Novel Hot Gas Cleaning/Heat Recovery System

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SUMMARY

Nearly all types of coal gasification based advanced power generation systems under development incorporate hot gas cleaning stages to remove particulates and gas phase contaminants prior to the gas turbine. These hot gas cleaning systems offer significant benefits over conventional wet scrubber clean-up systems. However the development of a continuous fully integrated process, in which gas cooling, sulphur/halide removal, using regenerable sorbents would give substantial benefits.

Systems of this type have a number of advantages: the use of regenerable sorbents produces less waste and reduces the operating cost associated with disposal of classified waste products; the fuel gas cooler is located in a benign environment and can therefore be used to generate superheated steam at supercritical conditions yielding a further improvement in cycle efficiency. In addition, the removal of gas contaminants early in the hot gas path will directly improve the environment for downstream components, e.g. hot gas filter parts. On the basis of the expected reduction in the corrosivity of the fuel gas, components' lives may be extended by up to ten times. This benefit would apply to all types of gasifier, including conventional oxygen blown IGCC's where the introduction of hot gas cleaning would otherwise happen downstream of the raw gas cooler and the hot gas filter, both of which would have to operate in a highly aggressive environment.

This project was targeted at developing such a novel integrated raw gas cooler and sulphur and halide removal process for gasification plant. The desulphurisation process is based on a twin fluidised bed system employing direct solids transfer between adjacent vessels. Halide removal is achieved by means of sorbent injection.

The first stage of the project developed a series of mathematical models for the twin-bed desulphurisation concept. Then a 2-D cold model was designed and manufactured to demonstrate the concepts and the validity of the mathematical models produced. After a series of modifications were carried out and their effects assessed, a twin bed unit was designed and manufactured that was capable of being used initially as a 3-D cold model and then being retrofitted to an existing atmospheric pressure gasifier. The 3-D unit functioned as anticipated as a cold model, demonstrating the expected particle flux between the twin beds, and also showed that there were low gas leakage rates between the two beds. After being retrofitted to an existing atmospheric pressure gasifier, the twin bed unit was used to demonstrate the effect of sulphur sorbent on real gasifier derived fuel gases. Limestone, a well known sulphur sorbent in oxidising atmospheres and reducing atmospheres, was selected to test the effectiveness of the twin bed unit in this project. The twin bed was operated with the outlet gases from the gasifier in one side (absorber side) and with air in the regeneration side of the system. Several operating conditions and variables have been studied in the system: gas velocity, bed temperature. The use of the limestone sorbent in the twin-bed reduced the H_2S level in the fuel gas stream under all the conditions investigated.

The twin bed system seems to be a promising technology for a heat exchanger system, due to the good particle flows between the two fluidised beds, and for the reduction in contaminant emissions. However, further work is required to improve the understanding of the twin-bed hydrodynamics, as well as to develop sorbents with operating temperatures that are compatible with the twin-bed concept. Two options for the twin bed system have been suggested as worth pursuing as viable use of this technology in gasification plant design. The first involve a twin-bed gasification-heat exchange

system where gas from a gasifier is fed to one vessel and heat is transferred to a second by means of re-circulating solids. The second option is a triple-bed adsorption-regeneration-heat exchange system, where the gas from the gasifier is fed to a vessel and the H_2S is removed. Catalyst/sorbent is transferred to a second bed for regeneration, and solids are transferred to a third vessel where heat is removed.

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1. INTRODUCTION AND BACKGROUND

Combined cycle power generating systems offer many potential advantages over conventional coal-fired systems, including increased efficiency of power generation and lower environmental emissions (specifically particulates, CO_2, SO_X and NO_X). A wide variety of systems have been proposed, based on coal gasification and/or combustion with associated gas cleaning technologies to meet systems and emissions requirements.

Most of the of coal gasification based advanced power generation systems under development incorporate hot gas cleaning stages to remove particulates and gas phase contaminants prior to the gas turbine. Currently a sequence of hot gas cleaning stages is envisaged after cooling the fuel gases. For example, this could involve halide removal (to avoid poisoning of sorbents in downstream components), particle removal (using ceramic candle filtration), sulphur removal (using regenerable sorbents) and ammonia decomposition (using catalysts) to reduce the risks of NO_X formation in the gas turbine combustor. The development of some of these systems (e.g. ceramic candle filtration) is further advanced than others and is currently being incorporated into operational demonstration plants. The hot gas cleaning approach leads to higher cycle efficiencies than the use of more conventional wet scrubbing and avoids the waste water disposal issues. Studies have also shown that this approach can lead to significant savings in capital costs and reduced electricity prices which will immediately benefit the competitive position of Integrated Gasification combined Cycle (IGCC) in the power generation market.
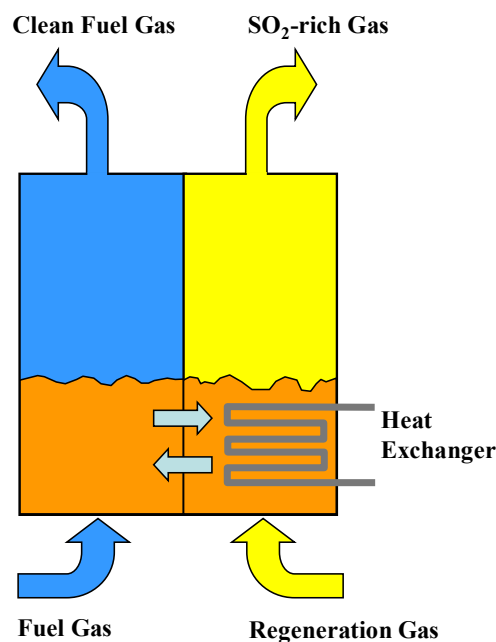
Figure 1 Schematic diagram of twin-bed gas cleaning / heat exchanger concept

This project provided an opportunity to achieve even greater improvements by starting the development of a continuous fully integrated process in which gas cooling, sulphur removal (using regenerable sorbents) and halide removal are carried out in a single process stage in a single pressure vessel (Figure 1). The approach, which is summarised below, will be applicable to all types of gasification plant handling a wide variety of fuels, e.g. coal, biomass and waste.

The sulphur removal system proposed consists of two adjacent fluidised beds operated respectively as an absorber and regenerator. The hot combustible fuel gas formed in the gasifier is passed through an absorber which contains a suitable sorbent to remove hydrogen sulphide. The sulphided sorbent is circulated to an adjacent air or oxygen blown regenerator, which contains immersed cooling surfaces, via an array of transfer ports located in the base of the wall dividing the two beds. The regenerated sorbent is recirculated back to the absorber. As the regeneration process is highly exothermic, additional heat recovery is possible from this bed. The sorbent in the absorber is maintained at an optimum maximum temperature of about 600°C for sulphur capture by the circulation of solids between the cooled regenerator and absorber beds. Halides can be removed by the injection of calcium or sodium compounds upstream of the sulphur removal process. Recovery of sulphur as a saleable by-product will be possible from the gases from the regeneration bed.

A hot gas filtration system would still be required downstream of such an integrated gas cleaning process, but the removal of gas contaminants early in the fuel gas path will reduce the erosion/corrosion potential for downstream components and reduce their cost as cheaper materials can then be used. This benefit would apply to all types of gasifier, but especially to oxygen blown IGCCs where sulphur removal would otherwise happen downstream of the fuel gas cooler and the hot gas filter, both of which currently operate in highly aggressive environments. In fluidised bed gasifiers it would avoid the necessity for in-bed sulphur removal, while not harming downstream components.

This integrated fuel gas cooling and cleaning process is the subject of a UK patent application (No. 9615603.9) assigned to Cranfield University. The twin fluidised bed system proposed was originally developed for a successful pyrolyser/combustor system which was used to generate high temperature process gases using versatile fluidised bed technology.

This final report on DTI Cleaner Coal Programme Project 109 outlines the successful progress made in developing the proposed integrated gas cleaning system.

2. AIMS AND OBJECTIVES

The overall aim of the project was to develop a novel integrated fuel gas cooler and sulphur and halide removal process for gasification plant.

The specific objectives of the programme were:
1. To prove the concept of using a twin bed reactor system suited to this application.
2. To assess the performance of available sulphur sorbents in the twin bed system.
3. To assess the effect of scale up on the performance of the system and the downstream effects on filter performance, residue characteristics and gas turbine performance.

This project aimed to supply the required underpinning scientific understanding of this integrated hot gas cleaning approach to allow the technology to move forward to subsequent industrial development and demonstration.

3. REACTOR DESIGN

3.1 Mathematical model
3.1.1 Introduction
The aim of the initial phase of the project was to develop a mathematical model of the process on which to base the design of the twin-bed system. The model provided data on the solids recirculation rates (between interconnected beds) required to maintain the regenerator and absorber at the optimum temperatures, and took into account chemical kinetics, attrition, segregation, heat transfer to immersed surfaces, vertical and lateral temperature gradients.

The computer model was developed in two distinct stages. The first stage used a 'simple' spreadsheet to determine the effects of heat transfer through the separation wall on the temperatures of the two beds and is discussed in section 3.1.2). This was then incorporated into the final program, (discussed in section 3.1.5) which was developed using Pascal. This model included the effects of sorbent activity, which is discussed in section 3.1.4.

The model developed is for a system that will consist of a central spouted fluidised bed (Bed 1) and a surrounding annular bubbling fluidised bed (Bed 2), with solids exchange between the two via a series of transfer ports (or slots). It was initially estimated that a likely internal diameter for the central reactor would be 150mm with a wall thickness around 6mm. After various combinations were investigated, the following emerged:

Internal diameter: 200mm
Internal wall thickness: 6.3mm
Annulus width: 37.5mm
Reactor diameter (not including outer case): 287.5mm

These dimensions give rise to inner and outer reactors of roughly the same volume.

3.1.2 Heat Conduction Through the Separating Wall
The first stage of the computer model was to write a 'simple' spreadsheet to determine how heat conduction through the separation wall affected the temperatures in the two fluidised beds.

Ideally, the wall between the reactors should be insulated, but a plain steel wall would simplify the design. However, preliminary calculations suggest that conduction through the wall might dominate heat transfer between the beds, so that the effect of particle migration on bed temperature would be marginal.

To investigate this issue, and to find out whether the above dimensions were realistic with respect to typical envisaged operating conditions, a spreadsheet model was devised which incorporating an elementary model of the rig. A list of all the notations can be found in section 10.

It is assumed that gas (taken to be air) enters Bed 1 at a high temperature. Heat is transferred to Bed 2 through the transfer ports and possibly through the separating wall. Equating heat input to heat output:

$$\text{gas}_1 \, cg_1 \, T_1 + ms \, cs \, [\, T_1 - W_1 \,] + hhA[\, T_1 - W_1 \,] = \text{gas}_1 \, cg_1 \, T_0 \qquad (1)$$

Gas (again taken to be air) enters Bed 2 at a low temperature. Here, as well as heat transfer via the transfer ports and separating wall, there is, additionally, heat transfer to in-bed tubes and heat losses through the outer wall:

$$gas_2 \, cg_2 \, W_1 + ms \, cs \, [\, W_1 - T_1 \,] + hhA[W_1 - T_1 \,] + hA_f[W_1 - W_f \,] + Loss = gas_2 \, cg_2 \, W_0 \quad (2)$$

These two heat balances can be rearranged to give the simultaneous equations with the solutions:

$$T_1 = (cd + be)/\Delta \quad (3)$$

$$W_1 = (bd + ae)/\Delta \quad (4)$$

where

$$\Delta = a \, c - b^2 \quad (5)$$

In this model, the fluidising velocities in the two beds are specified. Initial estimates of bed temperatures are made to find the gas mass flow rates. Within the spreadsheet, an iterative procedure is then invoked whereby the temperatures and gas flows are updated, until convergence is achieved. It was found that the heat conduction through the separating wall almost equalised the bed temperatures.

3.1.3 Physical Properties

The minimum fluidising velocity, U_{mf} [1], of the bed particles has an important effect on the nature of fluidisation within a reactor [1], e.g. whether the bed is a moving bed, bubbling bed, spouted bed, etc. It can be shown that U_{mf} decreases somewhat with temperature within the range of particle diameter of interest here (100 - 400 microns). Such considerations have an important bearing on cold-model simulations and process scale-up. Particle terminal velocity, U_t [1], has an influence on particle removal from the reactors, and decreases with temperature.

The quality of fluidisation (e.g. bubbling versus smooth fluidisation) has been hypothesised [1] to depend on the product of four dimensionless parameters:

$$U_{mf}^2/g \, d_p \, , \quad \rho_s \, U_{mf} \, d_p/\lambda \, , \quad (\, \rho_s - \rho_g)/ \rho_g \, , \quad L_{mf}/d_b \quad (6)$$

viz, Froude number, F_r, a Reynolds number R_e, gas/solids density ratio, R, and the ratio of bed height at minimum fluidising velocity to bed diameter, L, for a typical range of temperatures, assuming a particle diameter of 350 μm and particle density of 1100 kg/m^3.

An internal spout forms if a central jet is used. Stokes number, S_t, gas/solids density ratio, R, and Froude number, F_r, have been found to be sufficient to correlate existing data on vertical jet penetration [2]:

$$H_j/D_i = 26.9 \, F_r^{0.322} \, R^{0.325} \, S_t^{-0.124} \quad (7)$$

The data indicate that a vertical spout of height around 0.1m would form, above which a series of large bubbles will arise. In the case of absorption of contaminants, the reaction rate may be high; much of the heat generated is released within the spout region, possibly resulting in a local hot spot. Blake et al. [2] have derived an expression for the rate of solids entrainment into the jet, as a function of the above hydrodynamic parameters, together with the particle Reynolds number:

$$W_s/W_o = 0.19 \, F_r^{-0.451} \, R^{-0.384} \, S_t^{0.432} \, R_e^{-0.081} \, [z/ \, D_i]^{0.451} \quad (8)$$

Where the particle Reynolds number is given by:

$$R_e = \rho_g \, v \, d_p \, / \lambda \qquad\qquad\qquad (9)$$

A simple model, using the above work, was developed to estimate the temperature within the hot spot. It is predicted that a jet temperature around 797°C would arise, assuming a mean bed temperature of 770°C. Thus, the current internal spout has the advantage of minimising temperature gradients within the reactor. However, a possible problem might be the degree of attrition associated with such a jet.

