Simultaneous removal of CO₂, SO₂, and NO_x from flue gas by liquid phase dehumidification at cryogenic temperatures and low pressure

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Abstract: The current paper presents a new process for postcombustion carbon capture. An historical survey of the cryogenic techniques used in the chemical industry for the removal of acid vapours is given, with particular emphasis on two Ryan–Holmes-based processes. The paper suggests that these two processes have the potential to achieve CO₂ separation from flue gas with high second law efficiency. A further variation on these processes is then proposed enabling the simultaneous capture of CO₂, SO₂, and NO_x from flue gas produced in conventional or combined cycle power stations, burning pulverized coal or heavy bunker fuels. The proposed process absorbs these vapours by dehumidification using a cooled liquid absorbent, at low pressure (close to atmospheric) and cryogenic temperatures. A feature of the process is the use of direct contact heat transfer to perform the major cooling and heating operations thus reducing the plant size and cost while improving efficiency.

The paper starts with a discussion of the most suitable absorbent for the process; liquid SO₂ is suggested and a simplified analysis of an absorption column is conducted using the technique developed by Souders and Brown. This analysis shows that with only four theoretical stages and an acceptable liquid/gas ratio of two, SO₂ is able to absorb CO₂ and leave a residual concentration of CO₂ in the flue gas equivalent to 90 per cent carbon capture.

The final section of the paper describes the use of dilute H₂SO₄ as a precooling stream to reduce the temperature of the flue gas prior to it entering the CO₂ scrubbing section. It is proposed to produce the necessary H₂SO₄ from the constituents of the flue gas using similar reactions to those of the ‘lead-chamber process’. The H₂SO₄ stream is also used to reheat the flue gas before it is passed to the chimney. It is shown that an important attribute of the H₂SO₄ stream is its role as a ‘lean-oil’, reducing SO₂ emissions from the power station to well below the levels required by future legislation.

Keywords: CO₂, SO₂, carbon capture, post-combustion, sulphur, coal

1 INTRODUCTION

Carbon capture and storage (CCS) is likely to form a major part of man’s attempt to reduce his output of carbon dioxide into the atmosphere. A recent UK Government report, clearly indicates that legislators are intent on supporting CCS into the next phase of

its development, namely the construction of a full size demonstrator power station [1]. However, CCS is still a young technology and there is considerable scope for new ideas to improve efficiency, reduce capital cost and enhance station safety and ease of operation.

There are a number of competing technologies for carbon capture in power stations, but these can be grouped broadly into two types: postcombustion and precombustion systems. The current paper will not attempt to discuss the relative merits of each type of carbon capture, as the literature contains a

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number of such analyses [2–6]. Instead, a new cryogenic process for postcombustion carbon capture that utilizes as absorbents liquids extracted from the flue gas is proposed.

2 CRYOGENIC SEPARATION

2.1 Historical perspective

McGlashan and Marquis [6] showed that many of the postcombustion carbon capture schemes, as proposed in the literature, have a low second law efficiency. They stated that this was due to additional entropy generation in the scrubbing section caused by mixing processes. Hise *et al.* [7] confirmed that the energy consumption in the scrubbing sections of physical or chemical absorption systems was intrinsically high. Physical or chemical absorption departs considerably from equilibrium. This departure can be seen as the ‘driving force’ for mass transfer of CO₂ from flue gas to absorbent and is indicative of the irreversibility of such processes.

Mass transfer can be achieved with much lower irreversibility by a process of condensation at cryogenic temperature and/or high pressure [7]. Cryogenic processes for carbon capture operate by passing the flue gas through a cooling stage where the vapour pressure of CO₂ is reduced sufficiently to enable its condensation, preferably as a liquid. The CO₂ depleted flue gas is then discharged. Cryogenic technology has been largely ignored or summarily dismissed in the literature due to its perceived low efficiency and practical difficulties when compared with other technologies [2, 7], but this is principally due to two physical properties of CO₂, namely:

- (a) high temperature of its triple point: $-56.6\text{ }^{\circ}\text{C}$;
- (b) high vapour pressure at its triple point: 5.11 bara.

