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**Programme Area:** Carbon Capture and Storage

**Project:** Mineralisation

**Title:** Carbon Capture and Sequestration by Mineralisation (CCSM) Final Report

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**Abstract:**

This report summarises the findings of the Energy Technologies Institute's project studying the capture and storage of carbon dioxide using mineralisation, CCSM. Five major groups of CCSM technologies were defined and the so-called "aqueous multi-step with additives" group was selected for investigation. Ammonium compounds were utilized as additives, and the CCSM process studied in this project is referred to as an "Ammonium-based" CCSM. 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 CO<sub>2</sub> emissions. Minerals and CO<sub>2</sub> can react together to permanently store CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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.

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# Carbon Capture and Sequestration by Mineralisation (CCSM) Final Report

CCSM Programme Deliverable 4.1

Final Report

1<sup>st</sup> October 2012

ENERGY TECHNOLOGIES INSTITUTE

CCSM PROGRAMME

FINAL REPORT

# Carbon Capture and Sequestration by Mineralisation (CCSM) Final Report

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## 1 Introduction

This report summarises the findings of the Energy Technologies Institute’s project studying the capture and storage of carbon dioxide using mineralisation, CCSM. Five major groups of CCSM technologies were defined and the so-called “aqueous multi-step with additives” group was selected for investigation. Ammonium compounds were utilized as additives, and the CCSM process studied in this project is referred as an “Ammonium-based” CCSM.

The project has produced an extensive body of detailed work that can be found in the documents listed in the bibliography at the end of this report. The key substantive project reports are:

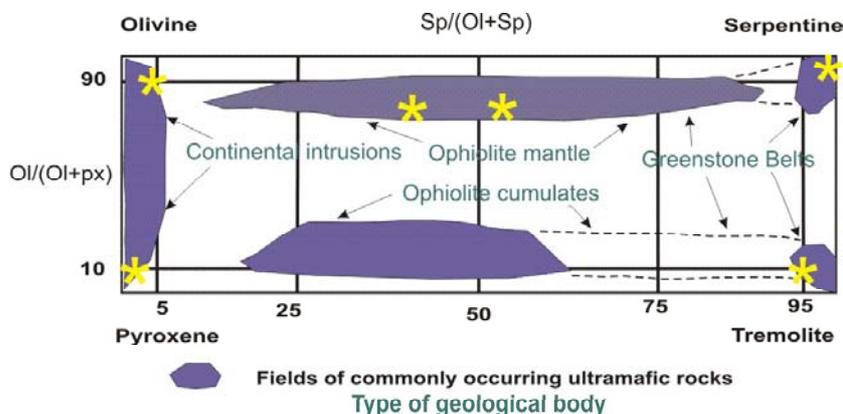
- Stage Gate 1<sup>1</sup>, 2a<sup>2</sup> and 2b<sup>3,4</sup> Reports
- Techno-economic Analysis 1<sup>5</sup> and 2<sup>6</sup> Reports

The objective was to investigate the potential for CCSM to mitigate at least 2% of current UK CO<sub>2</sub> emissions and 2% of worldwide emissions over a 100-year period. The project investigated:

- The availability of serpentinite rock to satisfy the UK target for CCSM. This equates to 22–33 Mt/yr of rock.
- Evidence of deposits of sufficient size, suitable minerals, and practically extractable rock outside of the UK for the application of CCSM.
- Whether a process could be developed to achieve 90% CO<sub>2</sub> capture from large sources (greater than 300 MW) of flue gas and 80% CO<sub>2</sub> capture from small sources (less than 300 MW) by 2050.
- If CCSM is likely to be cost competitive against alternative carbon abatement technologies including a quantified process design and economics coupled to improvement opportunities.

## 2 Mineral Suitability and Resource Assessment

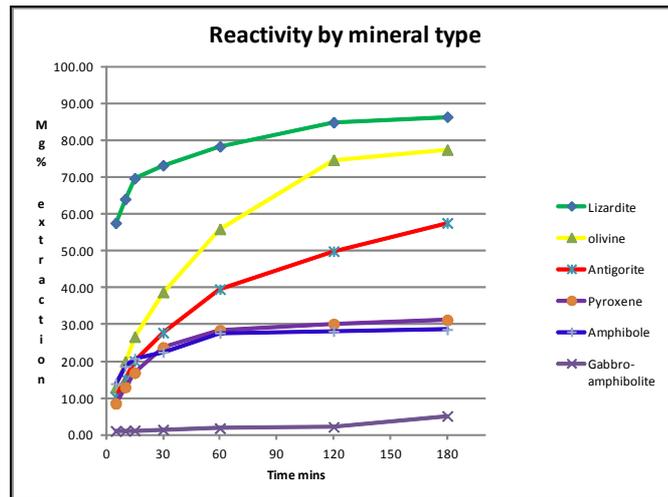
Previously, many laboratory experiments had been carried out to investigate the efficiency of the leaching of Mg from ultramafic rocks, but only a very limited range of compositions had been tested; either nominally pure olivine or serpentine. Moreover, in most cases, a full mineralogical characterisation was not completed. Here for the first time a range of mineral samples were selected to cover the broad range of ultramafic rocks shown in Figure 1, the basis of which was described in detail in the Stage Gate 1 report<sup>1</sup>. The figure shows the main minerals that are found in ultramafic rocks at the corners, and indicates the composition fields of the commoner rocks, with the composition of the actual rocks tested shown as stars.



**Figure 1. The range of compositions of ultramafic rocks and the samples tested shown by yellow stars [Copyright BGS, NERC]**

All samples used have been subjected to a detailed geological characterisation that included examination of hand specimens, study of thin sections by optical, petrographic microscope, bulk mineralogy by XRD and chemical composition by XRF.