If a bubbling-bed regime occurs in the reactor, then particle mixing affects the temperature profile within the bed. The main points here are the high values attained and the difference between axial diffusivities in the two beds. It is also worth noting that radial diffusivity is an order of magnitude less than the axial one. It follows that the nature of air distribution within the reactor will have an important bearing on bed temperature; for example, a single gas entry spout may be effective in a narrow reactor but may be inappropriate in a scaled-up version of the process.

At present elutriation is not considered, but in practice the solids in the bed will have a range of sizes and preferential separation of material from the bed is expected. Similarly, attrition is not taken into account at present. Together with elutriation, this could form part of a module dealing with 'particle population', i.e. the prediction of the particle size distribution within the bed [1].

In simplistic terms, heat transfer between a fluidised bed and a surface (e.g. wall or heat exchanger) may be considered to be a combination of convective (h_c) and radiative (h_r) components. A typical value for h_c is 230 W/m^2 K in a reasonably vigorous bubbling bed [1] and h_r is about 120 W/m^2 K for a bed temperature of 900°C. It may be assumed, simplistically, that h_c is proportional to fluidising velocity. More elaborate models can be invoked that take into account particle size, density, specific heat, thermal conductivity, etc.

Solids recirculation rate is clearly an important factor in the hot rig design: initially, estimates were made [1], e.g. a value of 20 kg/m^2/s was used in the development of the models. In practice, the transfer flux may be expected to depend on the fluidising velocities in each bed, the nature of the ports (e.g. height, width, and whether or not air jets are used in the ports), and position of the ports within the rig.

3.1.4 Sorbent Regeneration
Here, gasifier gas is assumed to be fed to the central reactor (absorber) and H_2S removal is assumed to take place. The solids exchanged through the transfer ports take the captured sulphur to the annular reactor (regenerator) and refreshed sorbent is returned. Sulphur is removed from the sorbent by means of a flow of oxygen-rich gas.

The sorbent is taken as Zn_2TiO_4, and combining the work of [4, 5] it has been possible to develop a program that carries out the calculations appropriate to zinc titanate, assuming nominal values of bed temperature, etc.

3.1.5 Overall Computer Model
This overall computer model is similar in form to the earlier one given in section 3.1.2. Whereas the simpler one takes fixed values of specific heats, etc, and assumes the input gases are single inert species, the overall model is more elaborate. The input and output gas and solid streams are

specified as vectors: the gas streams have the components H_2, CO, CH_4, CO_2, O_2, N_2, H_2O, H_2S, SO_2, and total molar flow rate; the solids vector components are Zn, Ti, O, S, MM, and total molar flow rate (MM, the residual, is assumed to have molecular weight 30).

In practice, the exit gas specific heats cannot be found before the reactor temperatures, T_1 and W_1, are known, so that, as before, an iterative procedure is necessary. Similarly, the fluidising velocities necessary to evaluate bed/surface heat transfer are dependent on gas density, which in turn varies with temperature. Additionally, the radiative component of heat transfer depends on temperature. Finally, reaction kinetics are considered.

A computer program has been written to carry out the above calculations. Gas inlet flow rates and compositions are assumed. Initial gas component molar flow rates are found and initial guesses of bed temperature made. If no chemistry is considered then the outlet gas streams are identical to the inlet ones; otherwise, in the case of sorbent activity, sorbent utilisation and regeneration are accounted for, giving rise to changes in the gas compositions, and releasing heat in each bed. The iteration procedure is continued until convergence is achieved.

3.1.6 Predictions

The model can be run to investigate any of the associated parameters, e.g. vessel dimensions, or input variables such as inlet gas flow rates and/or temperatures. For example, Figure 2 illustrates the effect on bed temperature of solids circulation rate, in the case where there is no conduction between the beds and no chemistry occurs. It shows that, as expected, the beds approach the same temperature for a high enough exchange rate.

Effect of Solids Exchange (no wall conduction)

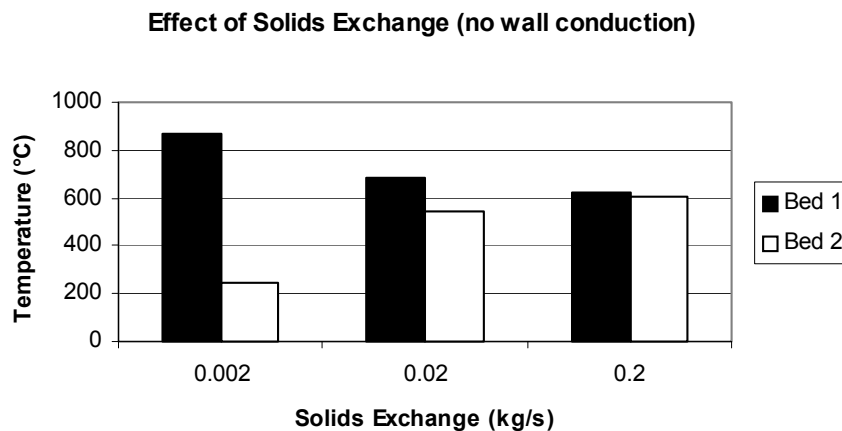**Figure 2 Effect of solids exchange on bed temperatures with no wall conduction**

If a reaction does occur, then the bed temperature will alter from the previous case, assuming there is a non-zero heat of reaction. Figure 3 summarises the case where a sorbent is present. Here, there is a net heat release in each bed, so that each bed temperature is greater than in the corresponding situation in Figure 2.
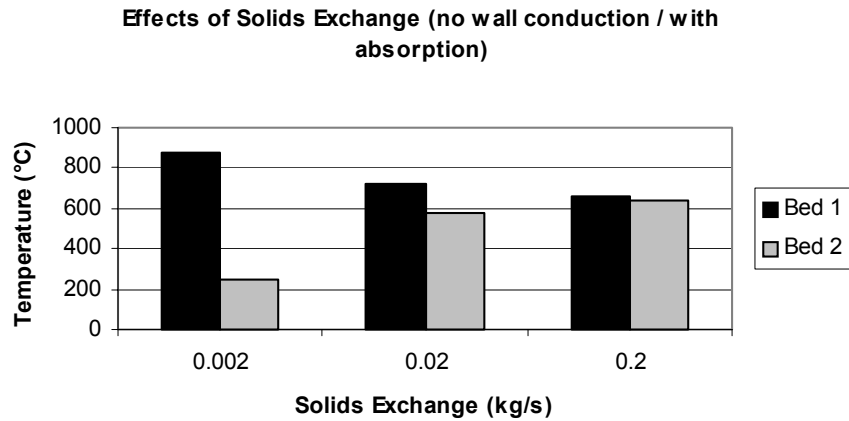
Effects of Solids Exchange (no wall conduction / with absorption)

Figure 3 Effect of solids exchange on bed temperatures with no wall conduction but with absorption

As noted previously, conduction through the wall between beds equilibrates temperatures and accounts for the majority of the heat transferred between the beds. However as can be seen from Figures 2 and 3 when there is no heat conduction through the walls of the vessel it is the solids exchange rate that determines the temperature in each of the beds.

Effect of Solids Exchange (wall conduction)
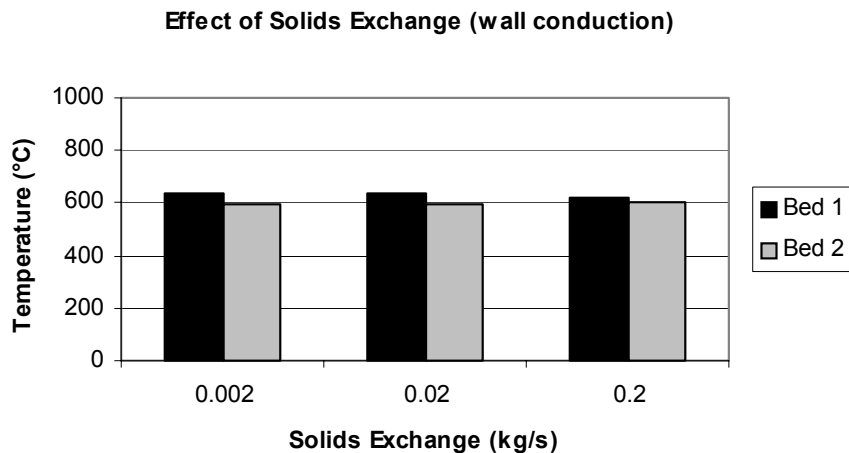
Figure 4 Effect of solids exchange on bed temperatures with wall conduction

Figures 4 and 5 are essentially representing the same data but presented differently. Figure 4 plots the effects of solids exchange while Figure 5 plots the effects of the number of transfer ports (slots). Since the solids exchange rate is a function of the cross-sectional area of the transfer ports one would expect the same results for an increase in solids exchange rate as found for an increase in the number of ports. In both cases the temperature of the first bed decreases while the temperature of the second bed increases. However the overriding affect is still form the heat transferred through the wall.

Effect of Solids Exchange (wall conduction)
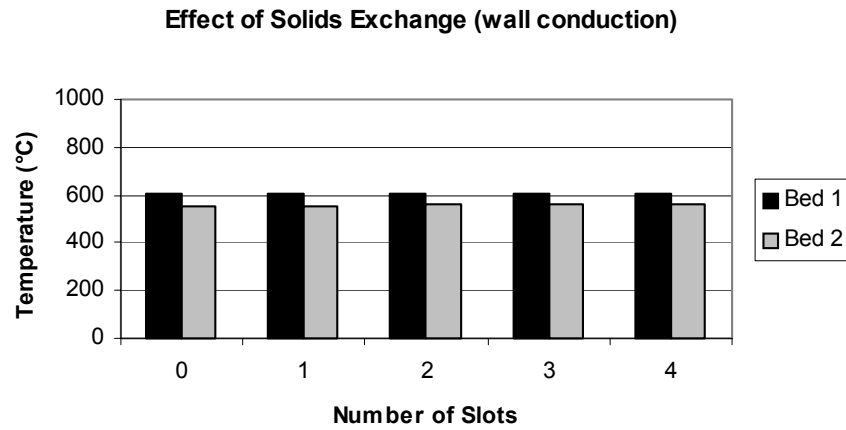
Figure 5 Effect of solids exchange on bed temperatures with wall conduction

3.2 Physical (Cold) Model Studies

A '2-D slice' model has been used to determine operating parameters for the twin bed system. It had been planned to modify an existing 2-D fluidised bed cold model to enable it to operate as a twin bed system. However, it was decided that a better approach would be to design and build a new 2-D cold model; which would allow easier modification of the twin bed arrangement. This decision resulted in the twin bed cold model being ready for use sooner than originally planned and being easier to modify for later tests. Figure 6 illustrates the first version of the 2-D cold model.

Figure 6 Photograph of the original 2-D 'slice' model

The 2-D cold model consists of the following basic features, as indicated in Figure 6:
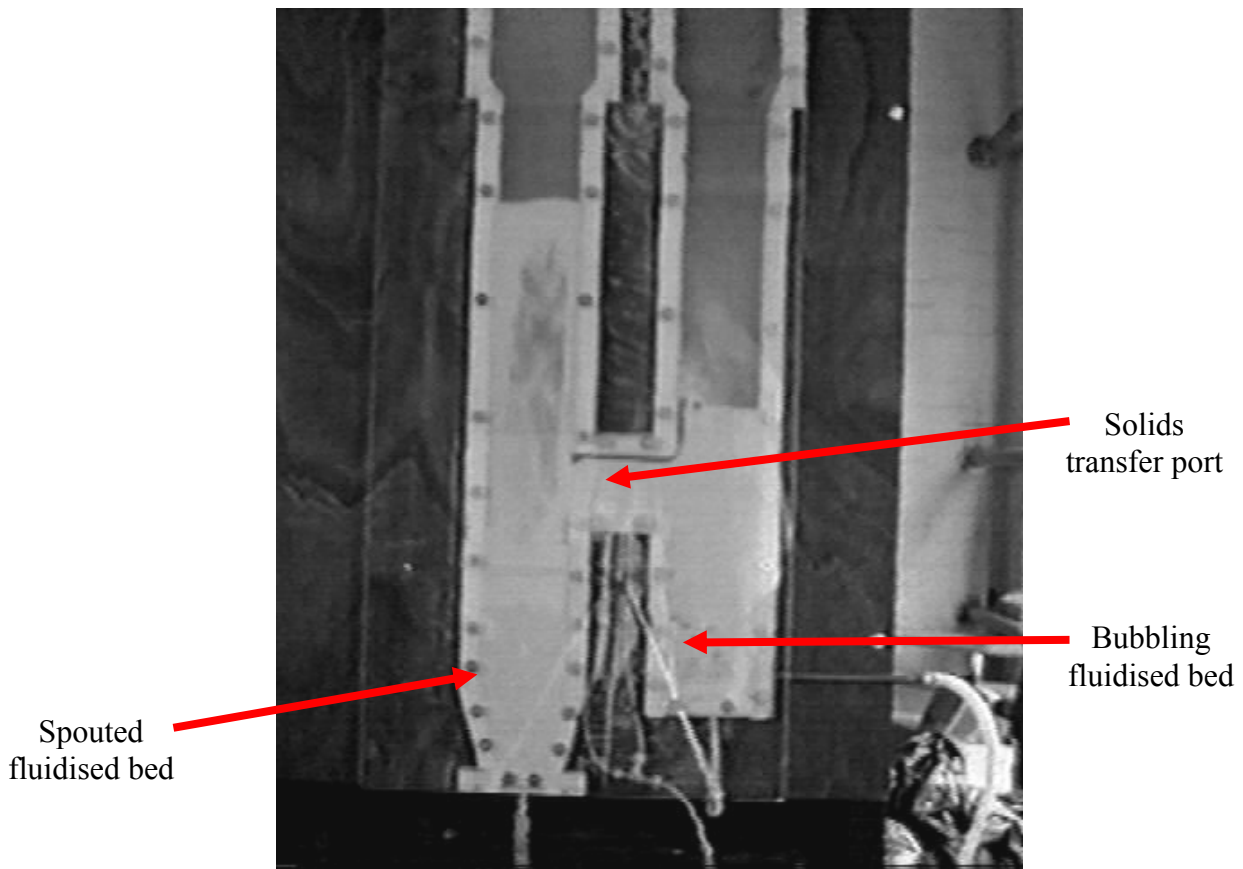- A spouted fluidised bed with its air inlet at its base
- A bubbling fluidised bed with its air inlet at its base
- A transfer port, which connects the two fluidised beds (with two air inlets).

