRL stage.

Similar sets of tests are to be performed using olivine samples prepared by mechano-chemical activation with NaOH:H_2O mixture. As it was mentioned above, NaOH will be used for simulation of various alkaline wastes containing Na. In addition, production of NaOH by electrochemical “chlor-alkali” method and its integration with CCS MC will be evaluated.

Overall, the TRL1 study made the following conclusions: (a) direct single-step CO_2 capture from flue gas without separation is feasible; (b) utilization of silicate minerals in combination with industrial alkaline wastes for CCS MC is feasible; (c) combined CO_2 and SOx capture is feasible as well.

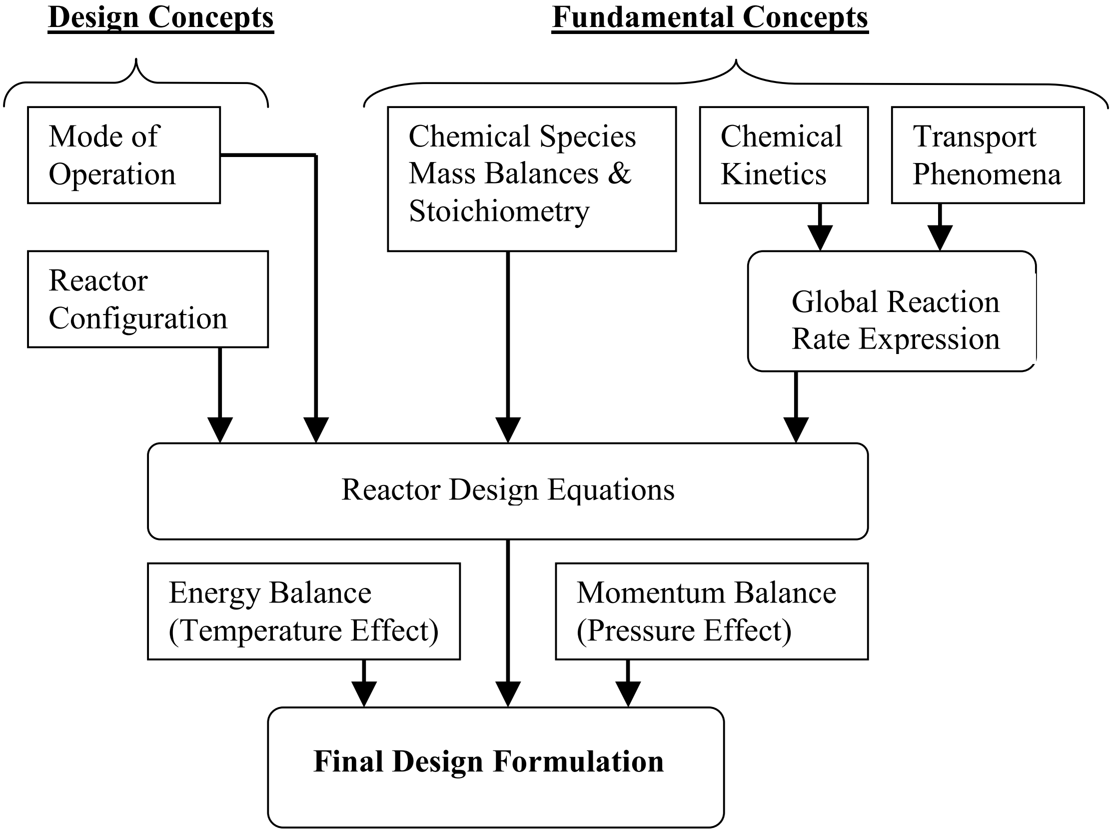
Level 2: Technology concept and/or application formulated.

Major control parameters for direct gas-solid CCSM. Non-catalytic gas-solid reactions (such as CAT CCS MC process) occur on the surface of the solid and involve heat and mass transport, and reaction kinetics. In the case of direct gas-solid CCSM, the gaseous reactant (CO_2) is transported to the interface, where it reacts with the solid reactant (minerals), and the solid products remain in the solid. Therefore, overall reaction rate depends on the surface area available and the rate of transfer of the gaseous reactant to the solid surface. Based on the results described above, it was concluded that activated "olivine-simulated flue gas" reaction rate quickly levels off and becomes diffusion layer limited. Consequently, the actual reaction rate (also referred to as the global reaction rate) is affected by the transport rates of gas species through the carbonate plus silica product layer. Incorporating the effects of species transport rates to obtain the global rates of the chemical reactions is a difficult task since it requires knowledge of the local temperature at the point of species interaction, flow patterns (hydrodynamics) and numerous physical and chemical properties. Major control parameters for direct solid-gas CCSM are the following:

Phenomena	Major control parameters
Product layer diffusion	gas velocity (P, T, CO_2 concentration, flow rate)
	solid product layer density and porosity (diffusivity)
	solid product layer temperature gradient (thermal conductivity)
	mass transfer coefficients
Carbonation kinetics	activation energy (P, T)
	available interfacial surface area
	gas species residence time
	CO_2 concentration
	Mineral: CO_2 ratio

Obviously, the carbonation product layer properties play an important role. On the other hand, due to the fact that the final carbonation solid products are to be the same regardless of the starting silicate mineral (serpentine or olivine or anything in between), the direct gas-solid CCSM should be less sensitive to the mineral variation in comparison with gas-liquid-solid processes complicated by both mineral and CO_2 dissolution kinetics. This is a significant advantage of direct gas-solid CCSM.

Large-scale chemical reactor selection. The major control parameters listed above govern the selection of the large-scale chemical reactor; in addition, they provide guidance for the process performance improvement up to its highest limits (will be discussed later). In order to finalize a high-level large-scale CAT CCS MC concept and its applications the following factors were considered as a common chemical engineering practice:



In addition, various currently employed large scale pollution control technologies were analyzed that utilize pipeline reactors, continuously stirred reactors, autoclave reactors, fluidized beds, “wet” and “dry” scrubbers and combinations of them. It was shown above that direct reaction of CO_2 with activated olivine quickly becomes diffusion layer controlled, therefore the following combination of steps should be considered: (a) short flue gas-mineral contact time; (b) removal of carbonation product built up and (c) unreacted feedstock re-use. Hence, a combination of spray dry absorber and cyclone (or bag house) was selected, where product “fines” (assumed to be mostly carbonates, sulphates and silica) can be separated from “coarse” products (assumed to be mostly unreacted olivine) in two consecutive cyclones (or filtration stages in a bag house). Previously, it was reported in the literature that SDA can be used for CO_2 capture with various alkaline aqueous solutions and slurries [Cheng, 2005]. The best capture of ~50% was demonstrated in a single step using a mixture of lime and NaOH. Overall, CAT CCS MC large-scale concept can be defined as adaptation of SOx scrubbing technology (“wet” or “dry”). The co-capture of other pollutants such as SOx, NOx, and CO (through oxidation into CO_2) can be achieved.

The technology process flow diagram (PFD) was shown previously. Two applications for CAT CCS MC were considered and preliminary cost analysis is described below15.

Level 3: Analytical and experimental critical functions and/or characteristic proof-of-concept

The TRL3 concept demonstration at the laboratory scale was performed using a commercial SDA machine from Yamato Inc. shown in Figure 131. It includes slurry injection pump, spraying nozzle, SDA chamber, single cyclone, and final product collector. The CO_2

concentration from an in-coming gas stream was controlled by the CO_2 pressure and dilution with ambient airflow. The current experimental set up does not allow separate control of the CO_2 concentration and gas flow rate, therefore these factors are compounded such that the lower CO_2 concentrations is achieved along with lower gas flow rate and therefore results in longer gas species residence time in SDA chamber.

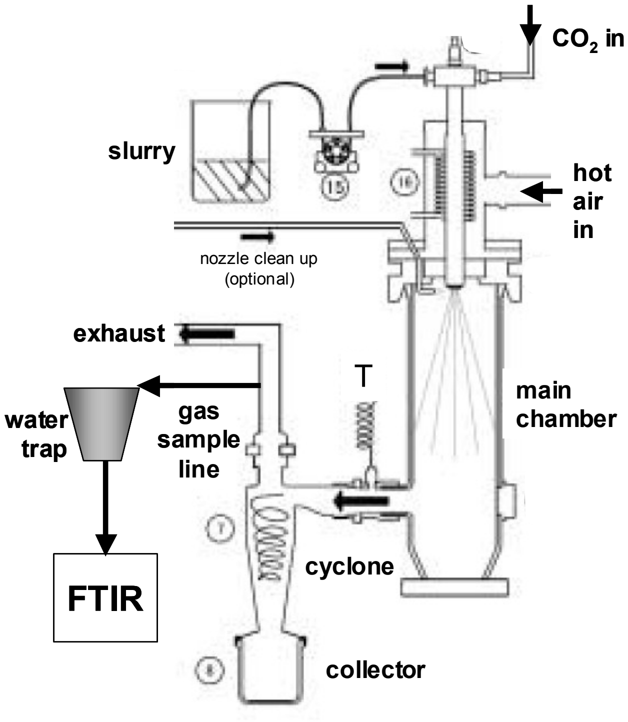


Figure 131 Experimental set up for demonstration of CAT CCS MC using SDA. [Copyright Caterpillar Inc.]

In a typical experiment diluted 5% aqueous slurry was used due to the limitations with the current commercial spray nozzle. The slurry injection rate was adjusted to provide an excess of mineral over the theoretical amount required to capture 100% of incoming CO_2 in gas stream. FTIR was used for continuous monitoring of CO_2 concentration in the gas stream. An example of the FTIR profile for a typical SDA test is shown in Figure 132. The CO_2 capture efficiency (CE) was calculated as

$$CE = (CO_2in - CO_2out)/CO_2in, \%.$$

First, the tests were performed with $CaO/Ca(OH)_2$ slurry to reproduce previous results published in the literature [Cheng, 2005] as well as to validate the experimental set up. Then, experiments were repeated with activated olivine samples.