A series of experiments, using an acid leach method (pH~1, NH<sub>4</sub>HSO<sub>4</sub>), was performed to investigate the liberation of Mg from a full range of rock compositions, and the results are shown in Figure 2. This is the first time a series of consistent experiments have been carried out on well-characterised starting materials. This is a major step forward in knowledge of the technology and enables the behaviour of many types of ultramafic rocks to be predicted.



**Figure 2. The Mg extraction rate for each rock type using 1.4M ammonium sulphate [Copyright BGS, NERC].**

The plot (Figure 2) of the efficiency of Mg extraction with time (reactivity) shows that lizardite serpentinites are by far the best (80% after 60 minutes) with olivine giving moderate results. Rocks rich in antigorite serpentine, pyroxene, and amphibole are not suitable.

## 2.1 UK resources

The composition and suitability of the rocks have to be taken into consideration, and after the less suitable types have been eliminated, a realistic estimate of resources can be made. The rock would have to be extracted from very large quarries, as big or bigger than any currently in operation in the UK, and hence logistics become important to minimize transport costs and environmental impact.

When all these factors are taken in to account the estimate of UK resources is 9.3 Gt, (roughly 4 times the project target) spread across six locations as shown in Table 1. The various locations were given a rating from A (best) to C (poor) in the detailed study for the Stage Gate 1 Report.<sup>1</sup>

**Table 1. The resources of ultramafic rocks suitable for CCSM in the UK.**

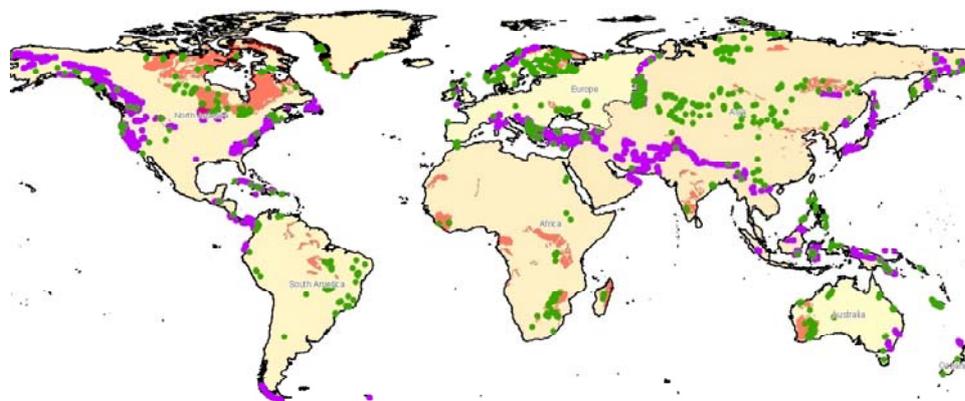
Location	Rock type	Rating	Area (km <sup>2</sup> )	Resource (Mt)
Lizard Peninsula, Cornwall	Meta-peridotite, serpentinite	A	32	3024
Ballantrae	Serpentinite	A	25	2363
Belhelvie	Meta-peridotite, serpentinite	A	10.3	951
Portsoy	Serpentinite	A/B	5.9	439
Shetland Isles (Unst)	Serpentinite, meta-peridotite	A	19.1	1750
Shetland Isles (Feltar)	Serpentinite, meta-peridotite	A	8.2	750
<b>Total resources</b>			<b>100.4</b>	<b>9276</b>

The relative location of the UK CO<sub>2</sub> emitters and rock resources is an important consideration in any CCSM system and was analyzed in this study. It was concluded that the emitters are not co-located with the rock resources. The costs and impact of the transport of large amounts of raw materials are therefore important. Transport by sea is far cheaper than any other method and the distance travelled, in terms of the UK region, is not important as much of the cost is in handling at both ends of the journey. This means that deposits with coastal locations are by far the most favourable and rock could be transported to any emitters at or close to the coast.

In the UK context, there are sufficient rock resources to capture 10% of current UK emissions for over 100 years. These are located in three main areas in Scotland and the Lizard in Cornwall; all are coastal locations. In several places, planning restrictions exist, and opposition to opening very large quarries is likely.

## 2.2 Global resources

A review of global resources was also undertaken to provide an estimate of the total amount of ultramafic rock available for CCSM. Figure 3 displays the global distribution of geological formations containing ultramafic rocks that might be suitable for CCSM, and shows that they are present throughout the world. In some areas, where there are oil and gas fields, geological carbon capture and sequestration (GCCS) may be an option, but in many other areas, this is not possible. In particular, the cratonic shield areas (shown in red on Figure 3) such as northern Europe, eastern Canada, and southern and central Africa are unlikely to have this choice. Many of the ophiolite belts, such as the Mediterranean region, eastern USA and Japan, similarly have poor prospects for GCCS. An additional factor for the ophiolite bodies is that many are in coastal locations, and shipping raw materials by sea, possibly quite long distances, may be an option.



**Figure 3. Global map showing the distribution of ultramafic rocks by geological environment: Ophiolites purple, greenstone belts red, and layered intrusions green.**

The estimate of resources, listed in Table 2, shows that there are around 30 Tt (tera [10<sup>12</sup>] tonnes) of potential resource from quarrying to a very conservative depth of 35 m, and this would be sufficient to capture about 300 years of global emissions at 2006 levels. The potential could be much greater.