In a real twin-bed system, the gasifier derived fuels gases would enter at the base of the spouted fluidised bed (the absorption part of the gas cleaning process), whilst air would be fed into the bubbling fluidised bed (the regeneration part of the system). The transfer port would be used to control the movement of solids between these beds by variation of its fluidisation by an inert gas.

Pressure tapping were added to the initial 2-D model (Figure 7) so it would be possible to determine the variation of pressure with bed height for different operating conditions and fluidising velocities. One of the aims of building the cold 2-D model was to help with the designing of a pilot scale twin bed reactor system (the 3-D rig) that could be connected to the gasifier at Cranfield University. Pressure readings have been a common method to determine the regime of fluidisation in fluidised beds in which visual observation was not possible.
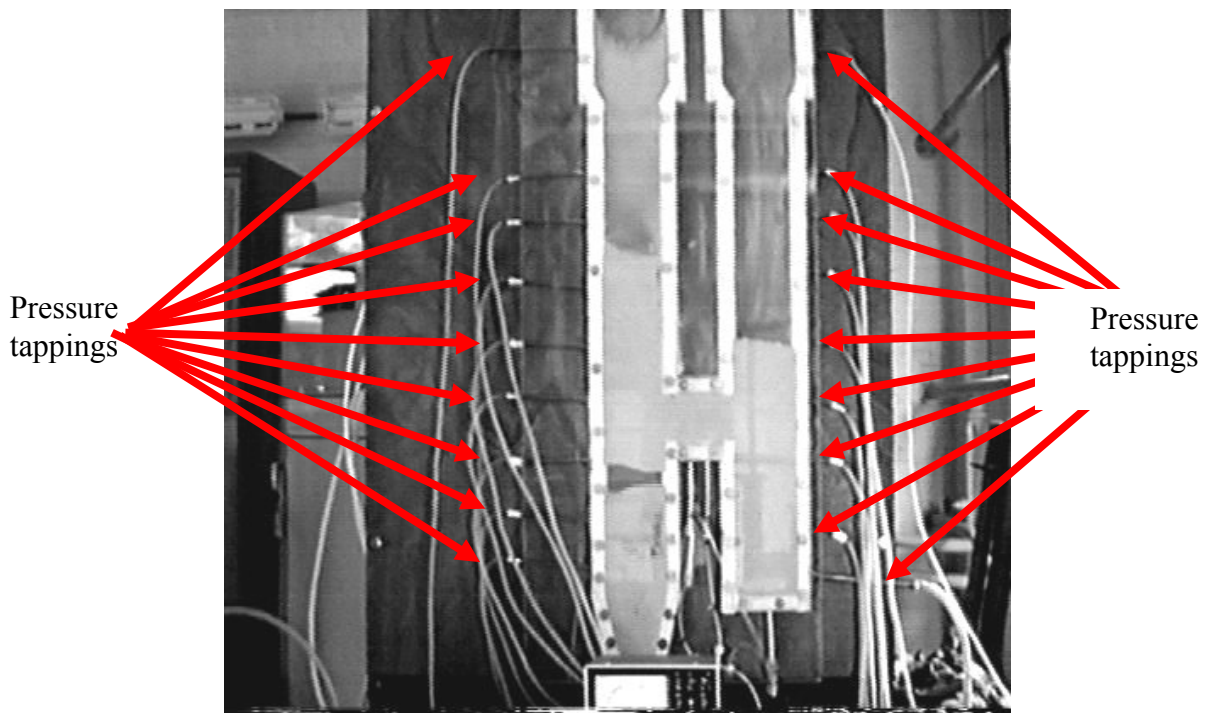
Figure 7 Photograph of the 2-D model with the first modification, the addition of pressure tappings

Characterisation tests were carried out on the 2-D cold model to determine the effects of the fluidising velocities on bed height, fluidising regime and bed pressure. These tests were done by systematically changing the fluidising velocities in the beds and the transfer port and measuring bed heights and pressures. The height of the spout and the bubbling regime in the two beds were also measured.

Figure 8 shows the effects of changing the spouted bed and the transfer port velocities. The transfer port velocity increases from left to right across the diagrams while the spouted bed velocity increases as you go down the diagrams. In all cases the bubbling bed was kept at a constant velocity.

Spout bed velocity 0.67 m/s
Bubble bed velocity 0.67 m/s
Port velocity 0 m/s

Spout bed velocity 0.67 m/s
Bubble bed velocity 0.67 m/s
Port velocity 0.2 m/s

Spout bed velocity 0.67 m/s
Bubble bed velocity 0.67 m/s
Port velocity 0.33 m/s

Spout bed velocity 0.67 m/s
Bubble bed velocity 0.67 m/s
Port velocity 0.5 m/s

Spout bed velocity 0.67 m/s
Bubble bed velocity 0.67 m/s
Port velocity 0.67 m/s

Spout bed velocity 0.89 m/s
Bubble bed velocity 0.67 m/s
Port velocity 0.2 m/s

Spout bed velocity 0.89 m/s
Bubble bed velocity 0.67 m/s
Port velocity 0.33 m/s

Spout bed velocity 0.89 m/s
Bubble bed velocity 0.67 m/s
Port velocity 0.5 m/s

Spout bed velocity 0.89 m/s
Bubble bed velocity 0.67 m/s
Port velocity 0.67 m/s

Spout bed velocity 1.11 m/s
Bubble bed velocity 0.67 m/s
Port velocity 0.2 m/s

Spout bed velocity 1.11 m/s
Bubble bed velocity 0.67 m/s
Port velocity 0.33 m/s

Spout bed velocity 1.11 m/s
Bubble bed velocity 0.67 m/s
Port velocity 0.5 m/s

Figure 8 Effect of changing fluidising velocities of the fluidisation of the 2-D model

It soon became apparent that the transfer port was positioned too high up the bed. For optimum transfer between the two beds the transfer port needed to be positioned in the region where both beds are operating in the spouted or bubbling mode. In order for this to occur a very high fluidising velocity was needed in the spouted bed which resulted in a high percentage of solids loss through the top of the spouted bed as well as a high degree of leakage through the port. Furthermore in the bubbling bed the transfer port was in the region of bubble coalescence which again is not optimum for solids transfer. Thus it was decided to lower the port to optimise solids transfer and bed fluidising velocities.

Figure 9 shows the modifications carried out in the twin bed to optimise the solids transfer and gas transfer between beds.
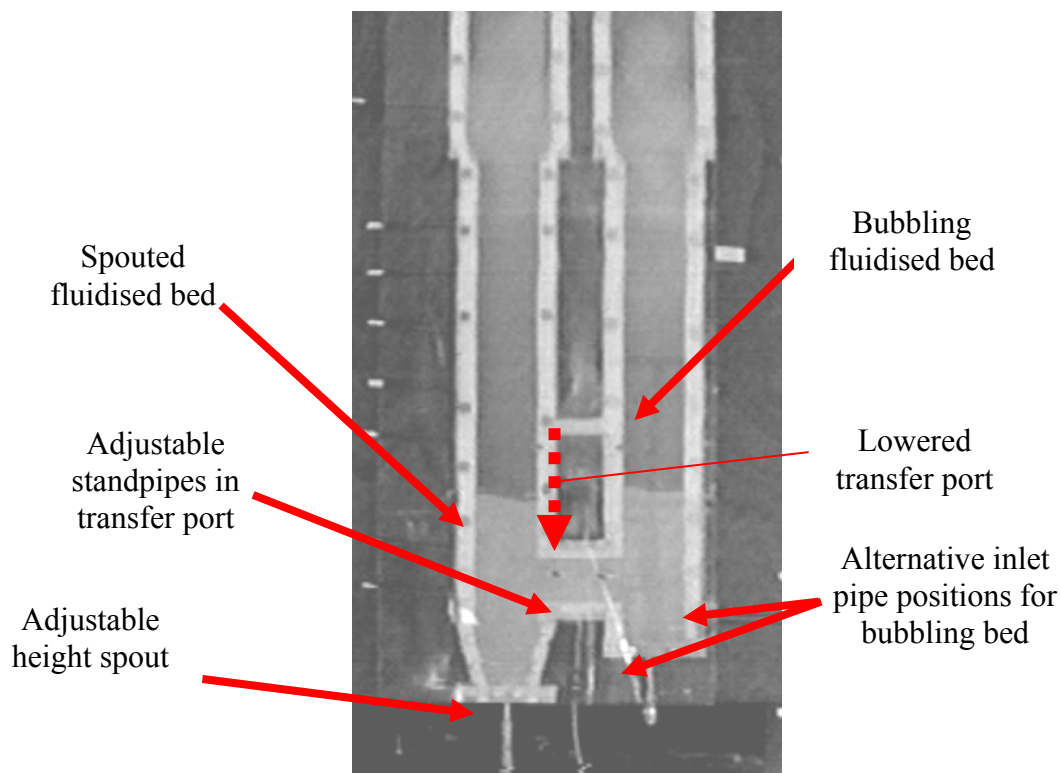

Figure 9 The second modification involved lowering the transfer port
(as can be seen by comparing the above photograph with those in Figure 8)

Other variables in the rig included:
- The height of the spout in the spouted bed can be varied.
- The position of the inlet pipe for the bubbling bed can be varied.
- The height and orientation of the stand-pipes in the transfer port can also be varied.

Initially the inlet pipe for the bubbling bed was across the whole width of the bed but this was later changed so that fluidising air was only introduced across 80% of the width of the bubbling bed to reduce the degree of gas leakage between the two beds. The air flow to all three fluidising inlet systems was controlled separately.

4 PILOT SCALE DESULPHURISATION STUDIES

4.1 Design Of The Twin-Bed System And Installation On An Atmospheric Pressure Gasifier

The idea of the twin bed system is that it would operate as two concentric beds interconnected via a series of ports. However, this design was not feasible for the pilot scale rig due to size constraints. Thus, it was decided to opt for a system consisting of two adjacent fluidised beds connected via a port, which would behave in a similar manner to a concentric system. Furthermore, it was decided to design the system on a modular basis connected by flanges such that the position (height) of the port could be easily changed. Due to the fact that the system was intended to be operated at high temperatures, (about 700-900°C) when connected to the gasifier, it was decided to build the rig out of 310 and 316 stainless steels.

Figure 10 is a diagram of the design of the twin-bed system and shows the main features of the dual bed design. The main modules of the two beds were constructed from 4 inch and 6 inch pipes with a 6mm wall thickness. The major design constraint on the size of the twin bed system was the capacity of the gasifier. The twin bed system had to be designed such that the spouted bed could be fluidised by the outlet gases of the gasifier. Thus, the twin bed system had to be designed around the output capability of the gasifier, effectively fixing the size (internal diameter) of the fluidising gas inlet pipe in the spouted bed. This then determined the size of the spouted bed and the bubbling bed.

It should be noted that the vessels increase in diameter just above the half-way point. This feature was added to ensure that if slugging occurred during the operation of either of the beds it would break-up at the point where the diameter of the vessel increases, thus reducing the amount of bed material that is lost from the rig.