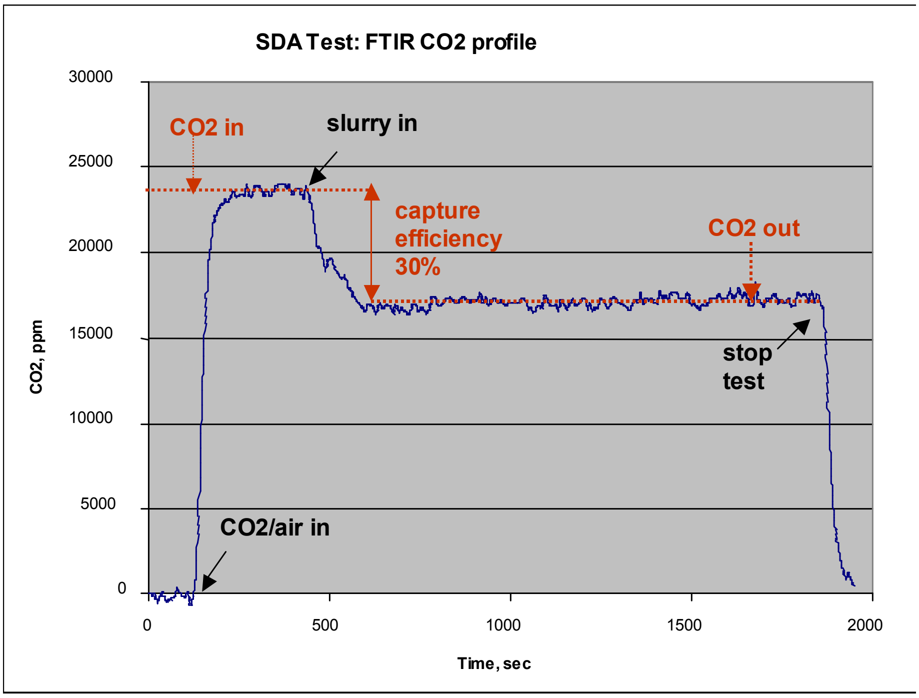


Figure 132 FTIR profile during CO_2 capture test with SDA. [Copyright Caterpillar Inc.]

Thus far, a limited number of tests were performed with activated olivine and the summary of all the experiments is shown in Figure 133.

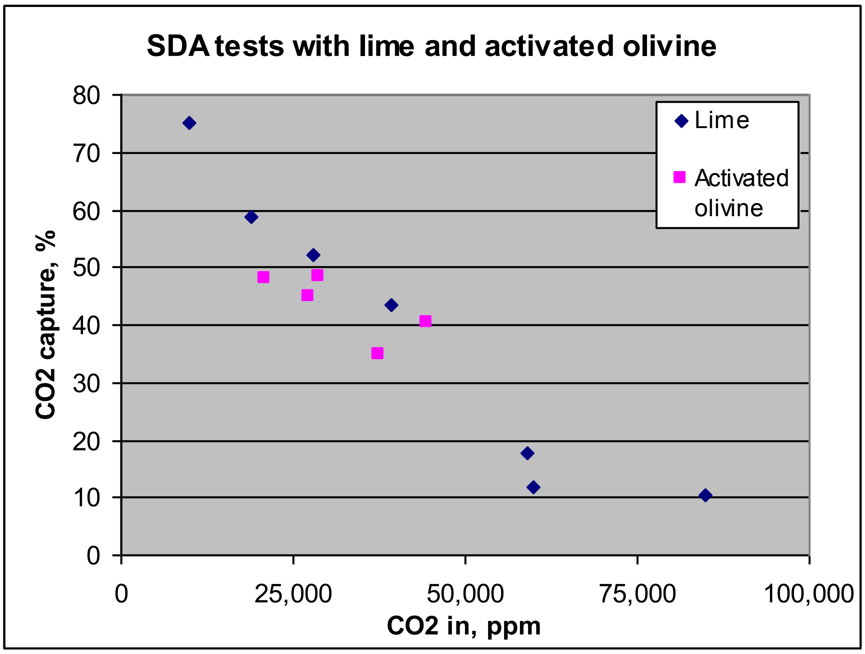


Figure 133 Summary of SDA tests. [Copyright Caterpillar Inc.]

Based on the limited number of tests the following observations are made:

1. The CO_2 capture performance of activated olivine is comparable to the performance of pure lime.
2. SDA method showed better performance in diluted CO_2 streams (<5%).

3. In order to increase the CO_2 capture performance in SDA, the incoming CO_2 concentration should be decreased as well as the residence time increased (or gas flow rate should be decreased). This observation is very different from the previous studies where not only pure CO_2 stream but also pressurised CO_2 stream was required in order to achieve high CO_2 capture and conversion. Our results require further investigation. Meanwhile, it should be mentioned that SDA method was originally developed and successfully utilized for SOx capture from flue gas where SOx concentrations are generally below 3%.

In order to estimate the amount of carbonates formed during SDA tests, final products from several SDA tests (incoming CO_2 concentrations between 2-4%, CO_2 CE between 35-55%, see Figure 133 above) were heated up to 800°C in airflow and the TGA weight loss curves were recorded. It is assumed that the observed weight loss was due to the decomposition of carbonates and CO_2 release. The results showed that in case of lime, ~ 80% of $Ca(OH)_2$ was converted into $CaCO_3$. In case of activated olivine the situation was more complicated: regardless lime and activated olivine showed comparable CO_2 CE in SDA tests, only 15-25% conversion of activated olivine into carbonates was estimated from TGA data. This result needs further investigation. It was mentioned previously that as-received olivine exhibited "temporary" CO_2 storage capability while exposed to CO_2 stream. It is plausible that activated olivine has similar behaviour.

The following tasks are planned for the completion of TRL3 and will be performed based on the conclusions and recommendations from the Consortium:

- Design of Experiments for optimization of SDA process using simulated flue gas mixture (factors – gas flow rate, type of mineral, mineral/CO_2 ratio, CO_2 concentration).
- Current SDA allows limited variation of carbonation temperatures, so an alternative test rig will be set up to study the impact of temperature on direct gas-solid CCSM process using simulated flue gas mixture at constant flow rate and CO_2 concentration.
- Define the carbonation rate equation based on the data collected.
- In-depth characterization of activated olivine and carbonation products (HR XRD, solid state FTIR, EXAFS/XANES, SEM/EDX, HRTEM).
- Design of Experiments for optimization of mechano-chemical activation of minerals (factors – type of mineral, type of "activator", solid/liquid ratio, energy input).
- Development of the energy penalty estimation tool for direct gas-solid SDA CCS MC.
- Next iteration of cost and energy penalty analysis.

Preliminary cost analysis

The preliminary cost analysis of the CAT CCSM technology is described in this chapter. The cost estimate is based on a number of reasonable assumptions derived from current knowledge and understanding of the critical technology parameters and their associated requirements. As the technology is developed, the cost model and estimates will be reviewed and updated accordingly.

Figure 134 shows a block diagram of the CAT CCSM process representing the system boundaries of the present cost evaluation.

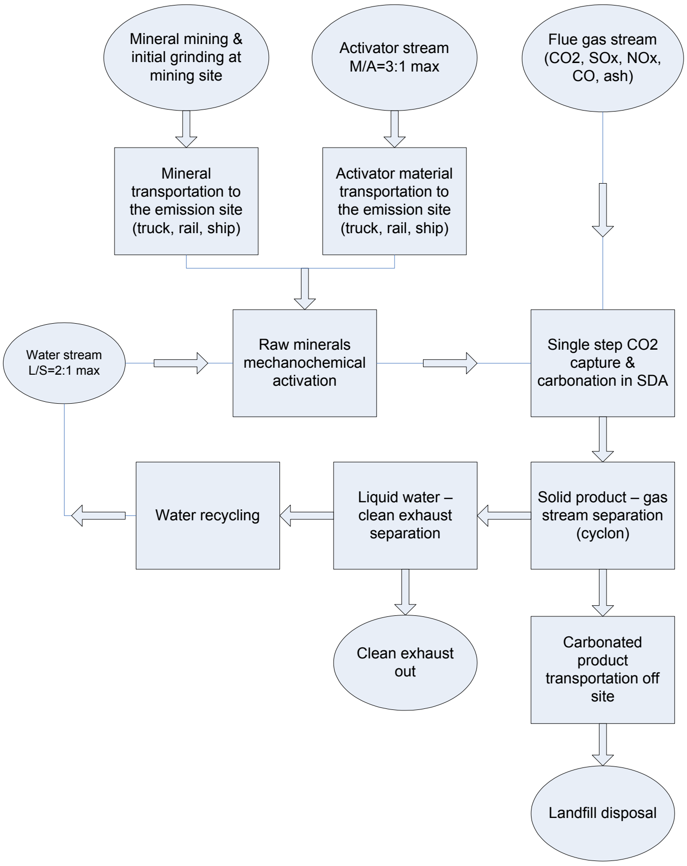


Figure 134 CAT CCSM Process schematics. [Copyright Caterpillar Inc.]

The process includes the following:

- mineral transportation to the CO_2 emission sites (limited to 100 miles),
- mechanical and chemical activation of minerals using activating additives (max 1 tonne per 3 tonnes of mineral, M/A=3) and water (max 2 tonnes per 1 tonne total solids, L/S=2),
- single step CO_2 capture and conversion in Spray Dry Absorber (SDA) main chamber
- final product separation in cyclone
- water condensation & recycling
- booster fan station to minimize backpressure in the system
- final waste product transportation to the landfill (limited to 100 miles)

Two applications for CCSM were considered in the cost analysis: the Caterpillar Heat Treatment facility located in East Peoria, USA and a Distributed Energy Resources Natural Gas Engine G3520 series. Estimates for the CO_2 emissions from the East Peoria Heat Treatment facility are based on a 6-month study of the energy and fuel consumption rates. The emissions range from 0.035 to 0.066 tonne of CO_2/hour per HT furnace (or 24,287- 44,287 tonnes/year for entire facility). This variation includes the type of furnace used as well as the manufacturing and furnace maintenance schedules. CO_2 emissions from the Caterpillar G3520C engine used for continuous power generation vary between 0.67-1.22 tonnes/hour (or 5.8 – 10.7 tonnes/year), and this estimate is based on the engine load range between 50% and 100%.

The Purchased Capital Equipment (PCE) includes the following:

- ➢ mineral storage tank
- ➢ slacker/ball mill combination

- slurry tank
- slurry pump
- SDA
- cyclone
- booster fan
- water chiller
- final product storage tank

Reference equipment, for which cost information as a function of capacity, was available from the literature [Wallas SM. Chemical process equipment selection and design, Boston: Butterwoth; 1988]. The Total Capital Investment (TCI) is estimated at 2.5 times increase over the cost of purchased capital equipment (TCI = 2.5PCE) and includes the installation, instrumentation & control, piping, electrical, land and site preparation, buildings, facilities, contractor fees, engineering & supervision labour and contingency. A cost simulation and sensitivity analysis using the Crystal Ball software was conducted at a 95% confidence interval to identify capital equipment cost variations.

Previous sensitivity analyses for the O&M cost for CCSM [Huijgen WJJ, Energy Conversion and Management, 48 (2007) 1923-1935] illustrated that the major uncertainties are due to raw material costs, market value of the final carbonation products and carbonation efficiency that controls total volume of raw materials to process. In addition, the transportation cost was generally not included in previous O&M cost estimates. Therefore, our O&M cost model has included the following:

- mineral cost (olivine) include the initial crashing & milling to ~75 micron size that is performed at the mining site on a large scale (Mt/year)
- activating additive cost
- mineral & final product transportation (truck, rail, ship) limited to 100 miles
- landfill disposal cost (conservatively, no value for the final carbonation products).