Thus, if CO₂ is condensed from flue gas at close to ambient pressure, it will do so as a ‘hoar frost’ of dry ice, whatever the temperature. If a liquid condensate is desired, the flue gas needs to be compressed to at least 5.11 bara. However, the concentration of CO₂ in flue gas is generally very low. As a result very little CO₂ can be captured unless the pressure of the flue gas is raised considerably. The mass flow of flue gas in power stations is substantial, so the gas compressors required to perform this compression would represent a substantial capital cost and consume a considerable fraction of the power station’s electrical output. Even if the flue gas (after passing through a CO₂ condenser) was expanded in an efficient gas turbine to recover as much of the compressor power as possible, such a system will inevitably incur considerable losses. One benefit of this process, however, is

that it would deliver liquid CO₂, ready for transport to the storage site without the need for an additional liquefaction plant.

Cryogenic cycles have been proposed in which condensation of CO₂ occurs, forming ‘dry ice’ at temperatures well below the triple point and crucially with the flue gas at or near to atmospheric pressure [8]. Frosting methods for removing CO₂ from gas streams are not new, having been used in the ethylene industry, for example, since the 1930s [9]. Such cycles necessitate the use of two condensers undergoing alternate frosting and melting cycles – the cold being generated by a separate refrigeration plant. This alternate freezing/deicing cycle suffers from the disadvantage of relatively low heat transfer coefficients in the frosting condensers making them substantial. In addition, the capital cost is doubled since two condensers are required. This makes this type of cycle less attractive for power stations where margins are thin and the huge capital cost of the very large heat exchangers required, would be prohibitive.

2.2 The Ryan/Holmes process

An alternative cryogenic cycle, the Ryan–Holmes process, is used in a number of plants in the chemical industry [10, 11]. This process was primarily intended for the ‘sweetening’ of sour gas and a schematic diagram is shown in Fig. 1.

Features of this process are as follows:

- (a) gas compression of the flue gas to a high pressure;
- (b) a recuperative heat exchanger to aftercool the compressed flue gas and reheat the CO₂ lean flue gas before its subsequent expansion. Additional cooling is also required due to the higher mass flowrate of the flue gas entering the plant, and is provided by an additional refrigeration plant (not shown);
- (c) a high pressure, cryogenic distillation/absorption column into which is injected an ‘additive’, designed to maintain the CO₂ as a liquid/slush stream at temperatures below the triple point of CO₂;
- (d) a second high-pressure column designed to recover the ‘additive’ as the column bottoms stream, while the overhead is CO₂;
- (e) CO₂ liquefaction plant (shown as a simple overhead condenser run at high pressure in the schematic);
- (f) an expansion turbine to recover as much of the work of compression as possible.

A variation on the Ryan–Holmes scheme is the CNG process that also uses an organic liquid to prevent solid CO₂ forming in a low-temperature distillation/

Fig. 1 Schematic diagram of the Ryan-Holmes process for removing CO₂ from flue gas

absorption column [7, 12]. Like the Ryan-Holmes process the absorption is conducted at high pressure, the variation is the use of fractional crystallisation, rather than distillation, for the removal of CO₂ from the additive stream.

Both of these methods use a combination of physical absorption and dehumidification to remove CO₂ from a carrier gas stream (this can be described as a process of extractive dehumidification). The advantage of this is that it offers a way of reducing the CO₂ vapour concentration in the out gas without resorting to excessively low temperatures since there is an added driving force for mass transfer – the solubility of CO₂ in the absorbent. This will clearly reduce the power lost in compressing and then expanding the carrier gas since lower pressures are required. In addition, although the refrigeration load required to condense the CO₂ will not be reduced as the latent heat of vapourization is only weakly a function of temperature, the refrigeration is required at higher temperature and so a refrigeration cycle of higher coefficient of performance can be used.

A key feature of both the Ryan-Holmes and CNG processes is the eutectic forming 'additive' (butane in the original Ryan-Holmes patent) designed to prevent the liquid CO₂ freezing and choking the various columns. This enables the columns to be run at a much lower temperature than the triple point without the column freezing. Consequently, the residual concentration of CO₂ in the out-gas will also be reduced, due to the lower vapour pressure at this temperature. As a result, the ambient pressure in the absorber can usefully be reduced, while maintaining the same degree of CO₂ capture.

2.3 Discussion

Both the Ryan-Holmes and CNG processes were intended for sour gas treatment. As a result the processes were optimized for the removal of both CO₂ and H₂S. In addition, in sour gas treatment, there is usually a requirement to remove almost all the contaminate vapours. Consequently, very high pressures are generally used in the absorption columns of such plant.