The various modules of the twin-bed system were manufactured by a sub-contractor and delivered to Cranfield University where they were assembled and attached to a support frame in position to be connected to the gasifier. Figure 11 is a picture of the assembled twin-bed system with key features labelled. The set-up shown is for operation using compressed air (carried out as part of the rig commissioning process), however the air inlet for the spouted bed can easily be changed over to use the gasifier outlet gases as they have identical fittings. The bubbling bed uses a distribution plate with the holes closest to the port blocked off to reduce air leakage between the two beds. The system was plumbed such that all three fluidising inlets can be operated independently. The transfer port can be fluidised via two low standpipes.
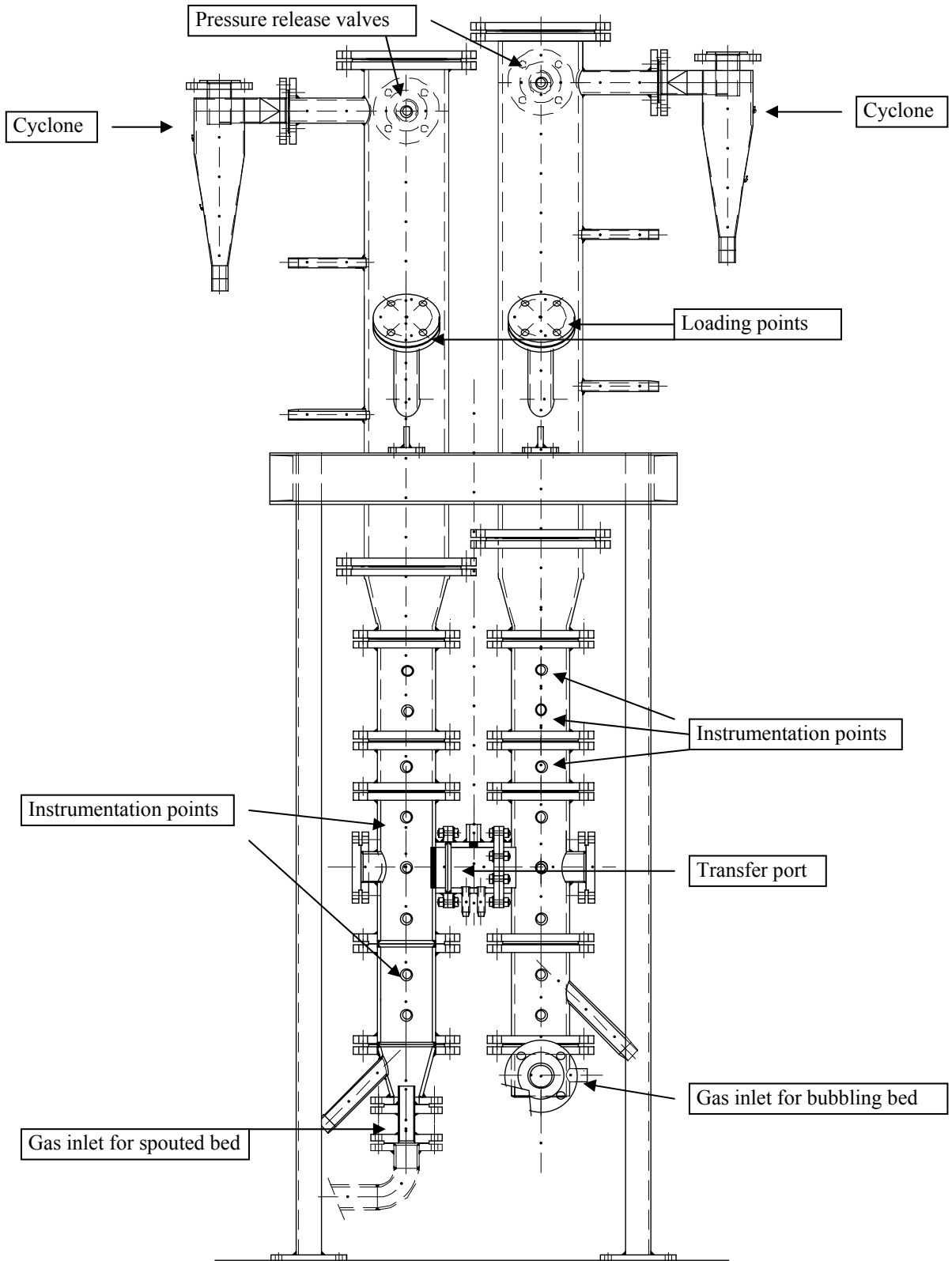
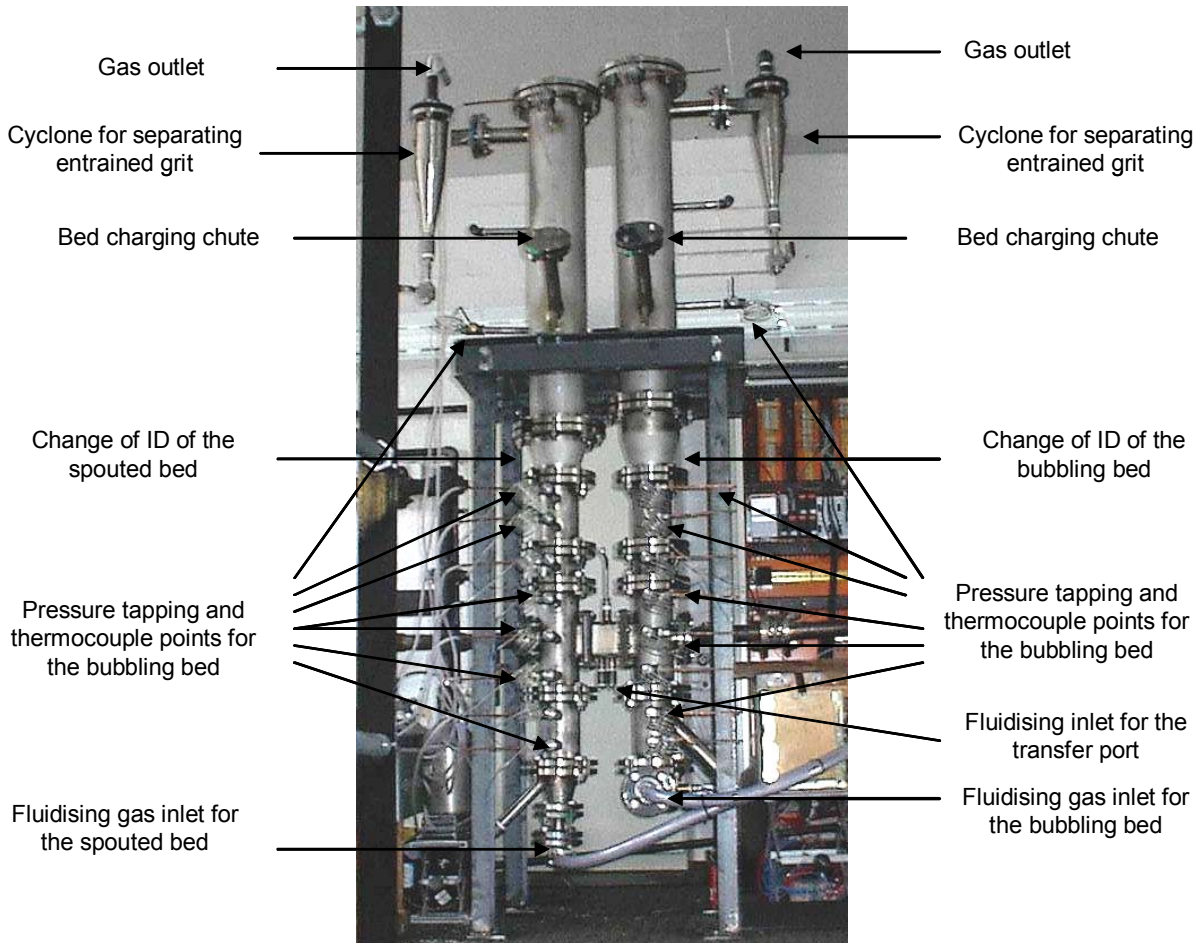**Figure 10 The basic design of the pilot scale twin-bed system**

Figure 11 Photograph of the pilot scale twin-bed system (before lagging)

Figure 11 shows the system as it was initially installed before it was connected to the gasifier and before the transfer port was lowered. Commissioning tests showed that the transfer port was in the region of slugging and had to be positioned lower to ensure that it was in the bubbling region of the two fluidised beds, as this is where maximum solids transfer occurs (as also shown by the cold modelling test work).

There are ten instrumentation ports on each of the fluidised beds, eight of which are below the expansion joint of the beds. Each of these ports has a thermocouple and a pressure tapping. Thus, during operation of the system, it is possible to determine how the pressure of the beds varies with bed height. This then enables the determination of the state of the fluidisation within the bed if the amount of bed material is known. The thermocouples extend into the centre of the beds allowing for the measurement of bed temperature as a function of bed height; this feature becomes important when running the system in series with the gasifier. The other minor modification was the addition of a secondary air inlet pipe to the spouted bed, which enabled the introduction of heated air into the spouted bed during trials investigating the performance of the twin bed system. This warm air supply enabled the spouted bed to be heated to approximately 80-90°C, so that when both beds were fully fluidised it was possible to calculate the solids transfer rate between the two beds by the change in temperatures of the two beds.

Figure 12 illustrates the integration of the twin bed gas cleaning system with the gasifier.
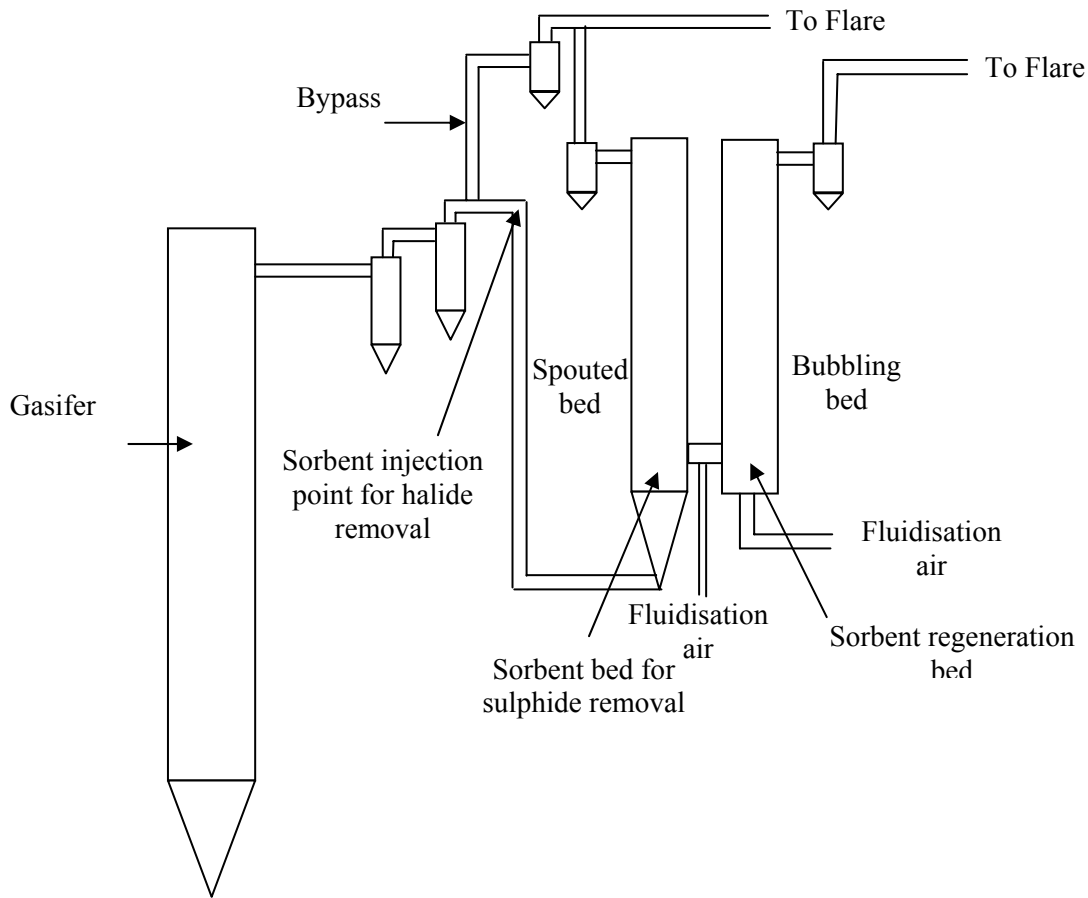
Figure 12 Diagram showing the integration of the twin bed gas cleaning system with the atmospheric gasifier.

4.2 Low Temperature Tests on Pilot Scale Twin-bed Reactors

A series of low temperature tests were carried out in the twin bed prior to its use together with the gasifier, in order to obtain solids transfer rates and to investigate the possible leakage of gas between beds. Due to the fact that the twin bed system was manufactured from stainless steel it was not possible to determine the solids transfer rate between the two beds by means of fluorescent tracers. Thus it was decided to use heat as a tracer between the two beds. In order to do this the spouted bed was heated to 90°C and then both beds were fluidised with the transfer port open. The temperatures in the two beds were monitored as well as the temperature of the inlet and the outlet gases for each bed. The information gathered was then analysed using an excel spreadsheet. From the heat capacities of the bed material, air and stainless steel it was possible to determine the mass transfer between the two beds by the increase in the temperature of the bubbling bed material and the outlet air. From these tests it was ascertained that the solids transfer rate between the two beds was in the range of 5-22kg/s/m^2.

The graph in Figure 13 shows how the temperature in the twin bed system changes with time after the spouted bed has bed heated up to 90°C. Series 1-3 and Series 5-7 are the temperatures of the bed material in the spouted and bubbling beds respectively, while the Series 4 and Series 8 are the exit gas temperatures in the two beds. As can be seen from the graph it takes about 80 seconds for the temperature in the spouted bed to equalise. The heat and energy balances were calculated from the data between 90 and 150 seconds.
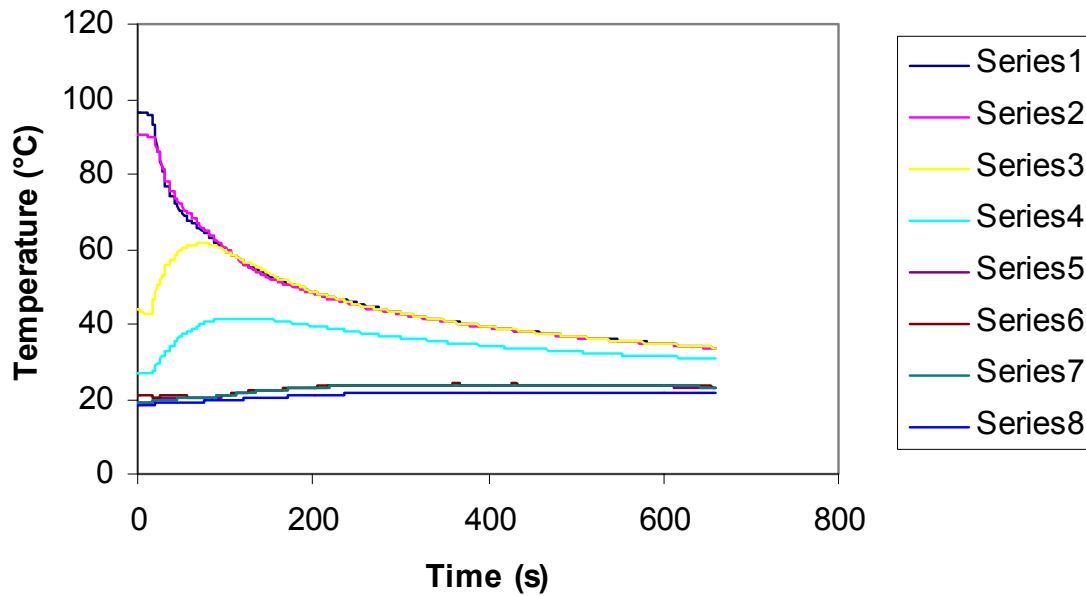
Figure 13 Change in temperature of the two beds with time
(Series 1-3 are spouted bed temperatures; Series 5-7 are bubbling bed temperatures; Series 4 and 8 are the gas exit temperatures for the spouted and bubbling beds respectively)

In most cases when using the twin bed system the desire is to attain as high a solids transfer rate as possible with a low gas leakage as the beds are likely to be fluidised from different sources. For example in the case of using the twin bed system as a heat exchanger for gasification the amount of gas leakage between the two beds is important and needs to be kept to a minimum. It would be undesirable to have oxygen leaking into a vessel containing high temperature hydrogen or high temperature hydrogen leaking into a vessel containing air. In order to measure the leakage between the two beds it was decided to use CO_2 as a tracer gas, as it is readily detectable and non-toxic.

Two different sets of tests were conducted to determine the leakage between the two beds. In the first set of tests 30 l/min of CO_2 was injected into the fluidising air of the spouted bed and the volume percent of CO_2 in the exit gases of the bubbling bed was measured. In the second set of tests 30 l/min of CO_2 was injected into the bubbling bed and the volume percent in the spouted bed was measured. The tests were carried out over a range of different operating conditions in order to determine their effects on the gas leakage between the two beds. The results of these tests are given in Tables 1 and 2.