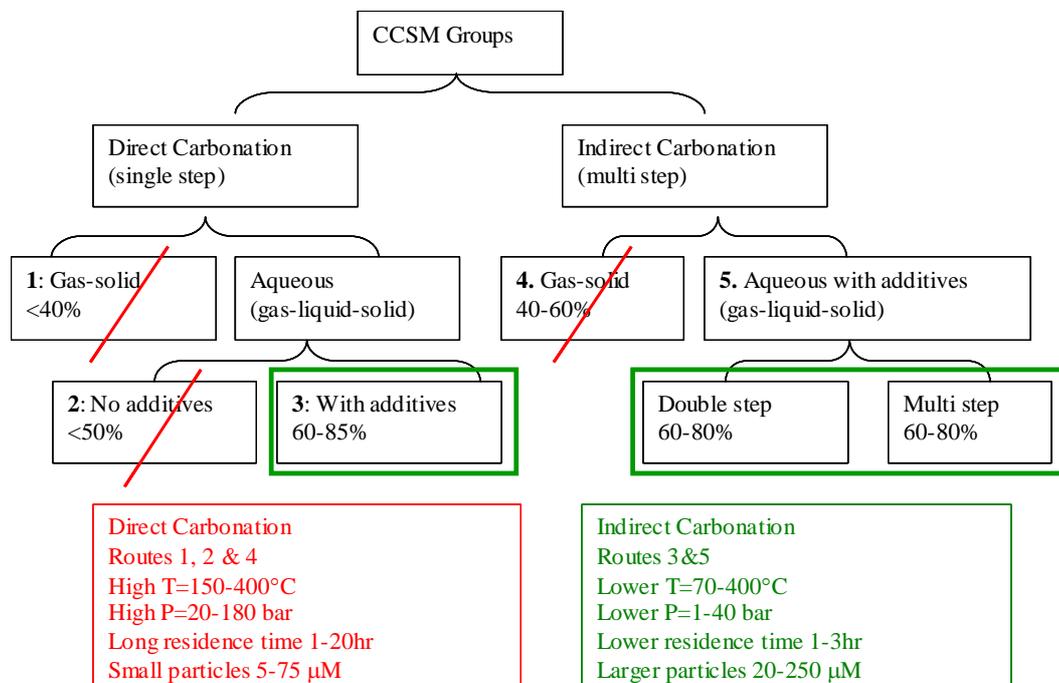
**Table 2. Summary of global resources (in tera tonnes [Tt]) of ultramafic rocks.**

		Geological setting			Total	CO <sub>2</sub> mineralising potential, Tt	Years of global CO <sub>2</sub> (2006)
		Ophiolite (including Urals)	Archaean greenstone belt	Layered intrusion (NRCAN data)			
Quarry depth 35 m	Mass serpentinised ultramafic rocks (Tt)	11.9	7.8	-	19.7		
	Mass unaltered ultramafic (Tt)	11.4	-	0.5	11.9		
	Total resources				<b>31.6</b>	<b>10.5</b>	<b>371</b>
Quarry depth 100 m	Mass serpentinised ultramafic rocks (Tt)	34.1	22.2	-	56.3		
	Mass unaltered ultramafic (Tt)	32.6	-	1.8	34.3		
	Total resources				<b>90.7</b>	<b>30.2</b>	<b>1,065</b>

Tt - Tera tonnes 10<sup>12</sup> tonnes; Global emissions 28.4\*10<sup>9</sup> tonnes

### 3 Technology Optimisation

The project assessed twenty-five CCSM process routes, with the respective CO<sub>2</sub> capture efficiency as shown in Figure 4, and these were reviewed during the early stages of this project<sup>1,2</sup>. The difference between direct and indirect carbonation is the addition of an independent process to extract Mg from the starting mineral for the indirect route. These technologies were ranked against various criteria, specifically described in Work Package 1. Overall, no single technology demonstrated ALL of the desired criteria required for the large-scale implementation. However, direct single step aqueous carbonation (Group 3) with additives, such as the Shell technology<sup>7</sup> and indirect aqueous carbonation (Group 5) with additives, such as the Ammonium-based technology showed significant improvements over the other direct CCSM routes. As a result, these two processes were studied in-depth.



**Figure 4. CCSM process routes.**

The main advantages (A) and disadvantages (D) of the two selected technologies are listed below.

*Shell process:*

- Direct flue gas mineralisation (A)
- Seawater performs better than fresh water (A)
- Technical feasibility demonstrated in batch and continuous process mode (A)
- Chemicals recyclability not addressed (D)
- Very large slurry volumes (D)

*Ammonium-based process:*

- Faster reaction kinetic in presence of additives (A)
- Does not require desorption and compression of CO<sub>2</sub> during capture (A)
- 99% of NH<sub>3</sub> and 95% NH<sub>4</sub>HSO<sub>4</sub> are in principle recyclable (A)
- Separation of products can generate saleable materials (A)
- Multiple heater/coolers, pumps and compressors (D)
- Material losses are unavoidable, including CO<sub>2</sub> slip (D)
- Additive regeneration has not been experimentally achieved so far (D)

Previous work over a number of years by Shell Global Solutions<sup>1</sup> has developed a plant design and specification, but significantly less data were available for the Ammonium-based process. In order to determine the reaction parameters for the plant design a series of technology optimisation experiments were undertaken and these are discussed below.

### **3.1 Rock Pre-treatment**

A range of samples was studied. They were assessed in grinding and/or thermal activation. It was found that:

- Conventional mining and grinding processes can be used for serpentinite pre-treatment. About ~33 kWh/tonne was required to grind a 5 mm starting feed to < 250 µm.
- The ammonium-based process, considered in detail in this summary report, requires a particle size of less than 250 µm. The undersize fines inherent to grinding can be used and will enhance Mg-extraction for no extra cost. Particles of this size can be sourced from the quarry, and the very small incremental cost would be captured in the cost of the raw material. As a result, the plant design contains no capital for grinding equipment.
- The Shell process requires thermal activation of the mineral, with a particle size of < 20 µm. Fine grinding and damage to the crystal structure enhances the activation and subsequent extraction of Mg. The plant design and capital estimates include grinding equipment to achieve this.