Two cost scenarios were considered:

1. Early Phase technology development that achieves 25% CO_2 capture efficiency and requires at least 10 years lifetime of capital equipment and,
2. Advance Phase of the technology development that allows 90% CO_2 capture efficiency and requires 30 years lifetime of capital equipment.

The Early Phase utilizes fewer raw materials (minerals, additives, water) and requires smaller capacity equipment to achieve 25% CO_2 capture. In addition, less expensive equipment materials can be employed for continuous operation in the 10-year lifetime. The Advance Phase requires much larger capacity equipment that is more costly as well as the utilization of more expensive durable equipment materials in order to meet the 30-year lifetime. The Early Phase of the technology development with lower CO_2 capture capacity is a required step in order to analyze various options for the Advance Phase implementation. These options include: (a) single flue gas flow through a single large scale SDA; (b) single flue gas flow through a series of sequential small SDAs; (c) split flue gas flow into several small streams. For the Advanced Phase technology, scenario (a) was considered for cost analysis in this report.

The cost estimates are summarized in the Table below. The data illustrate that TCI for HT application varies from \$189K to \$270K, while capital investment for DER is an order of magnitude higher \$1,777K-\$2,667K. For the comparison, the TCI for a 100MW power plant (60 tonnes CO_2/h emissions) was estimated at $45M [Huijgen WJJ, Energy Conversion and Management, 48 (2007) 1923-1935]. It should be mentioned that TCI (in $/tonne CO_2) drops significantly as technology moving from Early Phase to the Advance Phase for both applications.

HT Facility: 0.035-0.066 t CO_2 per hour per furnace, P=1atm, T =200-300 ºC				
	Early Phase		Advance Phase	
	Min	Max	Min	Max
PCE, $K	76	108	133	193
TCI, $K	189	270	333	483
TCI, $/tonne CO_2	33	86	20	28

Table 61 Heat Treatment TCI. [Copyright Caterpillar Inc.]

DER (G3520): 0.67-1.22 t CO_2 per hour, P=1atm, T= 450-550 ºC				
	Early Phase		Advance Phase	
	Min	Max	Min	Max
PCE, $K	711	1067	1108	1703
TCI, $K	1777	2667	2769	4258
TCI, $/tonne CO_2	66	182	10	15

Table 62 Distributed Energy Resource TCI. [Copyright Caterpillar Inc.]

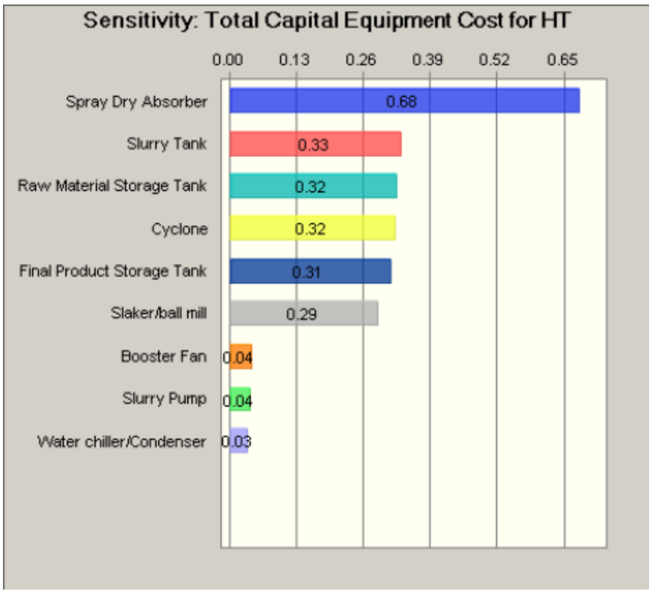


Figure 135 Sensitivity Analysis Results for the Heat Treatment (HT) and Distributed Energy Resource. [Copyright Caterpillar Inc.]

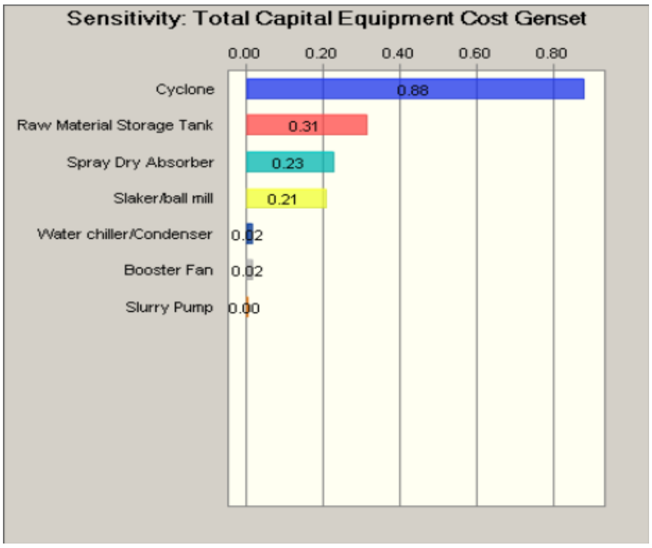


Figure 136 Sensitivity charts for TCI for HT and DER applications. [Copyright Caterpillar Inc.]

For HT application the SDA cost presents the highest uncertainty as well as highest absolute cost of a single capital equipment unit while for the DER application, the cyclone separator is the single most significant contributor for cost uncertainty and the highest absolute cost contributor. This reflects a major difference of two applications, namely, a much higher exhaust gas flow rate occurs in case of the DER when compared with the HT manufacturing process.

The O&M cost was calculated for three different transportation means – highway truck, ship and rail (min 10 miles, max 100 miles) based on available data in the literature [Stacy C. Davis, Susan W. Diegal, Transportation Energy Data Book, edition 26, US DOE, Oak Ridge National Laboratory, 2007. Bureau of Transportation Statistics, http://www.bts.gov]:

	Min, \$ / tonne CO_2	Max, \$ /tonne CO_2	Total \$ / tonne CO_2	
Raw Materials	6	31		
Landfill disposal	10	20	Min	Max
Truck	11.1	111.4	27.1	162.4
Rail	1.19	11.9	17.2	62.9
Ship	0.3	3.02	3.02	54.1

Table 63 O&M Costs Based on Different Transport Scenarios. [Copyright Caterpillar Inc.]

The results illustrate that the truck transportation could be considered only when a landfill disposal is nearby while rail transportation offers a more flexible and economic solution for inbound mineral delivery to the emission site. The transportation by ship is most attractive but limited to coastal areas and other large waterways. Various combinations of “ship-rail-track” transports can be considered based on specific locations of the mineral mine, emission source and landfill disposal site.

Based on the overall cost analysis the following recommendations are made to allow the process to be economically viable:

- CO_2 capture and conversion efficiency should be 90%+.

- Lifetime of major costly capital equipment components should be at least 30 years.
- Large-scale CCS MC utilizing silicate minerals (M tonne per year) would allow lowering the cost of raw minerals.
- Utilization of final products for mine reclamations, landfill beds etc. would eliminate disposal cost.

Summarizing, the following ranking (A-E) of the process is proposed based on the assessment criteria described previously:

	ARC	ARC	Brent, GF	Huijgen, W	Caterpillar Inc.
Feedstock	S	O	S	W	O
R real	3.39	2.22	5.25	4.06	2.8
Pre-treatment	M (75), H (630)	M (38)	M (75), H (630)	M (38)	M-C (10)
T max, C	155	185	155	200	500
P max, bar	120	150	115	35.5	1.2
Additives	0.64 M NaHCO3, 1M NaC	0.64 M NaHCO3, 1M NaCl	0.64 M NaHCO3, 1M NaCl	none	CKD, alkiline waste stream
Conversion, %	62	61	80	69	25 (SDA tests)
CO2 FE, %	77	100	75	76	tbd
Reaction time, h	1	1	1	tbd	0.16
Energy & Efficiency	B	E	B	B	B
Material amount	C	B	C	B	B
Product additives	D	D	B	C	C
Simplicity & Generality	A	A	A	A	A
Reliability proven	A	A	B	C	B

Table 64 technical paths to the improvement of direct gas-solid CCSM process efficiency.

The cost analysis of CAT CCSM technology illustrates that in order to decrease the cost the carbonation process efficiency would have to be at least 90%. The major control parameters for the direct solid-gas process were previously discussed and these parameters provide insight for optimizing the process efficiency.

Mineral pre-treatment. The available surface area of solid mineral (or particle size distribution) controls the gas-solid interactions, and the surface area is defined by the mineral pre-treatment process (wet or dry activation). The mechano-chemical activation is a prospective method, and it has not been fully explored to date. Results from a CAT study using mechano-chemical treatment of olivine-CaO-water mixture showed formation of brucite and $(CaMg)SiO_4$; carbonation of these products is more thermodynamically favourable than the parent olivine mineral. Various other mechano-chemical processes should also be explored which might offer further improvements in mineral activation or even a breakthrough solution.

Product layer removal. To maintain the fast carbonation rate observed during the TGA tests described above, the carbonation product layer ($MgCO_3$ + SiO_2) would have to be continuously removed. This can be accomplished by agitating the carbonation products with glass beads or pebbles of the same feedstock silicate mineral. Combining agitation with sieving would also allow separating the carbonation fines from the larger unreacted mineral particles; the unreacted feedstock would then be returned into the carbonation step. This is a simple and cost effective solid separation method that is well established in the mineral engineering industry.

Large scale chemical reactor and gas-solid interaction pattern. Once the product layer is removed, the gas-solid carbonation rate is controlled by the available surface area and gas-solid interaction pattern. The SDA presents an advantage over other gas-solid chemical reactors (such as fluidized beds) due to the unique spray atomization pattern. The process creates an intimate gas-solid contact that is required for an effective direct carbonation reaction and has shown a positive impact on process kinetics.

Finally, our preliminary SDA experiments suggested that in order to improve the SDA process efficiency, the gas flow rate and CO_2 concentration should be decreased; e.g. flue gas stream should be split into several parallel paths with smaller SDA sizes rather then go through a series of sequential SDAs. It was previously mentioned that the SDA process is successfully used for direct flue gas desulfurization (FGD) - up to 98% of SOx is removed from rather dilute flue gas (<3% SOx). Our preliminary SDA results suggest that the same technology can be successfully adapted for the CO_2 capture; assuming CO_2 concentration in flue gas ~10% on average, four parallel SDAs can be used to treat the split flue gas flow with ~2.5% CO_2 concentration in each leg.