Table 1 Results of the gas leakage tests

Test A	Spouted (l/min)	Bubbling (l/min)	Port (l/min)	CO_2 in spouted bed (l/min)	CO_2 bubbling bed Vol %	Leakage %
1	300	300	0	0	0.025	
2	270	300	0	30	0.28	2.60
3	270	300	50	30	0.22	2.17
4	270	300	75	30	0.2	2.03
9	320	300	0	30	0.26	2.40
6	320	300	50	30	0.19	1.84
7	320	300	75	30	0.21	2.14
8	320	300	100	30	0.22	2.33
10	320	350	0	30	0.25	2.68
11	370	350	0	30	0.18	1.87
12	370	350	0	30	0.19	1.98
13	470	350	0	30	0.19	1.98
14	270	350	0	30	0.25	2.68
15	270	350	50	30	0.21	2.38
16	270	350	75	30	0.22	2.58

Table 2 Results of the gas leakage tests

Test B	Spouted (l/min)	Bubbling (l/min)	Port (l/min)	CO_2 in bubbling bed (l/min)	CO_2 spouted bed Vol %	Leakage %
1	300	270	0	30	0.2	1.80
2	300	270	50	30	0.2	1.95
3	300	270	75	30	0.19	1.91
4	350	270	0	30	0.19	1.98
5	350	270	50	30	0.17	1.88
6	350	270	75	30	0.19	2.20
7	350	270	100	30	0.15	1.73
8	350	320	0	30	0.17	1.75
9	400	320	0	30	0.16	1.87
10	500	320	0	30	0.14	2.00
11	300	320	0	30	0.14	1.20
12	300	320	50	30	0.12	1.08
13	300	320	75	30	0.12	1.13
14	300	300	0	0	0.025	

As can be seen from the Tables 1 and 2, the gas leakage between the two beds ranges from 1 to 2.5 vol%. Due to the ±20% error in the measurement of the CO_2 it is difficult to determine any trends with the changes in the fluidising velocities. However, it does appear as though the degree of fluidisation of the port does affect the gas leakage. As shown in the following graph.
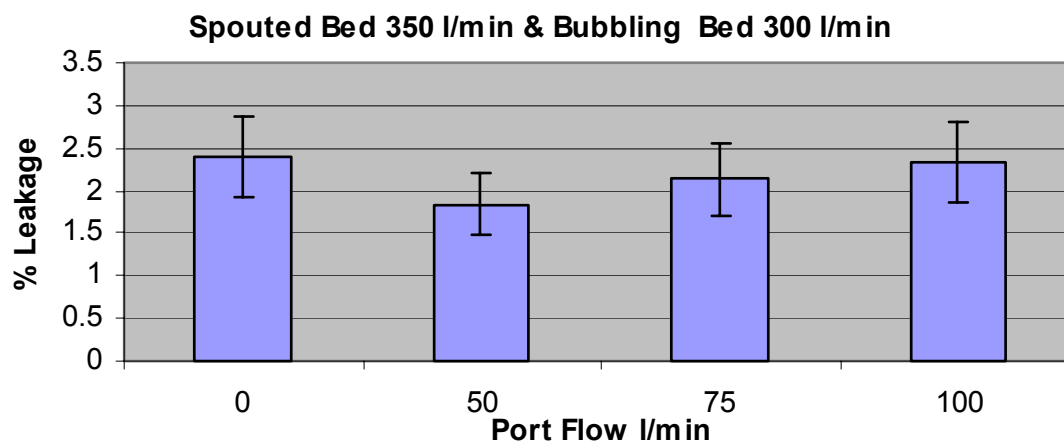

Figure 14 Effect of port fluidisation on the gas leakage

The general trend was that 50 l/min in the port reduced the gas leakage between the two beds. However, as the flow in the port is increased the leakage rate started to increase. Even this trend was not observed in all cases.

4.3 Operation of the Twin-bed Linked to the 0.15 m Atmospheric Pressure Gasifier
Once the performance of the twin bed had been assessed with the tests described in section 4.2 above, the system was integrated into the atmospheric pressure gasifier system (Figure 12) and a series of tests carried out to evaluate the performance of the twin bed system under more realistic operating conditions.

4.3.1 Sulphur Sorbent Selection and Experimental Parameters Investigated
It was originally intended that such tests would be carried out on a range of sorbents, but during the course of the project it became apparent that currently available sorbents would not work under the proposed twin-bed operating regimes. This information came from a combination of (a) other studies looking at sorbent performance [e.g. 12, 13] (Cranfield is involved in one of these projects, but detailed data provided by other partners can not be released due to confidentiality agreements [13]), (b) the assessment of twin-bed operating conditions carried out in the development of the mathematical models (section 3.1), and (c) the operating conditions achieved in the pilot scale twin-bed system.

Gasification fuel gas desulphurization is traditionally carried out by means of low temperature absorption processes. Low temperature H_2S absorption reduces the overall cycle thermal efficiency by a few percent as a result of the exergy losses in the cooling. The same residual H_2S levels can potentially be obtained through high temperature gas cleaning, thus avoiding this efficiency loss. H_2S removal at elevated temperatures can be carried out in a number of ways:
- Sorbent injection in the gasifier can serve as a bulk gas desulphurization. In situ desulphurization using limestone or dolomite can reach levels of 100 ppm.
- Desulphurization can be achieved too through the use of (regenerable) transition metal oxides.

One critical step in the use of these sorbents is the regeneration. At 400 ° C, nearly all transition metal oxides are suitable for desulphurization. At higher temperatures the H_2S residual levels increase with levels over 500 ppm over 500 ° C for many of them. Zn oxide seems to be the best sorbent capable of reaching the ppm level at high temperatures, however, metal volatilization can be a serious problem. Sorbent regeneration simulations have been carried out with different Zn-based materials and it has been proved that temperatures in excess of 700 °C are required to avoid sulphate formation and that the minimum regeneration temperature strongly increases with the partial pressure of oxygen. If desulphurization and regeneration temperature are much different, temperature gradients from one reactor to another can be expected and zinc evaporation is likely to occur in the reducing atmosphere of the desulphurization reactor (and zinc vapour species in the fuel gas stream would cause significant damage to downstream components, e.g. the gas turbine [15]).

In summary, the regeneration conditions required for available sorbents were incompatible with the use of the twin-bed system with a heat exchanger in the sorbent regeneration bed (i.e. the bed temperature would be too low). Existing regenerable sorbents would need to be used with a more complex set of reactors (which was outside the scope of this project), such as the triple bed reactor scheme suggested in the scale-up section of this report (section 6.1). It is known that alternative sorbents are being developed that may be more suitable, for example by Chinese workers developing them for the Smoven process, but these were not available to this project.

Therefore, it was decided to evaluate all the solid flow and heat transfer properties of the twin-bed system at a range of operating temperatures using limestone. This would provide real performance data to enable the best validation of the mathematical models that was currently possible and confirmation of the findings of the cold modelling programme. In addition, the sulphur adsorption of the limestone would provide data on the effectiveness of the twin-bed concept in removing sulphur from the fuels gases (again providing validation data for the mathematical model developed, section 3.1). The duration of each of the series of tests carried out was selected to allow stable operating conditions to be established throughout the gasifier/twin bed system at each of the different test conditions.

The parameters varied in these tests were:
- Spouted bed operating temperature
- Spouted bed fluidisation
- Bubbling bed operating temperature
- Bubbling bed fluidisation

4.3.2 Gasifier Operating Conditions
Full details of the atmospheric pressure gasification process are given elsewhere [6]. In brief, crushed coal (≤3mm) and air were injected into the bottom of the conical base of the 0.15 m diameter gasifier (Figure 12). Typical operating conditions for the gasifier are given in Table 3. The bed temperature of the gasifier was controlled by external electrical heaters, together with the coal and air (preheated to 300°C) fed into the spouted bed. The operating conditions of the gasifier (Table 3) had to be adjusted from their normal values to generate enough gas flow to allow the fluidisation of the spouted bed part of the twin bed system. This was achieved by supplying more nitrogen than usual to boost the gas flow (which also had the effect of diluting the product gas composition). For all the tests carried out, the gasifier was started up using an anthracite coal and then the fuel was switched to a bituminous coal (Daw Mill coal). Table 4 gives analyses of the Daw Mill coal.

Table 3 Operating conditions for the 0.15 m Gasifier

Feedstock – start-up	Anthracite coal (1 - 3.5 mm)
Feedstock – steady state operations	Bituminous coal (1 - 3.5 mm)
Coal Feed Rate	Typically 5 kg/hr
C:O ratio	2.5
Bed Temperature	980 ° C
Bed Height (fluidised)	0.6 m
Gas velocity	1 m/s
Fluidising gas	Air and nitrogen
Bed Off-take	1 kg/hr
Air preheated	300 ° C

Table 4 Chemical analysis of Daw Mill coal used in the gasification experiments (as received moisture basis)

Moisture %	6.1
Ash %	2.7
Volatile matter %	33.2
S %	1.21
Cl %	0.23
Gross CV (kJ/kg)	34180
DAF CV (kJ/kg)	35680
C	82.10
H	4.99
N	1.77
O	5.7

4.3.3 Twin-bed Operation

The twin bed was filled with limestone with a mean particle diameter of 450 μm. The experimental conditions for the twin bed are compiled in Table 5. Nitrogen has been selected as fluidisation gas in the transfer port between bed to minimise the gas leak between both beds and to reduce the chance of contact of a reducing atmosphere with an oxidising atmosphere.

Table 5 Operating conditions for the twin bed

	Spouted bed	Bubbling bed	Transfer port
Sorbent (maximum diameter)	Limestone (450 μm)	Limestone (450 μm)	Limestone (450 μm)
Sorbent loading	2.75 kg	2.75 kg	
Fluidising gases	Fuel gases from gasifier	air	nitrogen
Fluidising velocity	0.72 - 1 m/s	0.78 – 1.70 m/s	
Inlet velocity	~ 1 m/s	0.52-0.92 m/s	0.23 m/s
Bed temperature	325 - 525 °C	150 - 320 °C	
Transfer port fluidising gas flow *	-	-	35 l/min

* value fixed by findings of low temperature operation, section 4.2

The temperatures along the rig were monitored during the experiments, as well as pressure readings in the gasifier and in the twin bed. These pressure readings were used to control bed height inside the gasifier, (to start/stop taking solids out of the gasifier) and also to know the quality of the fluidisation in the twin bed.

Gas analysis sampling was carried out with the gasifier operating at stable conditions. The analysis of CO_2, CO, CH_4 and H_2 was carried continuously and the concentration of H_2S measured in batch analysis (bypassing the twin bed to obtain the concentration in the raw gas stream). Typical gas concentrations obtained are compiled in Table 6.

Table 6 Typical raw gas concentrations obtained with the gasifier operating in stable conditions with a bed temperature of 980°C

| Gas	% volume
H_2	4.28
CO	5.05
CH_4	0.77
CO_2	4.82
H_2S	400 ppm
HCl	70 ppm

Measurements to determine of H_2S levels were carried out using Draeger tubes. For each measurement, a known volume of gas (100cc) was pumped through a Draeger tube; to reduce uncertainties, this procedure was repeated at least three times.

Once the gasifier was operating in stable conditions the outlet gas stream from the gasifier was diverted through the twin bed. Temperature evolution in the twin bed from the time when it was connected to the gasifier has been compiled in Figures 15 and 16 for given fluidization conditions. The nature of the twin-bed system means that these data allow both heat and mass transfer between the fluidised beds to be determined for the specific operating conditions being evaluated.

The effect on the system of the fluidisation velocity in the bubble bed has been studied during these experiments by changing the air flow introduced in this bed and letting the system to stabilise again. As can be seen a change in the flow affects to the communication between both beds as well to the fluidization quality in the bubble side of the twin bed.

As can be seen in these figures a lower velocity in the bubble bed (the velocity in the spouted bed is determined by the gasifier operation conditions) gives a lower solids exchange between both beds. This is deduced from the slower heat transfer from the spouted to the bubble bed. From this heat exchange can be calculated the solids transfer between beds as it was done with the previous tests.