#### **3.1.1 Ammonium-based Activation**

A series of experiments were undertaken to evaluate the extraction of Mg from ultramafic rocks using acidic aqueous NH<sub>4</sub>HSO<sub>4</sub>. Leaching reaction time, temperature, concentration of reagents, particle size, and variability of feedstock resources were studied to create a set of operating parameters that can inform process design. It was found that the conditions that guarantee an average Mg extraction of 80% from lizardite serpentinite are a temperature of 100 °C for 60 min in 2M aqueous NH<sub>4</sub>HSO<sub>4</sub> using a particle size range of 75–250 µm and a solid to liquid ratio of 100 g/l. These parameters were used for the initial process design.

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<sup>1</sup> The CCSM consortium would like to express sincere gratitude to Shell Global Solutions for sharing the detailed analysis of their proprietary CCSM technology.

### 3.2 Carbonation

In the carbonation step, the Mg-rich aqueous solution ( $\text{MgSO}_4$ ) reacts with the aqueous solution from the  $\text{CO}_2$  capture step ( $\text{NH}_4\text{HCO}_3$ ) to precipitate Mg-carbonate (solid product). Carbonation reaction time, temperature, concentration of reagents, ratio of reactants, reaction effectiveness, reactor pressure and solid to liquid ratio were studied to create a set of operating parameters that can inform process design. It was found that:

- A temperature between 120 and 160 °C is preferred for the Mg carbonation process in presence of ammonium salt.
- Carbonation in a pressurised reactor (20 bara) improves reaction rates and product yield.
- Carbonation efficiency is similar with synthesized solutions and solutions extracted from actual mineral samples. The impurities in real mineral solutions (Fe, Ni, Cr, etc.) are precipitated during pH swing step (~ pH = 5–7) and therefore have little effect on the aqueous carbonation reaction rate and product yield at pH > 9.
- A solid to liquid ratio of 100 g/l reduces the carbonation reactor size while maintaining high carbonation efficiency.
- The Ammonium-based process has the potential to simultaneously remove  $\text{SO}_x$  and  $\text{NO}_x$  in addition to  $\text{CO}_2$ . This could reduce the capital and operating costs of the process.

For the initial process design work, the team used the following conditions to secure 90% carbonation efficiency: 80 °C for 30 min with Mg: ammonium salts:  $\text{NH}_3$  ratio of 1:2:2 and a solid to liquid ratio of 100 g/l in the dissolution step. Therefore, the Ammonium-based process could meet the goal of capturing 90%  $\text{CO}_2$ . These were revised following the initial design cycle described in Section 4.

## 4 Process Design, Economic Assessment and Impact

### 4.1 Introduction

The requirement for the process design was to remove 80% of the  $\text{CO}_2$  content in the flue gas from a 300 MW coal-based power plant. This equates to a feed rate of 1.99 million tonnes of  $\text{CO}_2$  per year with 1.6 million tonnes per year being captured. This project studied two processes:

- The process developed by Shell Global Solutions. This is based on the thermal activation of mineral prior to reaction with the flue gas (Shell process) in aqueous  $\text{NaCl}+\text{NaHCO}_3$  media;
- The process developed by this project team based on the work by the University of Nottingham. This uses ammonium salts ( $\text{NH}_4\text{HSO}_4$ , pH~1) for the mineral ore-leaching step (Ammonium-based process). The design basis for this process is summarised in the main reports.

The project team went through two iterations of the process design. These were based on the experimental data summarised above. The first design was an ambient pressure model producing hydromagnesite. After review, the team revised the design parameters to an increased pressure and temperature model to produce magnesite<sup>8</sup>. This reduced plant complexity. The Ammonium-based process design is at an early stage design and could be improved further, while the Shell process is well developed.

### 4.2 Process Overview

#### 4.2.1 Shell Process

The Shell process is summarised in the figure below. Shell's direct flue gas mineralisation technology is slurry based where finely ground, thermally activated serpentine is contacted with flue gas at ambient temperature in slurry mill and in a leaching basin. This is followed by precipitation and separation steps.



In brief, the Ammonium-based CO<sub>2</sub> capture and sequestration process includes:

- Acidic dissolution of the mineral (chemical pre-treatment) with ammonium bisulphate to extract aqueous magnesium from the rock,
- Separation of insoluble impurities such as silica, separation of iron impurities by pH adjustment with ammonium hydroxide,
- CO<sub>2</sub> capture with ammonium hydroxide,
- Carbonation reaction with flue gas and ammonium hydroxide,
- Precipitation and separation of magnesium carbonate product,
- Recovery of ammonium sulphate, decomposition of ammonium sulphate to ammonium bisulphate and ammonia,
- Recycle and reuse of ammonium bisulphate, ammonia and water.

The evaporation of water from the ammonium sulphate solution uses electrical power and imported low-pressure steam from the power plant as the energy source, and the decomposition of ammonium sulphate will use separate natural gas combustion as additional heat energy. These two steps are the most energy intensive steps in the Ammonium-based CCSM process.

This process handles large mass throughputs. The result is that the process equipment will consist of multiple plants operating in parallel. The process is based on experimental extraction data for a serpentine sample that is typical of the mineral available in the UK. Throughout the process design, heat and energy are integrated as much as is feasibly possible based on the data available. The detailed design is described in main report.