Cost effective CAT CCSM deployment scenario for small CO_2 emitters.

Many types of high-energy intensive manufacturing facilities fall into the category of "small" CO_2 emitters. The typical attributes of these facilities are as follows:

- Facility is located in the proximity of urban area (<100mi).
- Facility is located in the proximity of landfill disposal sites (<100mi).
- Facility has optimized transportation logistics for inbound delivery of raw materials and outbound transportation of manufactured goods.
- The facility has significant amount of industrial waste accumulated on site for years of operation. The industrial waste is alkaline and/or rich in Mg, Ca, Fe, and Na. (Recent study by Blencoe, 2008 showed that CO_2 can be sequestered in form of mixed Mg, Na carbonates).
- The industrial manufacturing process generates waste heat that can be recovered and utilized for mineral activation and/or heat supply for the carbonation process. As an example, hot slag (>1,000°C) is generally air cooled and dumped at the iron/steel manufacturing site. Instead, it can be used to generate steam for mineral pre-treatment.

Examples of these facilities include cement manufacturing, aluminium manufacturing, steel manufacturing, paper manufacturing, etc. Various types of wastes suitable for the CCSM were discussed in previous chapters. For economy of scale reasons, it would be advantageous to use a blend of industrial wastes with primary ores as a feedstock; waste materials tend to have a very important advantage of high reactivity due to chemical instability.

CAT foundries are a typical example of "small" CO_2 emitters, where extensive amount of fossil fuels are consumed for manufacturing, and a significant volume of by-product waste is accumulated on site. Using a CAT foundry as an example, the cost components for CCSM and GCCS are compared. The baseline cost of \$54/tonne CO_2 for GCCS (range \$17-91) and \$75/tonne CO_2 CCSM (range \$50-100) were estimated by IPCC, 2005. Additional important cost components are discussed below. In order to account for these cost components the categorical data analysis and comparison is applied. The following operational definitions and quantification methods were proposed:

1. Site selection, surveillance, and preparation for CCSM facility:

(+1) short <3 years; (-1) long >5 years.

As previously mentioned, the installation and operation of a CCSM facility for small emitters does not require special permits while permits are required for the installation and operation of the liquid compressed CO_2 pipelines for GCCS. The greatest uncertainty for the GCCS is the estimation of the CO_2 storage capacity of the selected site; therefore a site study takes ~5-7 years to complete.

2. Timeframe to implement the technology after successful pilot demonstration:

(+1) short <3 years; (-1) long >5 years.

CAT CCSM technology for small emitters (as an example) utilizes chemical engineering equipment that is well known in industry. Therefore, it does not require the development of novel materials and tooling and can be implemented in less than 3 years.

3. Flexibility for scaling technology up/down.

The value of CCSM technology for small emitters is its flexibility in downsizing based on the level of CO_2 emissions and amount and type of industrial waste available locally. The integration of CO_2 sequestration with the industrial waste treatment is the optimal solution for sustainable manufacturing.

4. Safety risk (carbonation site, pipeline, storage site):

(0) – low; (-1) – unclear.

The monitoring costs for CO_2 pipelines and storage sites were estimated in the literature. Here the safety risk associated with both technologies (CCS and CCSM) is considered. Obviously, CCSM caries minimum safety risk to ecology, flora and fauna, while the safety risks from GCCS are unclear at this point.

5. Rick of failure due to technology novelty (materials, tooling, training, unforeseen issues):

(0) – low; (-1) – high.

GCCS is rather novel technology, no previous experience exists; thus, technical failures and unforeseen technical issues are likely to happen.

6. Liabilities required:

(+1) – no; (-1) – yes.

This important issue has not been properly addressed yet and could be a major roadblock for implementing GCCS. How GCCS technology will impact flora and fauna over long term is presently not understood. Thus, the liability over time has yet been established for this novel technology. The CCSM technology for small emitters is void of these unknowns.

7. Public acceptance as of today:

(0) – neutral; (-1) – unclear.

This issue has been widely discussed in the literature. It is understood that there is negative public acceptance for GCCS technology when compared to CCSM due to the CCSM allows to reduce GHG emissions and neutralize industrial waste accumulated in local urban area.

8. Potential useful products (landfill beds and covers, non-load bearing and decorative construction materials, landscaping products):

(0) – no, (+1) – yes.

Generation of potential useful products is a great advantage of CCSM and has been discussed in the literature and in this report. It is understood that a specific economic analysis will have to be performed for every small emitter to analyse the amount of carbonation products produced, production/manufacturing of certain construction materials in the area and local demand. Here it is assumed that carbonation products can be used locally for landfill beds and covers, non-load bearing and decorative construction materials, and/or landscaping products. Therefore, carbonation products will be replacing gravel and natural rock materials while mining and processing of rock and gravel will be replaced by the carbonation product processing. This analysis will be performed at the end of TRL 3 for CAT CCSM technology using data for the foundry at Mapleton, IL.

9. Industrial waste utilization: (0) – no, (+1) – yes.

This issue has already been discussed above, and it is obvious that reclassification of hazardous industrial waste into non-hazardous by-product through CCSM plays an important role in sustainable manufacturing.

10. Environmental footprint: (-1) – increases, (+1) – decreases.

The environmental footprint here defined as the ratio of the CCSM technology footprint (including pipelines and storage site) to the footprint of a prime industrial facility such as a power plant or manufacturing site. Again, due to the possibility to eliminate a significant amount of accumulated industrial waste through CCSM, the environmental footprint of small emitters can be reduced dramatically.

11. The "Importance" of the various cost components discussed above is defined as an impact of a specific cost component onto the overall cost of the technology: 5 – significant impact, 3 – medium impact, 1- low impact. All cost components that directly impact sustainability, environment, and ecology were rated of high importance along with safety risk component and liability where human lives can be impacted. The cost components related to the technology were rated as medium or low, understanding that technical issues can be resolved as technology is progressing from the initial stage to the advance stage.

	Key Criteria	Importance Rati			CCSM		GCCS	
					Rank	Weighted Rank	Rank	Weighted Rank
1	**Site selection**	5			1	5	-1	-5
2	**Time to implement**	3			1	3	-1	-3
3	**Flexibility to scale**	3			1	3	-1	-3
4	**Safety monitoring**	5			0	0	-1	-5
5	**Rick of failure**	3			0	0	-1	-3
6	**Liabilities reqired**	5			1	5	-1	-5
7	**Public acceptance**	1			0	0	-1	-1
8	**Useful products**	1			1	1	0	0
9	**Waste utilization**	5			1	5	0	0
10	**Environmental footprint**	5			1	5	-1	-5
	Count of positives				7		0	
	Count of negatives				0		8	
	Count of sames				3		2	
	Total weighted sum				**27**		**-30**	

Table 65 Analysis of the additional cost components and comparison of the cost impact on GCCS and CCSM for small emitters. [Copyright Caterpillar Inc.]

The results of our categorical data analysis and comparison are shown in Table 3. It can be seen that these additional cost components result in a GCCS cost increase of 30 points (-30 points means negative impact on cost, e.g. cost increase), but 27 points decrease in case of the CCSM cost (+27 points means positive impact on cost, e.g. cost decrease). Using baseline data from IPCC 2005 for GCCS ($54) and CCSM ($75) and treating the cost adjustment points as percents, the adjusted average cost for GCCS increases up to $72/tonne CO_2, while adjusted CCSM cost for small emitter drops to $55/tonne CO_2. Obviously, CCSM can be cost competitive with GCCS in small emitter applications having the essential attributes mentioned above.

SHELL'S DIRECT FLUE GAS MINERALIZATION

A simplified sketch consisting of the different process steps for the base case (called case 1 later-on):

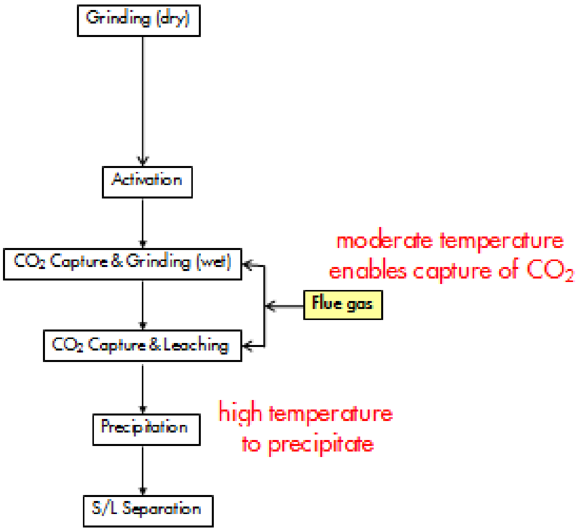


Figure 137 Direct flue gas mineralization process concept [© Shell Global Solutions]

Based upon this, an initial techno-economic assessment was carried out. The process was depicted in ASPEN PLUS. As mineral carbonation feedstock, serpentine (of 90% purity, rest inert) was used. Note that conditions prevailing in precipitator (better say conversion unit) would be such that olivine would also be converted, at least partially. The aqueous phase is water plus 0.1 M $NaHCO_3$.

The premises and battery limits are:

- Use of flue gas (10.2vol% CO_2, no contaminants)
- BOD for 1 $MtCO_2$ captured/a
- Process efficiency
  - High Mg-utilization
  - High degree of CO_2 capture
- Process effectiveness
  - Minimal parasitic CO_2 emissions

  - Plant @ CO_2 asset
  - Mineral mine @ minimal distance

- ➢ Proactive HSSE approach
- ➢ No end product valorization, nor CO_2 credits

An illustration of the BOD is given below.