Then, the solids exchange flow calculated from the data compiled in Figure 16 is 11 kg/m^{2}s, this flow is in agreement with the data obtained from the 2-D cold model rig and in the 3-D twin bed, respectively.
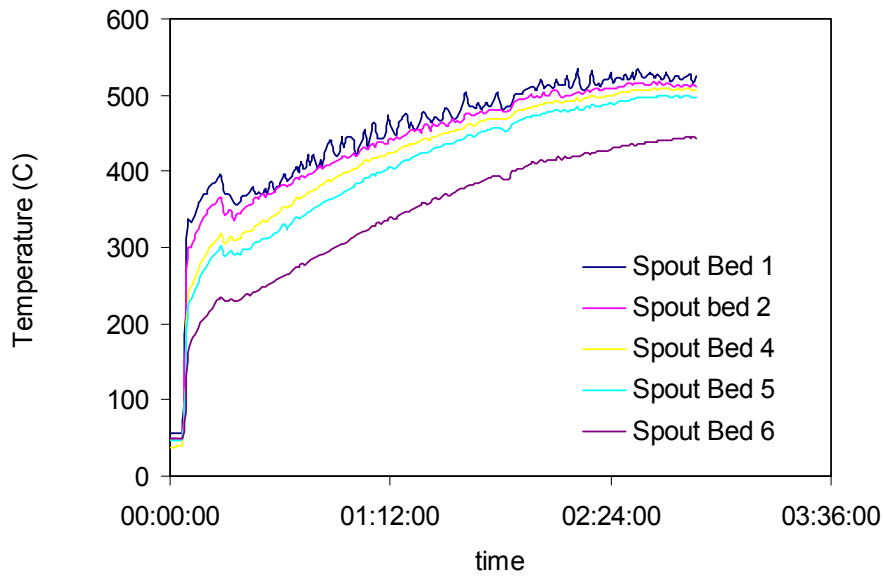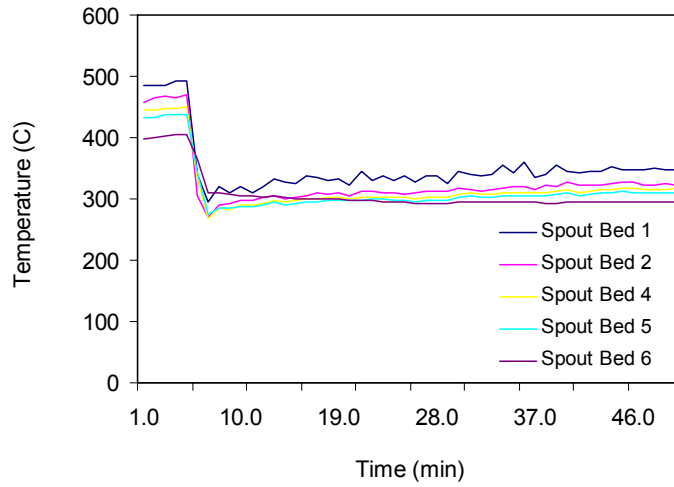
(a) Effect of exposure time on the heating of the spouted fluidised bed (1 – 6 are thermocouple measurements at increasing heights up the spouted fluidised bed reactor)
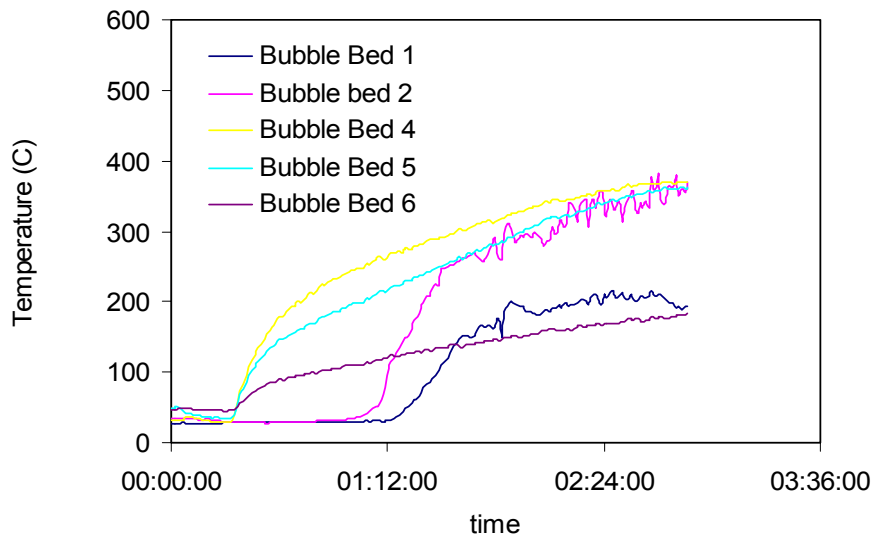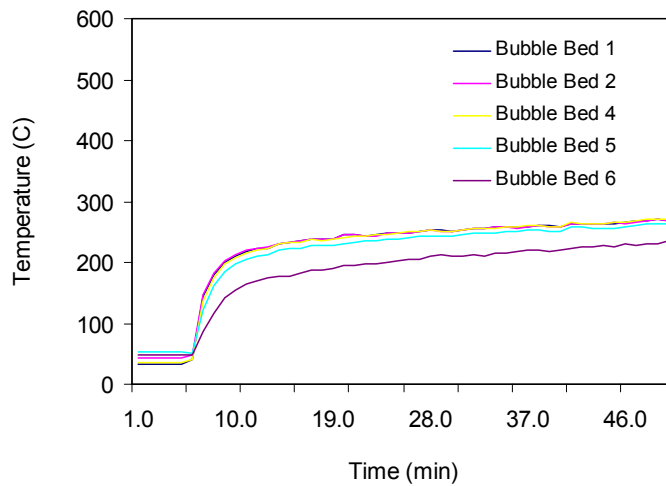

(b) Effect of exposure time on the heating of the bubbling fluidised bed (1 – 6 are thermocouple measurements at increasing heights up the spouted fluidised bed reactor)

Figure 15 Development of temperature profiles in the twin bed after being connected to the gasifier-derived fuel gas stream with $u_{spout\ bed} = 1$ m/s and $u_{bubble\ bed} = 0.55$ m/s

(a) Effect of exposure time on the heating of the spouted fluidised bed (1 – 6 are thermocouple measurements at increasing heights up the spouted fluidised bed reactor)

(b) Effect of exposure time on the heating of the bubbling fluidised bed (1 – 6 are thermocouple measurements at increasing heights up the spouted fluidised bed reactor)

Figure 16 Temperature profiles in the twin bed after being connected to the gasifier, with $u_{spout\ bed} = 1$ m/s and $u_{bubble\ bed} = 0.82$ m/s

As has been explained the analysis of gas composition was carried out continuously for CO_2, CO, CH_4 and H_2, and the results obtained during the operation of the twin bed are compiled in Table 7. The sampling point is located in the outlet of the spouted bed. Composition of the gas is very close to the gas obtained directly from the outlet of the gasifier; this indicates that the gas transfer between both sides of the twin bed is very low. This result is in agreement with the previous results obtained injecting CO_2 to the spout bed and measuring the concentration in the bubble bed, and is very important in isolating the reducing atmospheric from the oxidising atmospheric in the regenerating bed (bubble bed).

Table 7 Typical gas concentrations obtained in the outlet of the twin bed

| Gas	% volume
H_2	4.24
CO	5.48
CH_4	0.67
CO_2	4.65

To study the effectiveness of the twin bed as H_2S sorbent, several analyses have been carried out during the operation of this system. The analyses have been carried out with the same method as explained before, and the results are compiled in Table 8.

Table 8 H_2S concentration obtained during the operation of the twin bed

Test Condition	T Spouted Bed (º C)	T Bubble Bed (º C)	U Bubble Bed (m/s)	H_2S concentration (ppm)	Time (min)
1	325	260	0.92	300	45
2	350	300	0.82	100	75
3	360	320	0.61	183	130
4	400	150	0.55	225	140
5	500	300	0.55	175	180
6	515	295	0.68	150	270
7	525	318	0.86	325	310

As can be seen, the concentration of H_2S has been reduced in all the gas samples taken from the outlet of the twin bed. Three variables can affect to the sulphur removal from the gas stream in the operating conditions studied: gas temperature of both beds, velocity in the bubble bed and the time spent by the sorbent in contact with the contaminated gaseous stream.

The desulphurisation of reducing gases with limestone occurs according to the following reactions:

$CaCO_3 \rightarrow CaO\,(s) + CO_2\,(g)$
$CaO\,(s) + H_2S\,(s) \rightarrow CaS(s) + H_2O\,(g)$
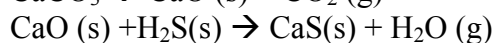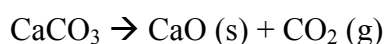
Although temperature seems to have only a little effect in the range of 600 to 800 ºC, below 600 ºC the reaction rate decrease strongly with decreasing temperature [7]. This tendency can be observed

in the results obtained in samples 4 and 5, for a given gas velocity in the bubble bed. The generalised trend in the whole set of samples is the reduction of H_2S emissions with increasing the temperature.

The second variable studied was the gas velocity in the bubble bed. The results reported above (e.g. Figure 15 vs. Figure 16) show that good fluidisation conditions are required in both fluidised beds to ensure sufficient particle movement between the beds. The better the fluidisation conditions, the higher the solids exchange between beds and so the higher the fresh sorbent supply is to the absorber bed (spouted). Test conditions 5 and 6 in Table 8 illustrate the benefits obtained in terms of lower H_2S levels after longer operating times from using a higher fluidising velocity in the bubbling fluidised bed. The effect of temperature and gas velocity can be observed as well by comparing the concentration of H_2S emissions for different bed 'life' times.

The benefits of lowering H_2S levels in the fuel gas stream on the lives of downstream components are discussed in section 6.2.

5. HALIDE REMOVAL STUDIES

The halide removal studies were targeted at evaluating the possibility of removing halide species (in particular HCl) upstream of a twin-bed gas clean-up/heat exchanger system using a solid particle inject. This would have the benefit of reducing the levels of HCl in the fuel gases that would be passing through the sulphur sorbent.

A literature review was carried out to identify potential HCl sorbents. This review identified Na based sorbents as the best to remove HCl. However, it also showed that Ca-based sorbents might also be satisfactory for HCl removal, particularly for atmospheric-pressure gasification systems [7]; but for Ca-based sorbents it has been seen that when trying to remove HCl in the presence of H_2S, the initial $CaCl_2$ is the displaced by the formation of CaS [8].

Therefore, as a result of the literature review, anhydrous sodium carbonate was selected as sorbent for these halide removal studies. The sorbent was injected upstream of the twin bed (as shown in Figure 12) entrained in a stream of N_2.The fuel gas temperature at this position in the gas path was 600 ºC.

A series of tests were carried out to evaluate the effectiveness of this sorbent. The parameters varied in these tests were:
- Sorbent injection rates (0 – 2.8 g / min)
- Carrier gas (nitrogen) flow rates (up to 10 l/min)

Gas sampling was carried out while the gasifier was operating in stable conditions both before and after the addition of the sodium carbonate, by pumping some of the fuel gas stream (sampled from downstream of the sorbent injection point) through bubblers containing distilled water. The solutions captured were later analysed to determine the HCl content of the fuels gases. The untreated fuel gas showed HCl concentrations of ~70 ppm. However, the samples taken from the gases treated with the sorbent did not show any HCl levels above the theoretical detection limit for this sampling technique (~2 ppm). In light of these analytical results from a wet chemistry method, tests were repeated using Draeger tubes (detection limit ~50 ppm), and similarly no significant levels of HCl were detected.

There are several potential reasons for these results:
- The sorbent removed all the HCl present in the fuel gas stream
- There was HCl remaining, but it was below the detection limits of both the sampling methods used
- There was further reduction of low HCl levels by interaction of the gas stream when it passed through new pipework (which at the pilot plant scale has a high surface area/gas volume ratio).

Further tests were carried out to evaluate the effect of the HCl sorbent (anhydrous sodium carbonate) on the H_2S levels both upstream and downstream of the twin-bed system. No changes in the H_2S levels were detected when the HCl sorbent was being used.

The use of the HCl sorbent did not have any measurable affect on the operation of the twin-bed system. One reason for this was that during the design stages of the twin-bed system, it had been decided to use the spouted fluidised bed for the fuel gas side of the twin bed system to avoid having a distributor plate in the fuel gas path. Such a plate would have been a potential blockage point when injecting solid sorbents upstream from it. Without a distributor plate, the fine HCl sorbent used in these tests would have been expected to have passed through the spouted fluidised.

6. SCALE-UP ISSUES

6.1 Scale up and Preliminary Design Specification
Scaling up the dual bed design requires a detailed understanding of the effects of operating characteristics on performance. This understanding, in the form of mathematical correlations and models, has come from the cold modelling and hot testing programmes pursued in this project. Work was done to develop these correlations and to upgrade the process models presented in section 3.1 in the gasification-heat exchange and S removal.

The basic criteria used for the scale up calculations for the system were:

- 100MW thermal
- Use reference coal properties
- 2 m expanded bed height
- Fluidising velocity 2 m/s
- Assumed inter-bed port transfer rate of 20 $kg/m^2/s$

Two options for gasification plant design were suggested as worth pursuing as a viable use of this technology. The first involves a twin-bed gasification-heat exchange system, where gas from a gasifier is fed to one vessel and heat is transferred to a second by means of re-circulating solids. Fluidising air is supplied to the second bed, and a portion of the heat is removed by a heat exchanger in the form of superheated steam. The second option is that of a triple-bed adsorption-regeneration-heat exchange system. Here gas from a gasifier is fed to one vessel and H_2S removed, catalyst is transferred to a second bed for regeneration, and solids transferred to a third bed where again heat is removed by a heat exchanger and by the sensible heat in the fluidising air.

In view of the different geometrical configurations, two theoretical frameworks have been devised, viz. one for the twin-bed design, and a completely different one for the triple-bed plant.
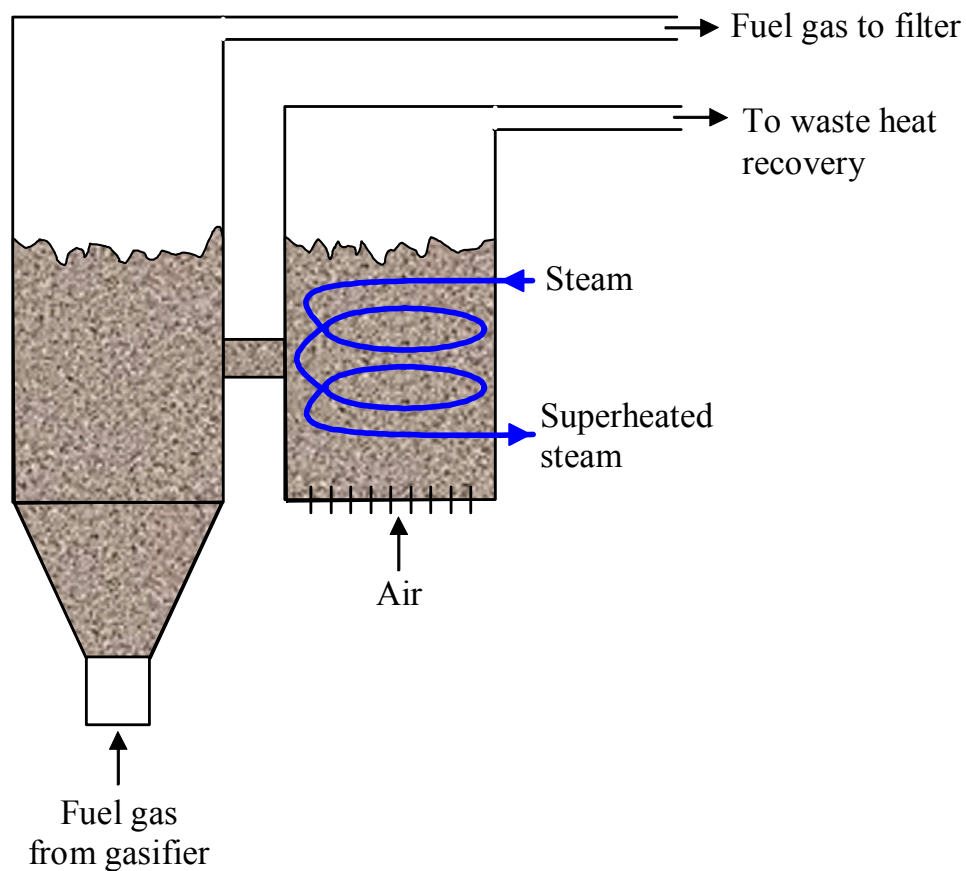
Figure 17 Schematic of the proposed twin bed system for the gasification heat exchange

Figure 17 is a schematic of the twin bed system that could be utilised in a number of different manners. In all three cases the superheater is in the 2nd bed and is thus separated from the corrosive gases thus increasing the life of the system and allowing the production of superheated steam. Currently due to the fact that the corrosion is too high, gasification systems can't be used to produce superheated steam. There is however the risk of agglomeration in the first bed due to the particles entering with the gasification gases.