### 4.3 Process Comparison

Table 3 compares the Shell process with the Ammonium-based process as applied to a 300 MW power station. The figures are scaled to an equivalent rate of flue gas CO<sub>2</sub> removal for the two processes. As mentioned, the Shell process cost does include mineral grinding, but does not account for any additive recovering options.

**Table 3. Comparison of Shell baseline to Ammonium-based CCSM process design.**

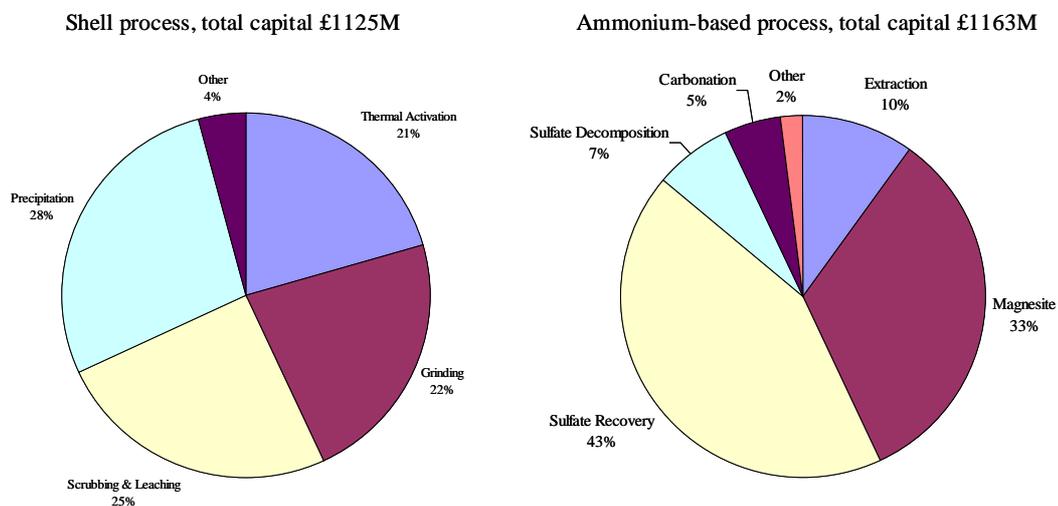
	Shell	Ammonium-based Process
<b>Capital (£M)</b>	1,125	1,161
<b>CO<sub>2</sub> captured</b>	80%	80%
<b>CO<sub>2</sub> parasitic load</b>	30%	88%
<b>CO<sub>2</sub> avoided</b>	50%	(-8%)
<b>£/Tc CO<sub>2</sub> avoided</b>	306	n/a
<b>Natural Gas firing (MW GCV)</b>	212	773
<b>Power usage (MW)</b>	156	147
<b>Significant energy users</b>	<ul style="list-style-type: none"> <li>• Thermal pre-treatment</li> <li>• Flue gas blower</li> <li>• Absorption column pump</li> <li>• Drying and additive recovery not included</li> </ul>	<ul style="list-style-type: none"> <li>• Sulphate recovery &amp; decomposition</li> <li>• Recovery of carbonate solution</li> </ul>

This shows that the processes are similar in many respects, but that the Ammonium-based process is less effective than the Shell process due to its additional energy usage. In this analysis, it has been assumed that the energy consumed comes from sources that do not have carbon capture. The

result is that the Ammonium-based process does not have a cost of carbon capture as it produces more CO<sub>2</sub> than it captures.

Figure 7 compares capital cost between the Shell process and the Ammonium-based process. Both have a similar total capital cost, but it should be noted that 50% of the cost of the Ammonium-based process is taken up in the ammonia recovery system. This shows that the core of the process is a significant improvement on the Shell process, but the recovery system has unacceptably high parasitic load. If it is possible to reduce the capital cost and improve the efficiency of the ammonia recycle, the Ammonium-based process has the capability to be more competitive than the Shell process. This would also have the added benefit of reducing energy consumption and improving the carbon capture performance of the process.

It should also be noted that the capital and operating costs of drying the slurry produced in the Shell process are not included in the analysis. If it were this would increase the capital cost, reduce the efficiency of carbon capture and increase the cost of carbon captured. The effect of this has not been evaluated in detail by the project team as the necessary data have not been available.



**Figure 7. Shell Process and Ammonium-based Process Capital Cost Distribution.**

#### 4.3.1 Process comparison and consideration of power supply from alternative carbon-neutral sources

The figures in Table 3 above have been calculated on the basis that power is produced from sources that inherently produce carbon dioxide. It is noted that potential alternatives are available such as nuclear or wind, which would result in the power being produced without producing carbon dioxide.

Two additional situations have been considered in Table 4 below. Firstly, the CO<sub>2</sub> avoided has been calculated assuming that the power required for the process (147 MW) is sourced from carbon free sources such as nuclear or wind. Secondly, the CO<sub>2</sub> avoided has been estimated assuming that additionally the carbon dioxide footprint arising from the large natural gas duty is instead sourced from alternative green electricity.