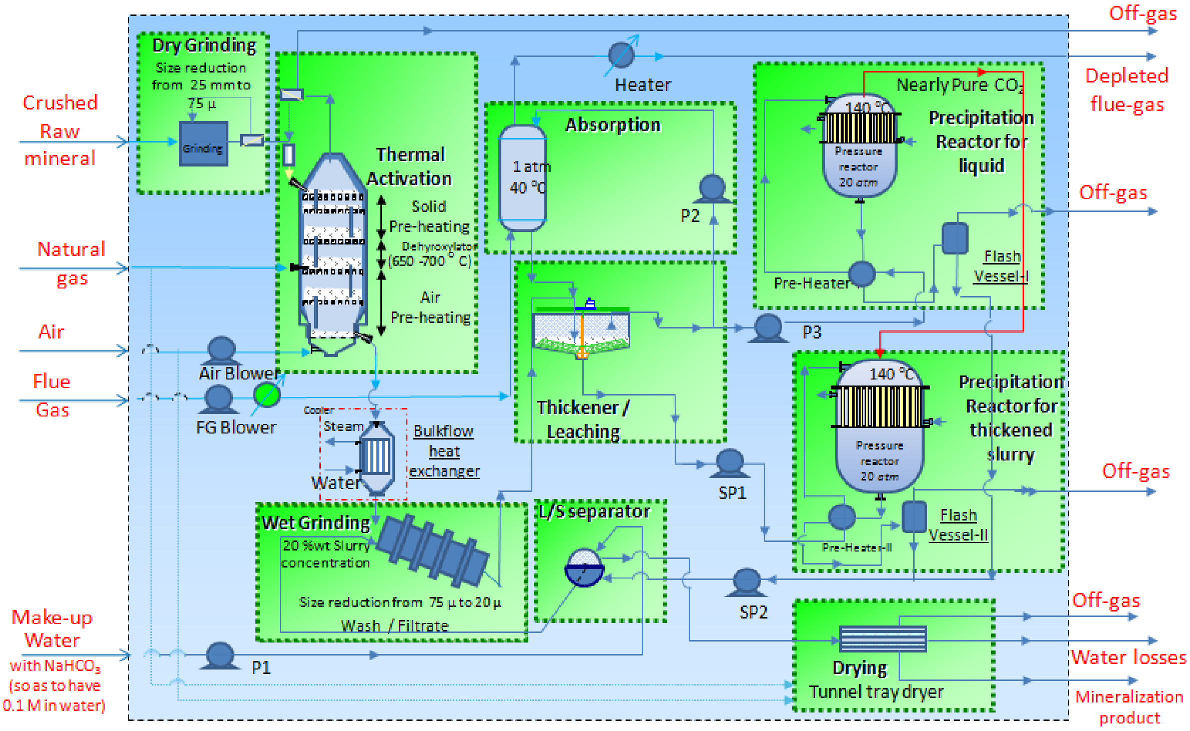


Figure 138 Process flow sheet for direct flue gas CO_2 mineralization – base case [© Shell Global Solutions]

In the experiments, a flue gas stream was fed to the wet grinding unit and to the scrubber. The reason why it is not depicted here is that wet grinding, as a reactor, cannot be modeled in ASPEN. However, it is equivalent to one equilibrium stage of our scrubber model.

As you see we are employing staged grinding (thermal activation of serpentine strongly reduces its tensile strength) and that there is a staged slurry concentration.

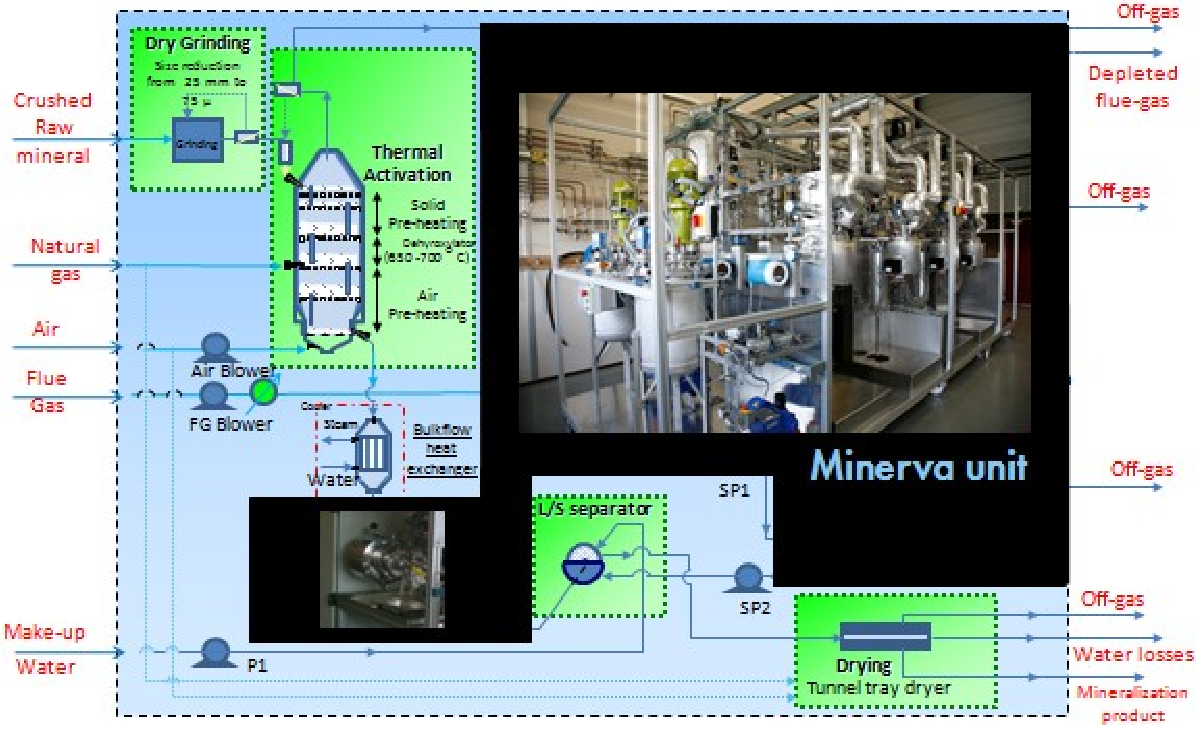


Figure 139 Process flow sheet with Minerva unit overlay [© Shell Global Solutions]

A step cost analysis was carried out in relation to the mineralization product form. This is sketched below. All mineralization product forms seem sustainable; all contain a solid that can be used (→ product valorisation).

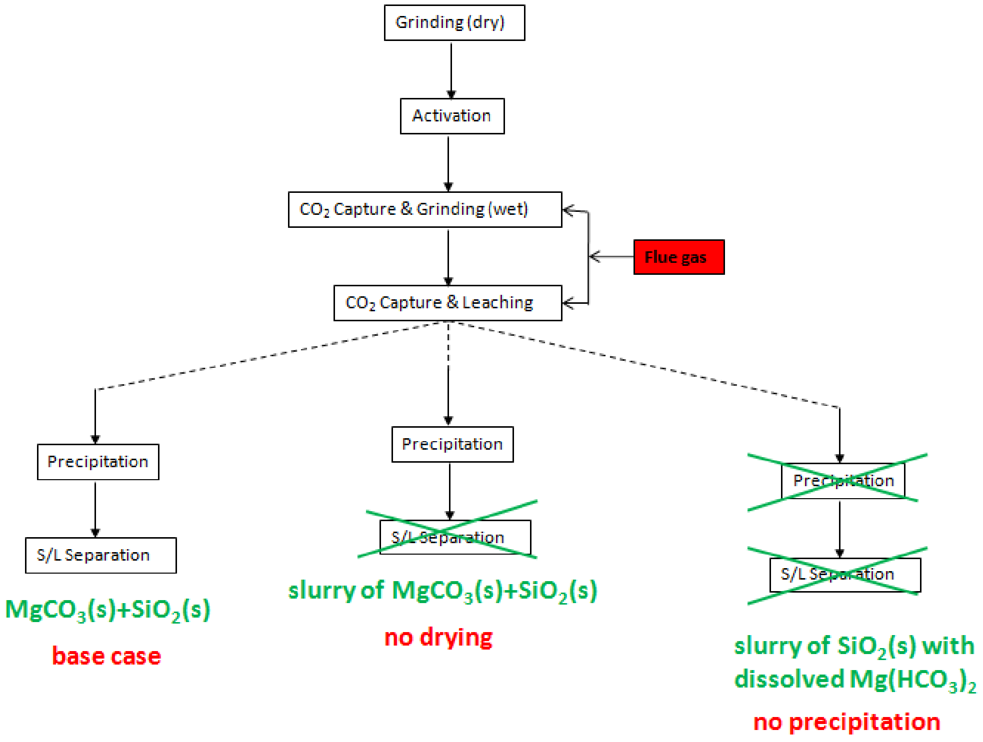
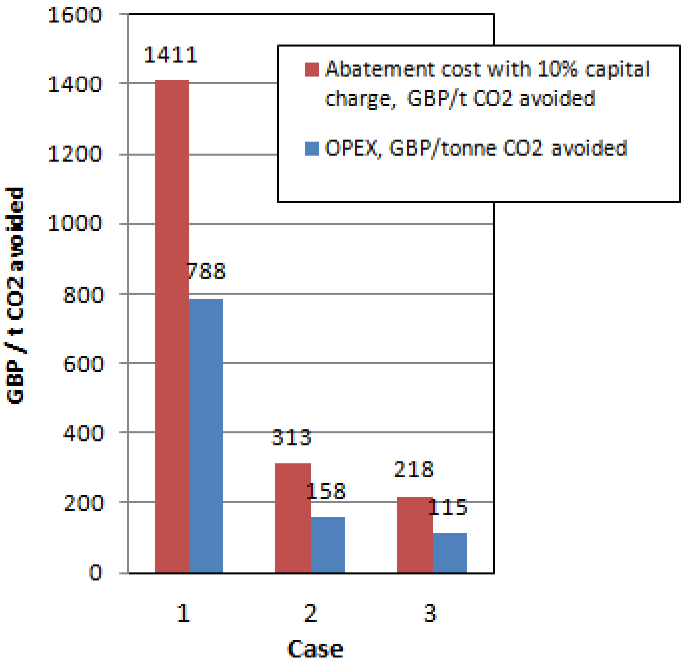
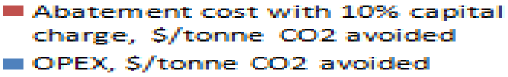


Figure 140 Overview of the different mineralization product forms and their processes [© Shell Global Solutions]



case 1 = base case, case 2 = no drying, case 3 = no precipitation



(GCAT cost estimates)

Figure 141 Different product forms can be obtained, lowering costs (including parasitic CO_2 emissions) whilst maintaining sustainable product applications [© Shell Global Solutions]

The abatement costs are the sum of capital and operational costs. Capital costs are taken into account through an annual capital charge of 10%. Operational costs are roughly equal to 50% of total abatement costs. Further reductions in capital costs require more advanced process integration. Current process has not been optimized in this respect. In this cost estimate, neither product valorisation nor CO_2 credits were taken into account. In addition, the costs of mineral transport have been left out of the analysis.