In the case of sulphur removal three beds would be needed due to the fact that adsorption and regeneration occur at similar temperatures. The adsorption would occur in the first bed, the regeneration in the second bed and heat exchange would occur in a third bed. A schematic of the triple bed system is shown in Figure 18.
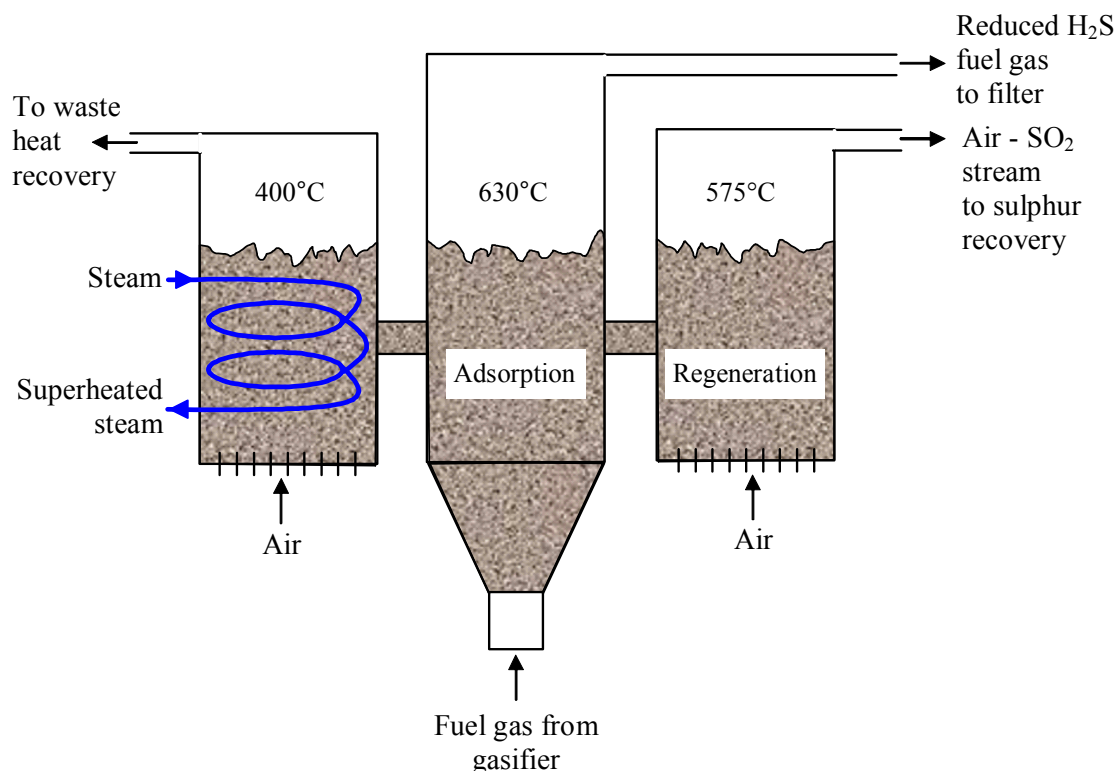
Figure 18 Schematic of the proposed triple bed system for removal of sulphur

The results of the mathematical model, cold modelling and hot testing indicate that the transfer rates are sufficiently high to warrant further studies in order to determine the full capabilities of the twin bed concept. The basic concept has been shown to work and all the results point towards a range of potential applications for the system. Theoretical frameworks were developed for two of proposed systems in the form of mathematical models presented as Pascal programs.

One model dealt with the cases of a gasifier gas-stream being fed to one bed and cooling air to a second, with solids recirculation between beds.

Another model examined the triple-bed adsorption-regeneration-heat-exchange concept. In this system gas from a gasifier is fed to one vessel and H_2S removed, sorbent is transferred to a second bed for regeneration. The solids are then transferred to a third bed where again heat is removed by a heat exchanger and by raising the temperature of the fluidising air. Again from certain input parameters the size and operating conditions/ temperatures of the system could be predicted.

For illustrative purposes, the models were run in order to carry out sensitivity analyses on certain parameters, for example the effect of bed diameter on cooling air flow rate, heat exchange between beds, etc. The models can now be used in design studies but would need to be supplemented by more detailed studies of fluidisation conditions within the beds.

6.2 Assessment of Potential Effects of Twin-bed Gas Cleaning Systems on Downstream Components

6.2.1 Introduction

The gas produced by a gasifier has a number of potential uses, for example, to fuel a gas turbine, internal combustion engine or fuel cell. Each use will have a specific requirement for maximum contaminant levels based on component, process and emission requirements that will need to be met by a gas cleaning system. To produce a suitable fuel gas for the above systems the twin-bed gas cleaning system will require additional downstream gas cleaning. The contaminants often have complex interactions, as illustrated in Figure 19, that can impact on the performance of gas cleaning systems and other hot gas path components. For example, the reduction of sulphur in the gas can change the dew-point temperature for trace metal species resulting in improved removal and/or enhanced corrosion. The effect of the twin-bed process on changing the fuel gas composition has been assessed for the components anticipated in a gasification combined cycle power plant (i.e. hot gas filters, ductwork and valves, and gas turbines) and is discussed below.

6.2.2 Hot Gas Filtration and Solid Products

The hot gas filtration systems need to operate in aggressive gasification environments at 250-700°C and at pressures of 10-25 bar$_g$, depending on the particular gasification system. In order to realise fully the cost and environmental advantages, it is essential that the systems provide not only efficient contaminant removal but also have the reliability and availability required of the overall system. Over the years, adaptations to system configurations and more realistic expectations of filter performance have led to the original choice of ceramics for the filter medium being questioned. It is now apparent that reliable, lower cost filter systems can be operated using metallic filter media, provided improved materials selection and advanced fabrication methods are developed. Metallic filter media provide a number of significant advantages over ceramics [14]. The potential for fuel gases to cause sulphidation, erosion and fouling raises concerns over the selection of materials and the lifetimes of filter components.
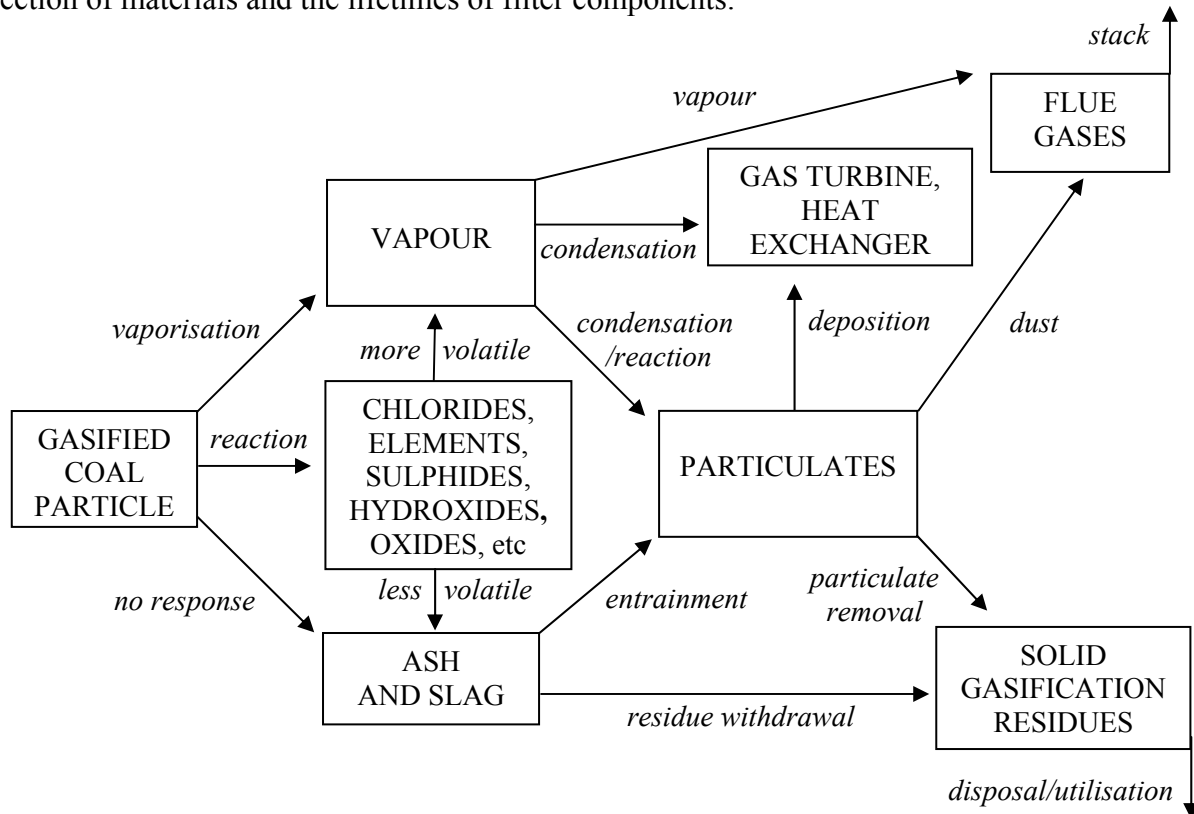

Figure 19 Flow Diagram of Fate of Trace and Alkali Metals in Gasification Systems With Hot Gas Cleanup

The twin-bed gas cleaning system could potentially add to the gas particulate loading (the particulate limits for a number of components are given in Table 9). Typically, filters are operated above 350°C to avoid problems with tar formation and ideally would be able to operate to at least 600°C. Materials selection for this unit is a complex issue but one major limiting factor is high temperature sulphidation resistance. Recent work [14] has demonstrated that for the materials studied the upper working temperature is strongly influenced by the hydrogen sulphide concentration in the gas as shown in Figure 20. Clearly, lower hydrogen sulphide concentrations in the gas may allow cheaper materials to be selected for some component parts.

Table 9 Examples of Gas Particulate Limits for Power Generation Equipment [16-18]

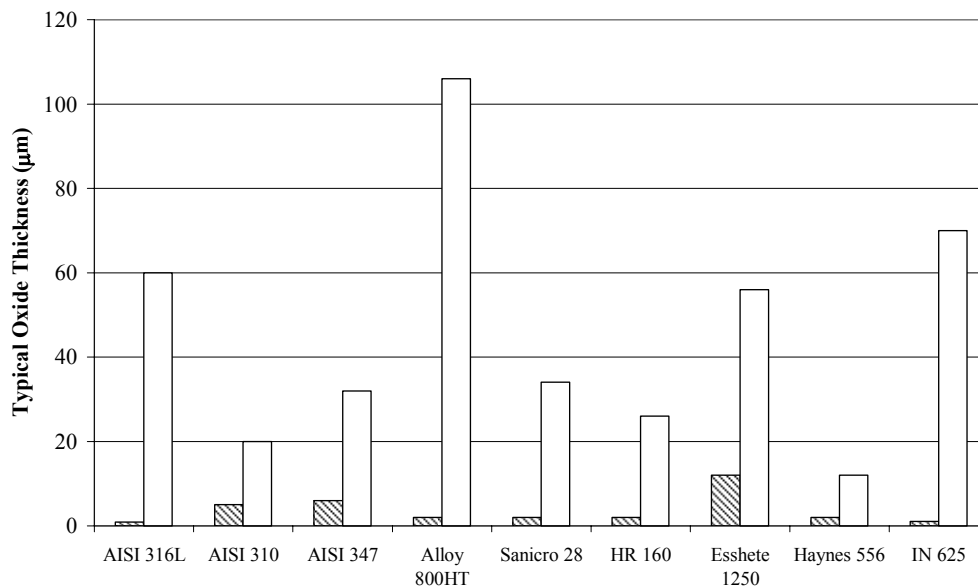| Component	Particle size	Limit
Internal Combustion Engine	<10 μm	<50 mg/Nm^3
Gas Turbine	>20 μm	<0.1 mg/Nm^3
	10 - 20 μm	1.2 mg/Nm^3
	5 - 10 μm	10-15 mg/Nm^3
	<5 μm	40-100 mg/Nm^3
Molten Carbonate Fuel Cell	>0.3 μm	<0.1 g/l

Figure 20 Comparison of typical oxide thickness for candidate filter materials tested at 550°C for 700 hours in simulated gasifier fuel gas containing either 0.02% H$_2$S (unshaded) or 1% H$_2$S (shaded).

The solid products that need to be removed from the hot gas filter and twin-bed reactors will all be influenced by the composition of the sorbent that is used in the twin-bed gas cleaning system. At present, no sorbent has been identified for this duty, so assessment of the residue properties in not possible.

6.2.3 Ductwork and Valves

On the clean side of the filter, the ductwork would be metal lined (to prevent refractory spallation from entering the downstream gas turbine) and there is a need for a fuel control valve. Lifing issues for these components were considered during the assessment of materials for an ABGC pilot integrated plant [19]. High temperature sulphidation was one critical degradation route for such components, and so reduced hydrogen sulphide levels will reduce the damage caused by this degradation route. If there is sufficient sulphur removed, then the dominant degradation mechanism can be changed to oxidation [e.g. 20], which occurs at much lower rates as illustrated in Figure 21.

6.2.4 Gas Turbine

All combined cycle power systems utilise industrial gas turbines, whatever the fuel. The successful development of economically viable advanced power systems relies on their gas turbines giving high efficiencies together with acceptable performance and availability. In particular, the blading materials for these gas turbines must give acceptable and predictable in-service lifetimes.