**Table 4. Comparison of Ammonium-based CCSM process design and the effect of sourcing of green power on the process economics.**

	Ammonium-based Process	Ammonium-based Process (Power from green sources)	Ammonium-based Process (Power and natural gas from green sources)
<b>Capital (£M)</b>	1,161		
<b>CO<sub>2</sub> captured</b>	80%		
<b>CO<sub>2</sub> parasitic load</b>	88%	69%	17%
<b>CO<sub>2</sub> avoided</b>	(-8%)	11%	63%
<b>£/T<sub>e</sub> CO<sub>2</sub> avoided</b>	n/a	1552	270

#### 4.4 Process Design Conclusions

The capital cost is similar for both processes. The core of the Ammonium-based process is significantly lower cost than the Shell process, but the ammonium sulphate decomposition stage, ammonium sulphate recovery, and the recovery and recycling of excess reagents from the precipitation stage mean the plant has high variable costs of operation, as it is unable to capture the carbon dioxide generated by the power station without significant additional energy usage. This energy usage equates to a carbon dioxide production rate that exceeds the amount of carbon dioxide the recovery plant is designed to capture. At this stage of development, therefore, the Ammonium-based process is less attractive than the Shell process although this may change if the full cost of product recovery is factored into the Shell process costs. However, there are a number of technology development options that can be explored. It is believed that these have the potential to reduce operating costs and increase carbon capture potential. Reduction of the process energy usage may also reduce the plant capital cost.

## 5 Life Cycle Assessment

### 5.1 Life Cycle Analysis

A programme of work was undertaken to quantify the life cycle carbon footprint of the selected Ammonium-based CCSM and GCCS technologies using Life Cycle Assessment (LCA).

The main energy inputs to the CCS life cycle are electricity, natural gas, diesel, etc. The range of energy sources and production processes available mean the carbon footprint can vary considerably. Internationally recognised standard values were used.

Mount Keith nickel mine has been used to estimate the emissions from serpentinite mining as reliable data are available and serpentinite is the host rock for the nickel in this mine. The analysis includes the energy consumption of drilling, excavating, loading, hauling and crushing. The waste generated from the mining process is about 1–2% of the serpentinite mineral mined. When capital equipment, explosives, and maintenance are not included, the carbon footprint of this process is around 2.5 kg CO<sub>2e</sub>/tonne serpentinite.

In the ammonium-based process, each tonne of CO<sub>2e</sub> removed requires 69 kg of fresh ammonium sulphate (38 kg CO<sub>2e</sub>), 0.7 MWh of electricity input, 3.6 MWh of natural gas higher heating value energy input, and 1.3 MWh of low pressure steam input. In this life cycle analysis, we assume the electricity input is from coal-fired power plant with carbon footprint of 1050 kgCO<sub>2e</sub> per MWh, and low-pressure steam input is from waste heat from the power plant with zero carbon footprint. Without milling and heat or chemical treatment, serpentinite mining is not energy intensive and has a small carbon footprint, similar to other mineral mining processes.

## 5.2 Ammonium-based Process

The Ammonium-based process is described above in Section 4.2. The resulting CO<sub>2</sub> inventory is shown below in Table 5.

## 5.3 Carbon Dioxide Transport

The mode and distance of transport for CCSM technology and GCCS technology are quite different. In the model used for GCCS analysis, CO<sub>2</sub> was captured from a coastal power station and transported through pipeline to an offshore storage location. The pipeline transportation distance was taken as 420 km with negligible carbon footprint. In CCSM technology analysis, CO<sub>2</sub> is captured and sequestered at the Fellside power plant, and the magnesite was transported 107 km by ocean barge to the original Ballantrae mine site.

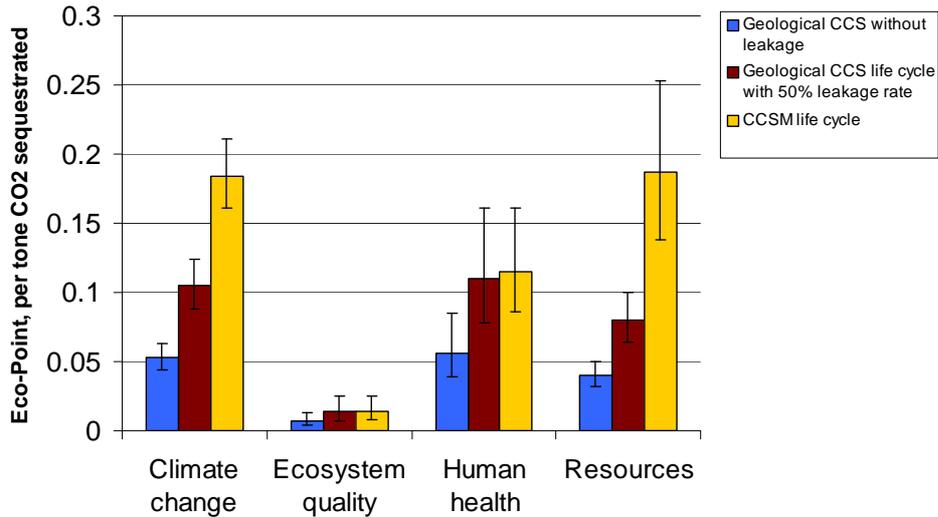
**Table 5. Ammonium-based mineralization process inventory (per tonne CO<sub>2</sub> sequestered).**

Material	Amount	Unit	Carbon footprint, kg CO <sub>2e</sub>
Ore	3.1	Tonne	
Flue gas	6.0	Tonne	
Water	0.6	Tonne	
Ammonium Sulphate*	0.069	Tonne	38.1
N <sub>2</sub> *	4.85*10 <sup>-4</sup>	Tonne	0.2
Magnesite	2.6	Tonne	
Other minerals	2.2	Tonne	
Flue gas	5.0	Tonne	
Electricity for CCSM process	0.7	MWh	779.3
Natural gas (HHV)	3.6	MWh	770.9
Low pressure steam	1.3	MWh	
Electricity for grinding	0.10	MWh	107.9

\* EcoInvent

Ocean barge transportation<sup>10</sup> of 214 km has a carbon footprint of 3.2 kg CO<sub>2e</sub>. With consideration of material, energy input and transportation of CCSM life cycle, the overall CO<sub>2</sub> avoided is 0.83 tonne CO<sub>2e</sub> per tonne CO<sub>2</sub> sequestered. Different electricity sources can have very different carbon footprints. Hypothetically, the carbon footprint of CCSM technology can be lowered dramatically when the CCSM process uses electricity input from a low-carbon intensity electricity source, such as natural gas power plant, nuclear power plant, etc. However, it is rather against the purpose of this technology development to sequester CO<sub>2</sub> emission from a low-carbon intensity electricity source.