UON ENERGY REQUIREMENT AND APPROXIMATE COSTS

The overall process including the capture step consists of 7 main steps:

1. NH_3 is used to capture CO_2 from power plant's flue gas and produces NH_4HCO_3
2. Serpentine particles are reduced to75µm by mechanical grinding
3. NH_4HSO_4 is used to extract Mg from serpentine in the mineral dissolution step. Mg-rich solution produced from mineral dissolution is regulated to neutral pH by adding NH_4OH
4. The impurities in the leaching solution are then removed by adding NH_4OH.
5. The solution reacts with the intermediate product (NH_4HCO_3) from the CO_2 capture step to precipitate carbonates
6. Evaporation of the aqueous ammonium bisulphate
7. Regeneration of the chemicals

All reactions in this process are spontaneous, except the regeneration reaction. The reaction of carbonate formation change is endothermic. In the usual capture process, the CO_2 is first absorbed by chemicals, such as monoethanolamine (MEA) or NH_3 then desorbed to recover the sorbents and the released pure CO_2 is compressed for transportation. Compression consumes about 25% of the total CCS energy consumption. This process combines capture and storage resulting in savings in CO_2 compression and transportation. The intermediate product in the capture step when NH_3 is used (NH_4HCO_3) can be used directly in mineral carbonation. Therefore, there is no need for desorption and compression of CO_2. The process is also able to separate three different products: silica, magnesite and iron oxide. The silica product is approximately 90% pure (magnesium silicate and magnetite are the main impurities) that, if this by-product were to be used in commercial applications, would avoid additional energy penalties associated with refinement. The magnesium carbonate has over 90% purity (silica and $FeCO_3$ are the main impurities) and FeOOH is the main formation of the Fe product, with a purity of about 40% (Wang et al, 2010). Ammonia-based wet scrubbing is similar in operation to amine systems. Ammonia and its derivatives react with CO_2 via various mechanisms, one of which is the reaction of ammonium carbonate, CO_2, and water to form ammonium bicarbonate (Figueroa et al, 2008). In 2007, Alstom, the Electric Power Research Institute (ERPI), and WE Energies launched a pilot plant that uses chilled ammonia to capture carbon dioxide (CO_2) from coal-fueled power plants. Also, Alstom and American Electric Power are jointly participating in the installation of a CO_2 capture Product Validation Facility at AEP's Mountaineer Power Plant, which is designed to capture and store 100,000 metric tonnes of CO_2 annually. In late 2009, AEP and technology provider Alstom began operating the pilot plant. Alstom's process uses chilled ammonia to capture CO_2 and isolates it in a highly concentrated, high-pressure form. The process operates at near freezing temperatures (0–10 °C), and the flue gas is cooled prior to absorption using chilled water and a series of direct contact coolers. This process has been demonstrated to capture more than 90% of CO_2 (from 3-15% CO_2 in flue gas) (Gal E, 2006) at a cost that is far less than other carbon capture technologies. Costs were assessed at \$20/tonne CO_2 avoided compared to \$51/tonne CO_2 avoided when amine scrubbers are used (Monoethanolamine). The steam consumption in the reboiler of the ammonia-based system is less than 15% of the consumption of the MEA system due to the lower heat of reaction and lower steam fraction in the regenerated CO_2 stream. The system presents very low emission of NH_3. Once captured, the CO_2 can be used commercially or sequestered in suitable underground geologic sites or mineralised by CCSM processes (Sherrick et al, 2008; EPRI, 2007). The energy penalty for 85% capture of CO_2 in the chilled ammonia system was estimated to be 477 kWh/tonne CO_2, whilst an estimate of 364kWh/tonne for MEA has been calculated, in which 60% of the energy penalty can be attributed to CO_2 regeneration. As a comparison, 44% of the energy penalty from using the chilled ammonia system arises from the refrigeration process (Kothandaraman A, 2010).

The two most energy intensive stages of the UoN process are i) water evaporation, and ii) thermal decomposition. The solid liquid ratio used was 200g/L. The evaporation step needs about 12kWh/tonne H_2O for water evaporation, and thermal decomposition 30kWh/tonne NH_4SO_4 for ammonium salts regeneration. Considering 90 % dissolution, 90 % carbonation and 95 % regeneration, at 200g/L solid/liquid ratio, to sequester 1 tonne CO_2 this process needs around 560kWh/tonne CO_2, not including the energy requirement for grinding (39kWh/tonne CO_2) and filtration (5 kWh/tonne CO_2). This figure may be subject to change depending on the specified conditions, and so it can only be considered as a preliminary estimation. The energy consumption, when considering the capture step, increases to 795kWh/tonne CO_2 where the capture step includes only 40% (191kWh/tonne) of the energy required in the chilled ammonia system because compression and desorption are not necessary (considering that 60% of 477kWh/tonne is not required to both compress and desorb the CO_2). Typically, geological sequestration with amine carbon capture stage requires between 470 and 640kWh/tonne CO_2 (Kodama et al, 2008). The cost of the process in energy terms was estimated to be £64/tonne CO_2 stored (£0.08/kWh) without considering the operational or capital costs. The energy consumption is lower than the ARC process that uses 1,010kWh/tonne CO_2 for activated serpentine (640kWh/tonne for activated olivine) (IPCC, 2005) but higher than other processes that state requirements of around 300kWh/tonne using mineral waste materials (Kodama et al, 2008). However, this last process reaches a lower efficiency of 60% compared to 80% and 90% of the two previous processes, respectively.

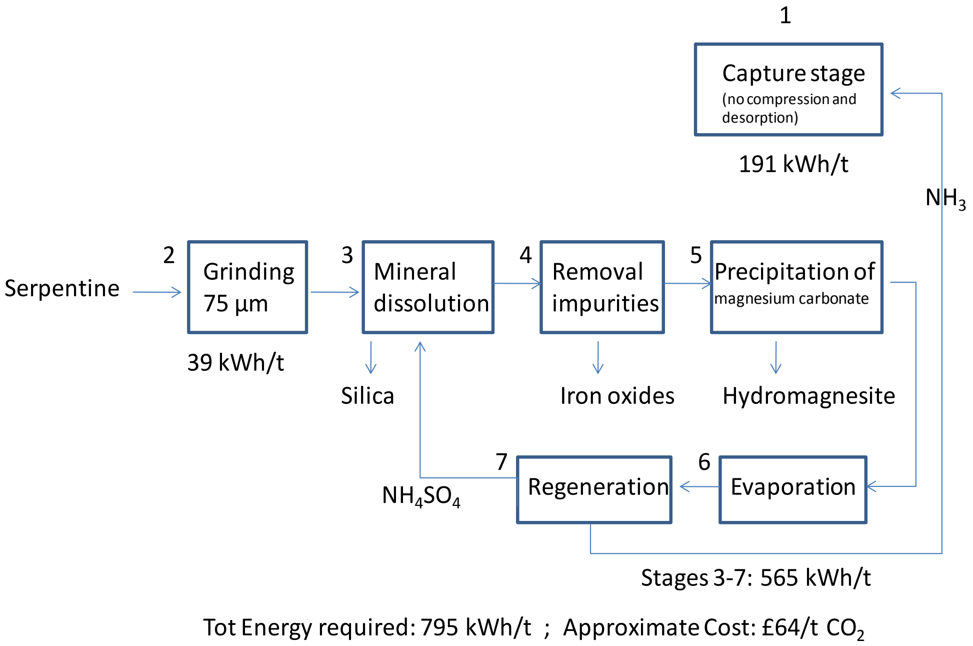


Figure 142 Scheme of UoN CCSM process and rough energy requirements and energy costs (Capital and operational costs are not included). [Copyright University of Nottingham]

ÅBO AKADEMI ENERGY REQUIREMENT AND APPROXIMATE COSTS

An estimation of the energy required for the Åbo A. CCSM process is given to show how a 1Mt CO_2/year mineralisation process would look and what it may cost for processing a CO_2 – containing flue gas stream.

The process as it is being optimised at ÅA is depicted schematically in the Figure below. It involves Mg-hydroxide production from Mg-silicate (serpentinite rock) using ammonium salt (which is recovered and reused) in an endothermic step (at ~ 450°C, 1 bar) combined with Mg-hydroxide carbonation in a pressurised fluidised bed (at ~ 500°C, > 20 bar). One specific objective of the work at ÅA is to balance the energy input requirements by using the carbonation heat release.

A 1Mt CO_2/yr process would require an input of ~3 Mt/y serpentinite, or 35kg/s CO_2 and 110kg/s mineral, if 90% of the Mg is extracted and the carbonation efficiency is 90%. (With 95%/95% the mineral amount needed is 95 kg/s.)

At this point the energy requirements are 4-5 GJ (1.1-1.4MWh)/tonne CO_2, mainly as ~ 500 °C heat.

For the carbonation of the $Mg(OH)_2$ a pressurised fluidised bed would be used, that would have a diameter of 3-5m and a bed height of 3-7m, for 20-50 bar pressure. So far, in the lab we worked on a bubbling bed, a circulating bed may have advantages.

For the reaction of serpentinite with ammonium sulphate a rotary kiln would be used, offering a residence time of 20 minutes at ~ 450°C. Since the mass of NH4-sulphate is ~ 1.5x the serpentine mass it would contain a mass of 300 tonnes solids.

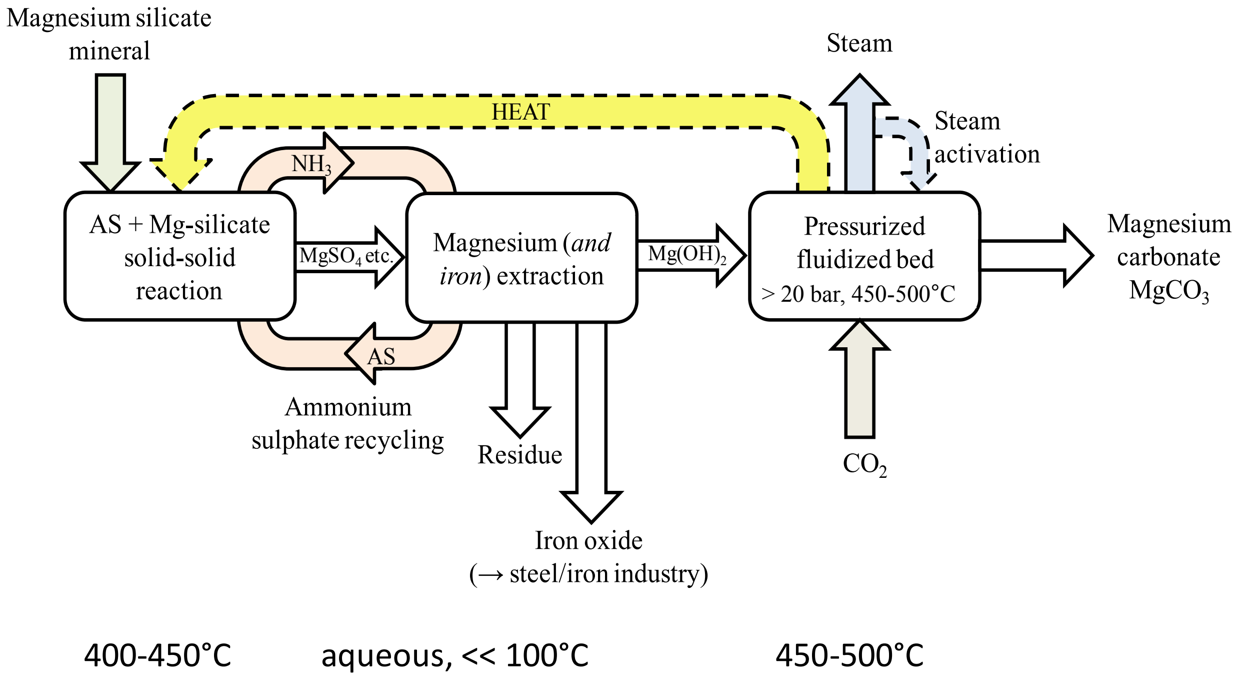


Figure 143 Åbo Akademi CCSM process. [Copyright Åbo Akademi]

About 5-10 heat exchangers are needed to preheat the CO_2, cool the H_2O/unreacted CO_2 gas from the carbonator, cool the solids from the kiln, preheat the $Mg(OH)_2$ that is fed to the carbonator, cool the $MgCO_3$ from the carbonator, preheat the serpentine (the NH_4-sulphate cannot be preheated, it would decompose). An expansion turbine would reduce the CO_2 pressure from transport pressure (100-140 bar) to carbonation pressure (> 20 bar), part of this energy is used to recompress unreacted CO_2 removed from the H_2O product from the carbonator using a flasher.