The gas turbine will receive a fuel gas from the gasifier that has been cleaned to meet a set specification to protect the turbine components and meet emission regulations. Gas turbine fuel specifications set limits on alkali metal and other trace metal species. Hydrogen sulphide in this gas will be oxidised to SO_X that can combine with alkali and other trace metal species and condense onto blades as sulphates. These deposits can increase the corrosion rate of the blade materials and reduce service lifetime.
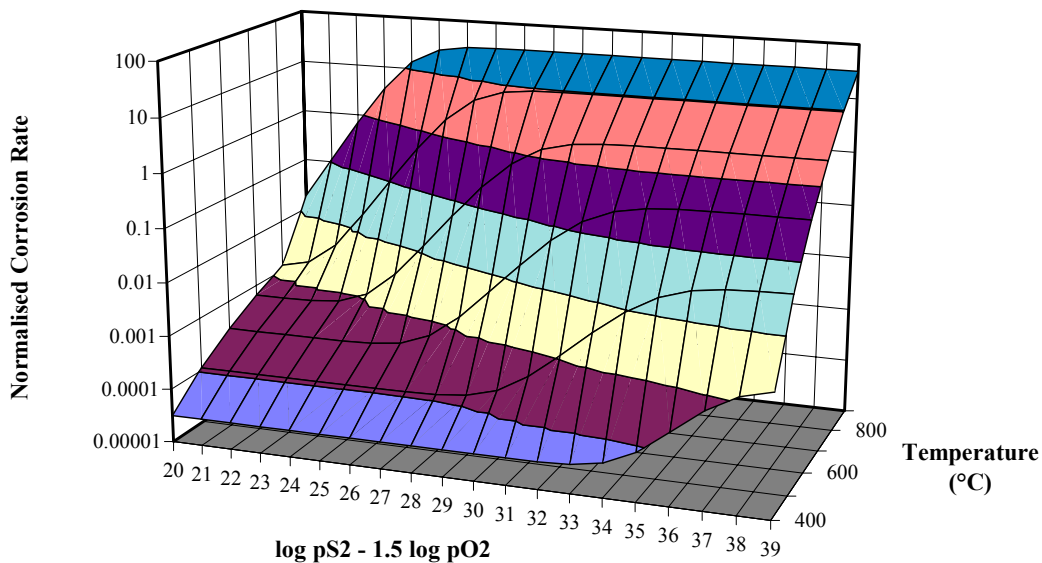

Figure 21 Example of corrosion map for gasifier fuel gases with variable sulphur contents
(materials behaviour varies from oxidation to sulphidation on moving from bottom left to top right of diagram)

Thermodynamic studies [15] have been used to predict dewpoint temperatures for potassium and sodium in a typical gas turbine. Figure 22 illustrates the dewpoint temperatures for potassium sulphate plotted as a function of contaminant levels for different SO_X and HCl levels and gas pressures. This example shows that the K_2SO_4 dewpoint increases with increasing K or SO_X levels in the gas stream, as well as gas pressure, but decreases with increasing HCl levels in the gas stream. Lower SOx levels will reduce the dewpoint temperatures for vapour phase derived sulphate deposit formation and therefore reduce the areas of turbine hot gas path components, especially aerofoils, that are likely to be covered by these deposits. Reduced fluxes of such deposits together

with the reduced SOx levels in the surrounding gas will result in reduced corrosion rates (Figure 23 [21]).
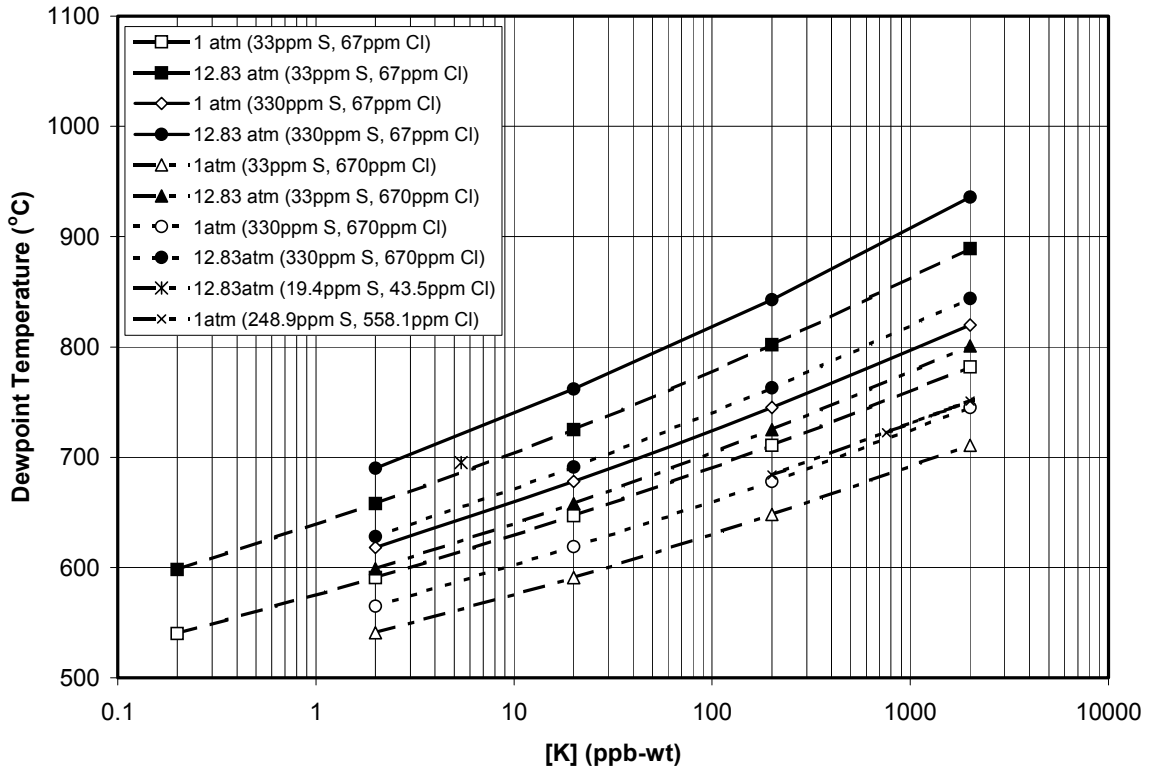

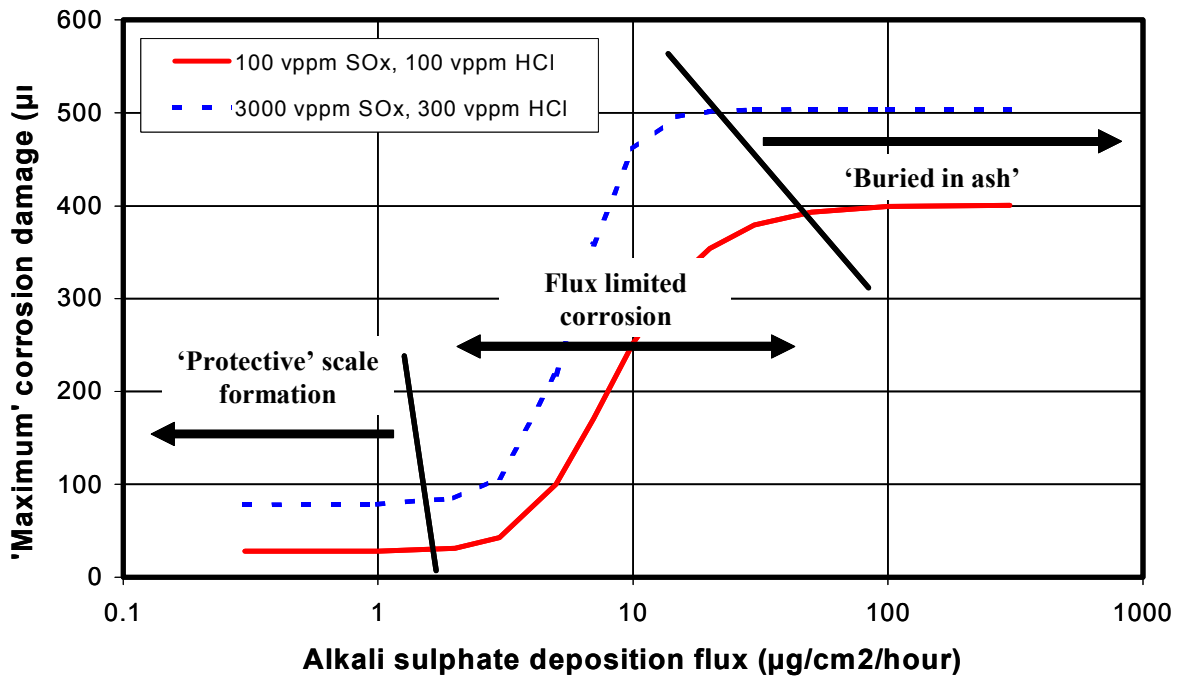**Figure 22 Dependence of K$_2$SO$_4$ dew-point on gas pressure, S, Cl and K levels [15]**

Figure 23 Effect of deposition fluxes and gas compositions on corrosion rates of a commonly used gas turbine material (IN738LC) [21]

7. CONCLUSIONS

The potential of a new type of hot gas cleaning/heat recovering system for gasification systems has been investigated.

This investigation consisted of a number of distinct stages:
- development of initial mathematical models
- design, construction and use of a 2-D cold model
- design, construction and use of a 3-D twin bed system, initially as a cold model, but then attached to a pilot scale coal gasifier
- consideration of scale-up issues using the mathematical models developed and tested.

The studies carried out with the cold model were the key issue to determine the height at which the transfer port between the beds should be located. Preliminary studies were done to determine the solids transfer between beds depending on operating conditions and to determine the gas leak from one bed to the other. From these tests was ascertain that the solids transfer rate was in the range of 5-22 $kg/s/m^2$ and the gas leakage between the two beds ranges from 1 to 2.5 % volume.

The final design of the pilot scale twin bed consisted of two adjacent fluidised bed connected via a port which would behave in a similar manner to a concentric system. The twin bed system had to be designed such that the spouted bed could be fluidised by the outlet gases of the gasifier. Thus the twin bed was designed around the output capability of the gasifier, effectively fixing the size (internal diameter) of the fluidising gas inlet pipe in the spouted bed. This then determined the size of the spouted bed and the bubbling bed.

The twin bed was operated using gas supplied from an atmospheric pressure gasifier to prove its effectiveness removing sulphur and halide from a gas stream. The gasifier was operated with air and nitrogen at a typical temperature of 980 ºC and with a coal feed rate of 5 kg/hr. The H_2S concentration in the outlet gases from the gasifier was 400 ppm.

Limestone with a mean particle diameter of 450 μm was selected as sulphur sorbent. The twin system was filled with 0.2 m of solids on each bed. Once the conditions in the gasifier were stable the outlet gas from the gasifier was diverted to the twin bed. The evolution of the temperature profiles in the twin bed showed that a good communication between the two beds exists. Solids transfer rates in the order of 11 $kg/s/m^2$ were determined, which make the system suitable to act as a heat recovering system. H_2S concentration was measured at different operating conditions in the outlet of the twin bed system. In all the cases the sulphur emissions were reduced compared with the raw gas stream.

The H_2S retention increased with increasing the temperature in the spouted bed, although the temperature in the experiments was still too low to achieve the best results in sulphur capture. Higher velocities in the bubble bed resulted in increased particle flows between the two beds, increasing the 'fresh sorbent' flow to the spouted bed and so increasing the efficiency of the system both in sulphur emissions and 'life time' of the system.

Potential issues that could be encountered in scaling up the process were considered using the mathematical models developed and tested during the course of this project. These were useful to indicate the sensitivity of the twin bed system performance to dimensional and operating condition changes.

8. RECOMMENDATIONS

The twin-bed gas cleaning system shows promise for use on gasification systems, as has been demonstrated by inter-bed heat flux and reduced H_2S emissions in all the experiments carried out in the pilot scale hot test rig during this project. However, further work is necessary to understand the complex nature of this installation. A few modifications need to be made in this test system to obtain a better control of sorbent performance and regeneration. For example, the prototype twin bed should be externally heated to achieve higher temperatures. Temperatures in the order of 600-800 °C in the spouted bed would maximise the sorbent performance. The heat transfer to the regenerator would be increased by improving the sorbent regeneration.

Topics for further investigation could include:
- development of sulphur sorbents specifically for use in twin-bed operating conditions
- development of catalysts to reduce NH_3 emissions
- cleaning combustion derived gases
- increased understanding of inter-bed hydrodynamics
- scale-up of twin bed process for industrial development and demonstration

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10. MEANINGS OF SYMBOLS

A   Area of separation wall between the concentric beds (m^2)

A_f Area of the heat exchanger tube (m^2)

cg_1 Heat capacity of fluidising gas in bed 1 (kcal/kg C)

cg_2 Heat capacity of fluidising gas in bed 2 (kcal/kg C)

cs   Solids heat capacity (kcal/kgC)

d_b Bed diameter (m)

d_p Particle diameter (m)

gas_1 Mass flow rate of fluidising gas in bed 1 (kg/s)

gas_2 Mass flow rate of fluidising gas in bed 2 (kg/s)

h   Heat transfer coefficient of heat exchanger tubes (W/m^2K)

hh   Heat transfer coefficient of the separation wall (W/m^2K)

Hj   Jet height (m)

F_r Froude number

L_{mf} Bed height at minimum fluidising velocity (m)

ms   Solids mass flow (kg/s)

R_e Reynolds number

S_t Stokes number

T_0 Temperature of the inlet gas in bed 1

T_1 Temperature of the outlet gas in bed 1

u_1 Average superficial gas velocity in the spouted bed (m/s)

u_2 Average superficial gas velocity in the bubbling bed (m/s)

U_{mf} Minimum fluidising velocity (m/s)

$V_{1,2}$ Volume of the spouted/bubbling beds at minimum fluidisation (m^3)

W_0 Temperature of the inlet gas in bed 2

W_1 Temperature of the outlet gas in bed 2

W_f Temperature of the cooling fluid in the heat exchanger

ρ_s solids density (kg/m^3)

ρ_g Gas density   (kg/m^3)

λ Gas viscosity   (kg/ms)