There are three stages in GCCS: capture, transport, and storage. The carbon footprint of capture stage depends on the type of power plant and the capture technology. For the Ammonium-based process, the energy required to capture CO<sub>2</sub> from flue gas is 258 kWh/tonne CO<sub>2</sub> captured. CO<sub>2</sub> compression for pipeline transportation and injection will require 238 kWh/tonne CO<sub>2</sub> at 239 bar.<sup>11</sup> The carbon footprint of these two steps is 325 kg CO<sub>2e</sub>/tonne CO<sub>2</sub> captured. Initial capital financial cost of construction of pipeline and maintenance can be significant, but the carbon footprint impact of those steps is rather limited when operational lifetime of a geological sequestration site is considered, and therefore not included in this analysis. Overall life cycle impact of GCCS with hypothetical leakage scenarios is compared to CCSM in the figure below. Even with an unrealistically high leakage rate of 50%, >50x the expected rate, GCCS has less impact than CCSM technology.



**Figure 8. Life Cycle Assessment comparison of Ammonium-based CCSM and GCCS.**

Climate change impact is largely determined by the carbon footprint of the technology life cycle; therefore, CCSM technology has much higher climate change impact than GCCS. In addition, because of the additional mineral and ammonium sulphate required, CCSM has a higher resource impact over GCCS.

#### 5.4 Life Cycle Analysis Conclusions

This preliminary analysis concludes that:

- GCCS has a lower carbon footprint than Ammonium-based CCSM technology.
- The high heating and electricity demand of the Ammonium-based CCSM process can result in a negative carbon footprint.

The Life cycle assessment (LCA) was conducted in line with the ISO standardized process.

#### 5.5 CAPEX analysis for aqueous CCSM

The capital cost estimated in this project for “multi-step” processes such as Shell and Ammonium-based technologies was compared with the capital cost of the “single step” technologies developed by Energy Center of Netherland<sup>12</sup> and Albany Research Centre<sup>13,14,15</sup> that were scaled to the same power plant size.

**Table 6. Capital cost analysis of “single step” and “multi step” aqueous CCSM technologies.**

CCSM Technology	ECN	ARC	Shell	Ammonium
Power plant, MW	300	300	300	300
Mineral feedstock	wollastonite	Olivine	serpentine	serpentine
Total fixed capital cost (TFCC), £M	112.1	514.9	678.3	700.0
TFCC per tonne CO <sub>2</sub> , £/tonne	74.2	265.6	324.9	335.3
Total power consumption for capital equipment, MW	50.8	35.4	107.0	143.1

It can be seen that the “single step” processes exhibit lower capital cost and lower energy consumption in comparison with the “multi step” processes. Overall, wollastonite feedstock does not require heat activation or chemical leaching, provides fast carbonation kinetics and complete

mineral conversion. However the feedstock is expensive and the global resources are so small in comparison to serpentinite and olivine that the process is not viable. “Single step aqueous” CCSM utilizing olivine could be economically attractive for small emitters co-located with these minerals deposits. Serpentine minerals, although rather abundant, require chemical or heat activation resulting in significant increase of capital cost and energy consumption. SO<sub>x</sub> and NO<sub>x</sub> removal in direct flue gas mineral carbonation

The simultaneous removal of SO<sub>x</sub> and NO<sub>x</sub> with CO<sub>2</sub> is a separate research topic that was outside of the scope of this study. General proof-of-concept experimental work was carried out to quantify the SO<sub>x</sub> and NO<sub>x</sub> removal efficiency in direct flue gas mineralisation and establish whether capture of these three pollutants could be integrated. The preliminary results were as follows: SO<sub>x</sub> removal was 42% and 54% at 80°C and 140°C, NO<sub>x</sub> removal efficiency was 24% and 18% at 80°C and 140°C, respectively. The low removal efficiency of SO<sub>x</sub> and NO<sub>x</sub> is linked to inadequate oxidation of NO and SO<sub>2</sub>, since NO and SO<sub>2</sub> cannot directly react with NH<sub>3</sub>. In order to maximize the SO<sub>x</sub> and NO<sub>x</sub> removal in direct flue gas mineralisation, an oxidation step using agents common in water treatment would be needed before the removal step.

## 6 Overall Project Conclusions

- The principle of CCSM, providing safe, long-term, stable storage of CO<sub>2</sub> is a highly attractive proposition.
- Globally there are ultramafic rocks that could be used as a feed material that could capture total global CO<sub>2</sub> emissions for over 300 years, and the use of industrial waste materials further increases the potential.
- Currently, CCSM is a less mature technology compared with GCCS; the economics of two technologies investigated in this study cannot offer a cost and/or net CO<sub>2</sub> sequestration advantage over GCCS. In the table below, it is noted that the GCCS figure of £152 /te is in the context of considering small, remote, industrial emitter such as a CHP, cement plant or a gas-fuelled small power station.

As improvements are made, CCSM developments should be re-assessed and mass and energy balances developed prior to large scale deployment.