The costs of operation would partly depend on whether a market is created for Mg-carbonate or other products, the price tag for the mineral (currently valued as a mining waste) and losses of NH_4-sulphate (cheaper than ammonia or sulphuric acid).

The construction costs of the process plant are difficult to give or estimate since the first plant of this scale has not yet been built. The First Plant will be 5-10 times more expensive than the Second, third, ... plant. The central part of the plant are a 300 tonnes, 450°C rotary kiln, a 450-550°C > 20 bar pressurised fluidised bed, three water tanks for hydroxides precipitation, 5-10 gas/solid heat exchangers, one or two flashers, an expander/compressor combination for CO_2. Based on this estimation, a first impression of costs for constructing such a plant can be approximated with a high degree of uncertainty.

For the operation costs (Communicated to the consortium by Pr Ron Zevenhoven, 11/01/11):

1. Mineral 5-10 US \$/tonne × 3 tonne/tonne CO_2 = 15-30 US \$/tonne CO_2
2. Assuming costs for make-up ammonium sulphate (losses few %) ~ 40kg/tonne CO_2 at 150 US\$/tonne ammonium sulphate (alibaba.com) = 6 US \$/tonne CO_2
3. Not considered: revenues from product sales:

4. Energy input 80% as heat (30 US \$/MWh), 20% as power (60 US \$/MWh) gives 36 US \$/MWh = 40-50 US \$/tonne CO_2
5. Costs for CO_2 separation not included and transport
6. Power generation from pressure reduction of CO_2 (from transport pressure to 20-50 bar carbonation pressure) not included

→ Total costs material input + energy input, for a CO_2 stream: 50-85 US \$/tonne CO_2

Note: if operated on flue gas: with x% CO_2 in the gas, pressurisation to (at least) 2,000/x bar is needed for (at least) 20 bar CO_2 partial pressure.

A cheaper form of ammonium sulphate than agricultural-grade can probably be used.

Appendix 11 Stakeholder Consultation Workshop

INTRODUCTION

Gathering stakeholder requirements through a robust "voice of the customer" process is a vital part of developing appropriate critical customer requirements and metrics for any technology or product. To that end, a Stakeholder Consultation Workshop was organised by the consortium on the 12th of July 2010, at the ETI offices in Loughborough. Appropriate stakeholders were identified from industries at each step in the energy value chain of CCS Mineralisation. A detail attendee list is included in the appendix to this chapter.

- Geological resource identification:
    - BGS
- Extraction
    - Finning (the Caterpillar UK dealer)
    - Lafarge
    - Tarmac
- Large Power Generation
    - E.On
- Distribute Power Generation
    - Caterpillar
- Potential customer industries
    - Lafarge – Cement production
    - Tarmac – Cement production
    - Corus – Steel production
    - Shell – Petrochemical/Refineries
- Technology Developers
    - Caterpillar
    - Shell
    - University of Nottingham
- Useful waste-material suppliers
    - Corus – Steel slag
    - Lafarge – Quarry waste, construction & demolition waste
    - Tarmac – Quarry waste, construction & demolition waste
- End Product Markets – Construction
    - Lafarge
    - Tarmac

This group of stakeholders gave good representation of typical organisations at each point in the value chain. One of the points that the list highlights is that certain key organisations such as those involved in the cement industry also have quarrying businesses and established routes to market for construction materials. This meant that the workshop was able to foster discussions about the system needs from a highly interconnected viewpoint. The result is that some valuable lessons have been taken on board by the consortium to guide resource and technology development needs assessment activities.

EXTRACTION

Exploration and Planning

The extraction industry representatives highlighted that the permitting process for a new quarry site is expensive and takes many years to complete. One of the keys to minimising the cost of this process is to have well defined criteria for the mineral requirements of the CO_2 mineralisation process. This is a clear need for the technologists to address from their work so one of the requirements of the technology assessment laboratory work in Stage 2 should be to present what the critical customer requirements of the carbonation process are from the point of view of the mineralisation process. The corollary to this is that anything that can be done to make the process more flexible in terms of acceptable input material will have the potential to increase usable resource or reduce resource cost.

The experts also recommended that the consortium analyse for suitable resource located near to locations of existing quarry sites since this would help expedite the planning and permitting process.

Logistics

The location of resource relative to the location where of use will be a key consideration when evaluating transport costs. The opinion was expressed that land-based supply routes, such as rail, are running at, or close to, capacity. This combined with the cheaper nature of water-based shipping have the effect of making mineral resources at coastal locations particularly attractive.

The existing international raw material shipping supply chains also bring resource outside of the UK into play. The consortium was therefore advised to carry out an assessment of the total cost of imported minerals versus local sourcing and transport within the UK. By doing this it will be possible to assess the trade-off between the economies of scale of large-scale operations in other countries and the lower cost of short distance shipping around the UK.

By way of example aggregates typically cost about £10 - £12 / tonne without transport costs in the UK and costs double every 30 – 40 miles. As a result, UK quarries normally serve industry within 35 miles of the source. In the UAE aggregates typically cost £3/tonne and long distance shipping of coal by sea today costs about £7/tonne.

WASTES

Quarry Wastes and Mine Tailings– “Under-utilised products”

Crushing of quarried rock produces material that is of unsuitable size for typical construction and road-building applications. “Fines” are defined as particles smaller than 5mm in size. A substantial quantity of this waste (~25%) is in the form of dust (< 63 micron particle diameter). Since so much small material is produced as a by-product of the process already this could have a significant cost and grinding energy reduction opportunity for the mineralisation process which relies on small particles.

The expert stakeholders pointed out that the majority of mine and quarry wastes in the UK are used on site for things such as site infrastructure such as roads. As a result, the suggestion was made that “under-utilised products” might be a more appropriate term than “wastes”. The additional point was made that it is unlikely that suitable quarry wastes exist in the UK because existing quarries are not extracting the magnesium silicate minerals required for the mineralisation process in the same way as platinum, diamond and other mines are known to.

These mine tailings are typically suspended in water but settle out with time. The cost of handling these tailings can be up to 3.5% of mine operating costs. The magnesium silicate tailings associated with existing mining nickel and platinum group element (PGE) mining operations would be sufficient to mineralise all of the UK energy CO_2 emissions.

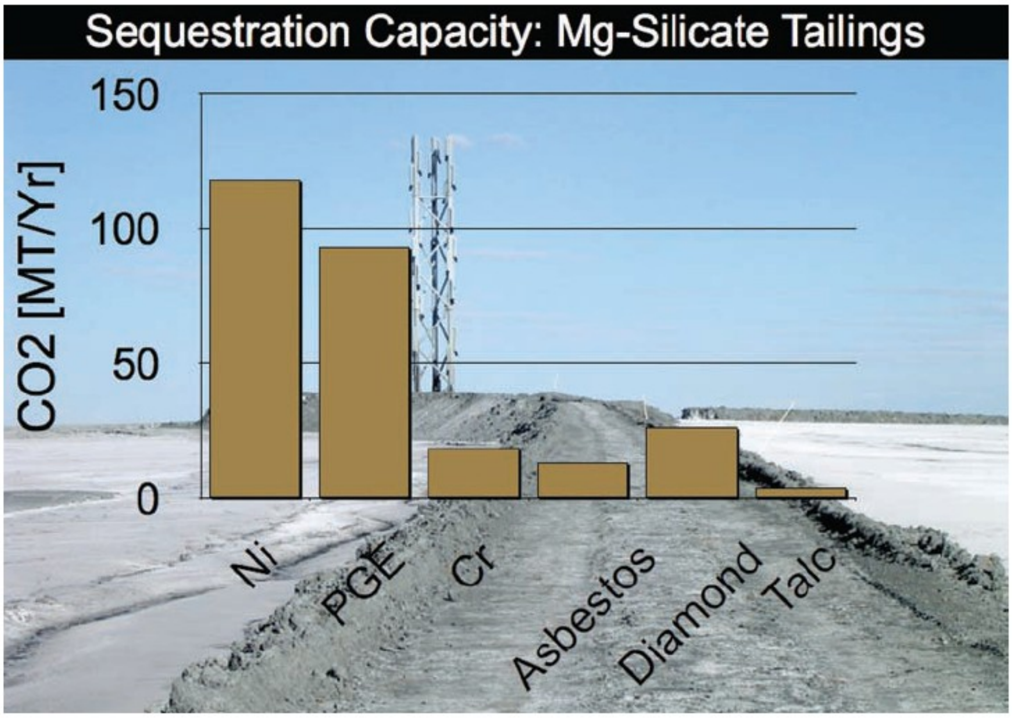


Figure 1 - Relative sequestration capacity of Mg-Silicate tailings with wastes from other commodity mines (courtesy of G. Dipple, Dept. of Earth and Ocean Sciences, University of British Columbia, Vancouver Canada)

Figure 144 Sequestration Capacity of Magnesium Silicate Tailings from Commodity Mines [Carbon Capture Journal, July-August 2009, pp 24 –26]

One of the proposed possible business cases for quarrying is to open a quarry to produce aggregate and sell the fines as a by-product to the CCSM industry. Since it is unlikely that a quarry would be opened specifically to supply CCSM so if a by-product can be sold to CCSM users for more than £5 per tonne then this could be used to offset the aggregates levy tax (£2.10 per tonne) and provide an attractive new product to sell.