	Cost per tonne of CO <sub>2</sub> avoided (£/te)	Data source
GCCS	152	Stage 2a TEA
CCSM (Shell process)	306	Table 3 above
CCSM (Ammonium based process)	Not applicable	Table 3 above

- GCCS is not possible in many parts of the world, and alternative strategies are required including reduction of carbon dioxide at source, eg by using nuclear, wind or wave technology for power generation. When considering suitable abatement techniques, CCSM could be part of the solution if technology improvements can be made. CCSM may have niche applications, especially in areas that are already mined and where mine waste can be used as significant amount of the industrial processing has already been done.
- The major individual components of the Mg-extraction and carbonation using the Ammonium-based process have been demonstrated at the laboratory scale with high efficiency (80–90%).
- The core of the ammonium-based process developed by the consortium has great potential to simplify the operations and would be simpler to operate. The core process is also significantly

lower capital cost than the Shell process. However, the recycling of the ammonium salt adds a significant cost and energy penalty. If this recovery cycle can be improved, the process still has the potential to be an attractive CCSM process.

- Combining these components in to a model plant shows that there are major problems with the recycling of the reagents, and this creates unacceptably high energy penalties leading to no net CO<sub>2</sub> avoided. If the process energy consumption is reduced, the parasitic CO<sub>2</sub> burden will come down. In order to be competitive, it will need to reduce to the GCCS figure of £152/ te CO<sub>2</sub> avoided.
- The consortium process has assumed filtration characteristics that would produce a solid output containing around 14% moisture. This can be transported to its final location and stored easily.
- The Shell process assumed different filtration characteristics and defined a product slurry concentrate with a moisture content of 50%. This can be transported, but would require further drying for long term storage. Atmospheric drying is not feasible because of the large volumes. Also the water consumption to run the process would be prohibitively large at ~28,000 t/day scaled to the plant rate given in Table 3. It would be operationally necessary to recover and recycle the water. To make the processes directly comparable, the filtration characteristics of the solid products from both processes need to be determined to allow a more accurate assessment capital cost carbon footprint and size of the respective plants.
- A major breakthrough in ammonia recycling technology is required to make an Ammonium-based process viable.
- There may be scope using other processes that were not investigated during this project that could make CCSM viable. However, during the early stages, the project assessed twenty-five CCSM process routes as shown in Figure 4 and the subsequent development work was based on the most promising technological routes.
- This project did not investigate the possibilities of making useful products from the CCSM process. This is being pursued by other research groups and companies. This could have a major impact on the economics, but may reduce net CO<sub>2</sub> benefits.

## 7 Future Steps

The major problem area for the Shell process is the use of imported heat to activate the mineral prior to the CO<sub>2</sub> mineralisation reaction and the drying required to create a handleable product. The Ammonium-based process avoids these loads, but the ammonium bisulphate recovery circuit consumes so much energy that no net CO<sub>2</sub> capture occurs. However, the capital required for the Ammonium-based process is significantly lower than for the Shell process if product drying were included in the Shell estimates. The major problem area for the Ammonium-based process is the ammonium sulphate decomposition stage, ammonium sulphate recovery, and the recovery and recycling of excess reagents around the precipitation stage. These account for 50% of the capital and the bulk of the operating costs.

Development of the process within the existing design concept will yield some reduction in energy usage and capital cost, but the project team's view is that the gains are unlikely to fundamentally alter the underlying picture. Seventeen improvement opportunities are noted and summarised in Table 7. Seven of these have a good chance of improving the capital or operational costs and thereby improving the carbon capture performance.

**Table 7. Areas for potential improvement of CCSM.**

Improvement opportunity	Improvement actions	Potential capital cost impact	Potential variable cost impact	Likelihood of technical success
<b><i>Incremental Improvement</i></b>				
Optimization of Mg extraction	Change reactor type (e.g. batch operated trickle bed reactors)	Medium	Medium	Medium
	Optimize particle size, solution concentration & utilization of bisulphate solution	Low	Low	High
	Operating temperature and materials of construction	Medium	Low	Medium – High
Optimization of precipitation stage	Reagent use, residence time & per pass efficiency	Medium-High	Medium	Medium
Direct precipitation of Mg by flue gas		High	Medium	Medium
Refinement of the heat and power integration scheme		Low	Low	Low
Cost/benefit analysis of potential energy reduction schemes	Power recovery from letdown of precipitation reaction liquors	Low	Low	High
	Power generation from sulphate decomposition vapours	Low	Low	Medium
	Options for combined power/heat generation & integration of heat recovery from sulphate decomposition	Low	Low	Low
Further integration of energy with other plants on the same site.	Potential to use LP steam from the power plant itself	Low	Low	Low
Materials of construction for extraction reactors		Medium	Zero	Medium – High
Operation of the sulphate decomposition stage & the impact of pressure on performance		Low	Low	Low
Filtration characteristics of the leached ore & magnesite, wash efficiency, the selection & sizing of the filters		Medium	Low	High
<b><i>Radical Redesign</i></b>				
Develop process to deal effectively with mixed serpentine-olivine rocks		High (increase)	Medium (increase)	High
Separation of MgSO <sub>4</sub> from the leachate solution	Avoid neutralization of unreacted bisulphate Separate carbonation & extraction solution cycles	Medium	Medium	Medium
Direct reaction of ammoniated MgSO <sub>4</sub> solution with flue gas		Medium	Medium	Low – medium
Application of bipolar electro dialysis in place of bisulphate regeneration	Simultaneous regeneration of bisulphate and alkali solutions Avoid evaporative crystallization of ammonia sulphate	Medium	High	Medium

It can be seen from the table that although there are a number of potential opportunities to improve the process, no one of them has the potential to change the economics of operation or the efficiency of carbon capture alone. However, a number do have potential for limited improvement and if implemented in parallel could have value. These could be worthy of further investigation at a later date.

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