Industrial, Construction and Demolition Wastes

The slag from steel processes is cooled in pits and produce bits of slag of 20mm and smaller size. A typical UK steel works produces about 300,000 tonnes/year of slag. Some of this has a use in cement already and as a result, relationships exist between cement manufacturers and steel producers where the cement manufacturer will handle the use and disposal of the steel slag produced.

The construction industry experts at the workshop highlighted that a number of government initiatives and taxes drive the use of construction and demolition waste already. This insight led the consortium to revisit the initial assessment of identified construction waste figures and led to a downward revision of the available waste resource for application to CCS Mineralisation to a more realistic figure, as discussed in the first chapter on resource availability.

From the industrial sector, one of the main sources of waste is steel slag but while these present an attractive source of reactant for the CCSM process they also have existing uses and so the consortium had to revise down the available material estimate from that which was initially indentified.

LARGE POWER GENERATION

Logistics and disposal

The issues associated with moving the large quantities of magnesium silicate required for the CCSM process and the subsequent magnesium carbonate and silica products of reaction to and from a power station is one of the key challenges seen by the large power generation sector. Power stations served by rail for their coal supply are running at peak rail capacity already, which is why they have to build up coal stockpiles through the summer months.

The other key issue for these potential users of the CCSM process is having a market to sell the products of reaction to to avoid disposal costs. The existing process for flue gas desulphurisaiton (FGD) is a good example of the model that would be most appropriate to deploy for CCSM. In this case, the gypsum produced from FGD is sold to plaster board manufacturers. The goal isn't necessarily to make a profit on the process as such but rather to avoid sending anything to landfill. This necessitates good process design and control to ensure that product of the required quality is produced from the FGD step. In this case, whiteness is the key metric and so good particulate removal upstream of the FGD step is key.

Similar metrics for the usefulness of magnesium carbonate and silica from CCSM will therefore have to be considered when designing and implementing the process.

Customer Requirements

Current locations for power stations will be the most likely locations for new-build due to the difficulty in getting green-field planning permission. Coastal locations are of interest for geological CCS already to reduce pipeline length requirements. This plays well for the favoured transport route for magnesium silicate for CCSM, namely by sea, to minimise transport costs and impact on surface transport infrastructure capacity.

Flexible fossil fuel fired power stations will be highly desirable for two reasons:

- Flexible response to demand is the highest value power generation and so is good for revenue
- Flexibility from fossil fuel power stations will also be necessary to allow increased deployment of intermittent renewables while maintaining grid stability

The consequence of both of these critical customer requirements is that any CCS system will have to be flexible too. The footprint of an amine scrubber system, including regeneration and CO_2 compression, is expected to match typical power plant size.

Decision Drivers and priorities

The following are the key decision drivers from the point of view of large power generator operators for deploying a CCSM system:

- Risk has to be very low before power generators will take up a technology

- Ability to handle flue gas directly without the need for pure CO_2 stream will be a key selling point for a CCSM process able to operate directly on flue gas
  - Geological CCS capture and compression process carries ~22% power production sacrifice
- In general opex is more important than capex in relative terms
- The legislation metrics will be key to technology decisions:
  - CO_2 per m^3 of flue gas?
  - Tonne CO_2 per site?
  - CO_2 per kW.hour?

The priorities for CCSM processes expressed by the large power sector stakeholder at our workshop can be summarise as follows:

- Direct conversion from flue gas
- Low energy requirement (at least comparable with Amine scrubbers)
- Flexible operation
- Feedstock understanding
- Minimal product quality variation (as per gypsum from FGD today)
- Low risk
- High reliability

DISTRIBUTED POWER GENERATION

Customer requirements

Distributed energy system assets have much tighter space constraints than large power stations since they often have to fit in around the primary industrial process system components or in available space in buildings. This is especially true for retrofit devices. ISO container scales are good since gen-sets are sold in these already. In this regard, modular solutions are particularly desirable. It is understood that this is an end-game scenario when the technology is very well understood.

For most distributed energy system customers highly automated systems with minimal user input are most appropriate. Some industrial customers can handle greater complexity and intervention since they are used to running complex processes, such as cement manufacture or steel manufacture, already. For all other customers “plug and play” systems will be vital. For these customers remote activation of the reactant would be desirable to reduce the footprint, on-site parasitic loads, and complexity.

The historical precedent of urea SCR implementation for NOx reduction shows that the market will bear ~30% additional capex for exhaust gas aftertreatment solutions.

Decision drivers

As for large power systems, the specific metrics for any CO_2 legislation or targets will drive particular system requirements. Based on how regulated emissions are managed today there could be two likely systems:

- Limitation on total hours based on level of emissions, or

- Capped tonnage (as for NOx today)
    - In this latter case flexibility of the CCS process will be vital to respond to exact CO_2 output at any given time

STEEL WORKS

An integrated steel works has a number of CO_2 streams, some of which have uses in the process already. Steel production results in about 2 tonne CO_2 per tonne steel and CO_2 floor price of €40 pre tonne is seen as the minimum required to trigger CO_2 reduction capex investment. This price not expected before 2020. Steel producers are some of the largest individual consumers of electricity. This exposes them to the cost of CO_2 reduction at their own facilities as well as in electricity production.

The expectation is that geological CCS is the main option on the table for this sector but there is a desire to have more options and in this regard, CCS by mineralisation and algae were cited as being on their radar already. The application of geological CCS to a steel works is expected to triple the land required compared to current facilities and there is a requirement that power plants for steel works have to be “CCS ready” when renewed now.

The initial goal is to reduce CO_2 from steel plants by between 5 and 10 percent with and ultimate target of between 80 and 90 percent. While it is clear that some facilities do not have space for the footprint expected of geological CCS it is also clear that Greenfield new build is unlikely to be possible. The current model of locating steel works at coastal locations for access to shipping ports fits well with the implementation model for CCSM proposed in this study since ship based movement of magnesium silicate is the preferred option identified in the first chapter.

PRODUCT USE

The CCSM process produces two potentially useful products of reaction, namely magnesium carbonate ($MgCO_3$) and silica (SiO_2). The potential uses of these products will be discussed in this section.

Magnesium carbonate

The most useful form of magnesium carbonate would be as an aggregate. A requirement of aggregates is that they are coarse and hard. Most CCSM processes rely on a fine powder form of the reactant and so the resulting magnesium carbonate is going to be in fine powder from too in most instances. Very fine powders are only useful to the construction industry as filler in cement and in order to produce something of value as an aggregate an agglomeration process will be necessary to convert the resulting powder into aggregate-size units. The subject matter experts consulted at the workshop pointed out that agglomeration processes have historically proven to be too high to make conversion of powders into useful aggregate affordable compared to the cost of conventional aggregate.

When considering the use of magnesium carbonate in cement it is important to remember that cement is a heavily regulated product and anything which effects the chemistry would be unacceptable. The cement industry is currently based around calcium-based materials and so a significant quantity of any new material would be needed to displace incumbents. Furthermore, the construction industry does not like variation so the product would have to be consistent and produce cement with the same performance as before.

Another potential market for the magnesium carbonate product would be in paper production. Entry to this market would require displacement of calcium carbonate used in paper production already. The barrier to entry to this market is the fact that magnesium carbonate is harder than calcium carbonate and if 100% substitution occurred then printer and copier components would wear faster. It would therefore be an important piece of work during the later technology development stages to ascertain what level of displacement could be achieved without negative durability impacts on existing printer and copier hardware. In the longer term, identifying the required hardware changes and the costs involved would be vital to securing a significant deployment path into this industry.

Silica

During the course of the workshop event and the analysis work for this report by the University of Nottingham, it became apparent that the silica product of reaction might actually be the most useful product of the CCSM process. This is because silica sand is a relatively high value raw material.

It is predominantly used in the glass industry where consistency and quality are the key acceptance criteria. Any iron content would present a problem so the CCSM process would ideally have to ensure that iron was separated out. If a high quality SiO_2 product could be precipitated from the CCSM process then that would have significant value as a raw material for high grade glass manufacture. If the cost-benefit trade-off of producing silica of such high quality at the end of the CCSM process didn't make commercial sense then the focal point would have to be consistency. The guidance from the subject matter experts was that as long as the process creates a consistent product then lower grade glass could be produced from it. What glass manufacturers don't want is to have to adjust their processes to respond to changing inputs.

Another important potential application of silica is as a pozzolanic material in concrete. In this application, the very fine form of the material that will arise from the CCSM process will be an advantage since this is desired state (also known as silica fume) for silica to be used in the pozzolanic reaction. The concrete resulting from this reaction has much greater strength than conventional concrete and so enables the construction of more complex concrete structures. As a result, this may make the silica product of the CCSM process more desirable to the construction industry than the magnesium carbonate product, contrary to historical focus.

CONCLUSIONS

The stakeholder exercise fulfilled its purpose of providing the consortium with an opportunity to gather hear the "voice of the customer" in order that the input can be used to guide technology development appropriately. The key conclusions that were drawn from the stakeholder input are as follows:

- Recycled concrete aggregate and other construction demolition waste is already used extensively and so may not actually be available as a reactant for the CCSM process in significant volumes
- The exploration and permitting process is expensive and can take many years to complete
- It is therefore essential that technology developers define resource requirements as fully as possible so that clearly defined exploration criteria can be set
- The corollary to this is that mineralisation technologies may need to be flexible to the variety and inhomogeneity of minerals which exist in reality
- Coastal resource and coastal emitter locations are the ideal combination to minimise transport cost and infrastructure demand
- Steel works tend to be in coastal locations to facilitate the logistics of raw material shipping already

- For large power stations the CO_2 capture and compression process for geological CCS is expected to have a footprint equal to the power station itself
- For steel works geological CCS is expected to triple the land requirement
- For distributed power systems:
  - Space requirement constraints are significant,
  - Modular CCSM systems would be highly desirable
  - Highly automated CCSM systems with minimal user input would be key to successful deployment for most users
  - Provision of an activated reactant to the user would be highly desirable
- The exact metrics chosen for any CO_2 reduction targets or legislation will have a significant impact on the system requirements
- The end use options for magnesium carbonate arising from the CCSM process are constrained by:
  - The expense of agglomerating into an aggregate form
  - Establishing its acceptability as a cement additive in a highly regulated industry
  - The challenge of its increased hardness compared to calcium carbonate mean that component wear on printers and copiers would be increased if substituted into paper production
- By contrast the market opportunities for the silica product may be greater and more lucrative
  - Silica sand is a relatively high value raw material
  - If consistency can be achieved with no iron content then the glass manufacturing industry would be a potential market
  - In the construction industry silica is useful for the pozzolanic concrete reaction resulting in higher strength concrete