Flue gases from power plant do not typically contain H₂S, and in a carbon capture plant a much higher percentage of CO₂ can remain in the flue gas – carbon capture plants are typically specified to remove only 85–90 per cent of the flue gases' CO₂. So, one option for a carbon capture process would be to adapt either the Ryan-Holmes or CNG process, but use an alternative 'additive' capable of keeping CO₂ liquid (or at least a slush) down to lower temperatures. This would make possible the operation of the process at, or around, atmospheric pressure and eliminate the requirement for flue gas compression. As is shown later, there are a number of binary mixtures between CO₂ and both organic and inorganic compounds, which are capable of remaining liquid at sufficiently low temperatures.

An additional weakness of both the Ryan-Holmes and CNG process is the scale and extent of the recuperator. If either of these processes was applied to a power station, the recuperator would need to cool down then heat up a large mass of the uncondensable constituents (mainly nitrogen) from the flue gas. Considering that the mass flow of flue gas in a typical power plant is of the order of tons per second, the recuperator would need to be vast, especially

allowing for the small 'approach' temperatures required to make the plant thermodynamically efficient. Building such a large recuperator would represent a significant cost, even if cheap materials like carbon steel could be used in its construction, but the presence of SO_2 , SO_3 , and H_2SO_4 as well as nitrogen-based acids represents a severe corrosion problem for carbon steels. Carbon steel may also suffer from embrittlement at low temperatures. A partial solution to the corrosion problem could be the use of plastic materials for the recuperator's shell. For instance, glass-reinforced plastic (GRP) is now commonly used in flue gas desulphurization plant [3] and is able to resist the dilute acids that condense from flue gas. A problem with many plastic materials is their reduced toughness at the low temperatures of interest, although reinforced plastics are generally considered less susceptible to this problem [13, 14]. However, even if metals can be avoided for the shell of the heat exchanger the material for the heat exchange tubes (or plates) clearly needs to have reasonable thermal conductivity and therefore probably will be made of metal. This will necessitate, at least in parts of the recuperator, the use of specialist corrosion resistant alloys with their associated cost.

To avoid the use of metal surfaces, an alternative to indirect heat exchange is clearly desirable. The Ryan–Holmes process performs much of its heat transfer using direct contact heat exchange. The advantages of direct contact heat transfer are detailed in reference [15] and reproduced here in modified form:

- (a) high heat transfer coefficient, due to excellent mixing;
- (b) simplified construction and maintenance;
- (c) elimination of metal walls with attendant thermal resistance and corrosion problems (and cost);
- (d) simultaneous heat exchange and absorption can be achieved.

Figure 2 shows a schematic of a proposed carbon capture plant embodying the principles of the Ryan–Holmes process, but using exclusively direct contact heat exchange. In operation, flue gas, driven by an enlarged forced draft fan (not shown), rises up a packed tower and is first cooled and then reheated by direct contact with a recirculating fluid. Due to the recirculation of the liquid stream, heat is extracted then returned to the flue gas regeneratively. This results in the need for a relatively small additional refrigeration load to overcome the latent heat of vapourization of CO_2 as well as any irreversibilities in the system.

Mass transfer of CO_2 from the flue gas to the recirculating fluid occurs simultaneously with heat transfer. Side distillation columns are used to remove the CO_2 from this fluid to avoid build-up. In the proposed plant these distillation columns are also used to

Fig. 2 Schematic diagram of generic absorption system

provide much of the refrigeration of the recirculating liquid; the columns are operated at low pressure and refrigeration is provided by flash of CO_2 vapour from the liquid stream followed by compression and subsequent condensation of this vapour. Thus a vapour compression refrigeration cycle is formed. Only a small additional refrigeration cycle would be required to provide the extra refrigeration necessary to cover losses.

The process shown in Fig. 2 is generic and it is assumed that a suitable absorbent can be found to maintain the absorbed CO_2 liquid. The choice of absorbent, however, is critical to the success of this process and will be discussed in the following section.

3 CO_2 ABSORBENT

3.1 Choice of absorbent

Treybal [16] gives a list of ideal properties for an absorption solvent used in a conventional absorption column. Different constraints apply in this case since the absorbent also needs to perform heat transfer duties and maintain CO_2 as a liquid. Hence, the following features are considered important:

- (a) gas solubility: the absorbent must be a good solvent for CO_2 vapour;

- (b) freezing point: the mixture of CO₂ and the absorbent needs to exhibit a low freezing point at least at some concentrations;
- (c) molecular weight: ideally the absorbent requires a low molecular weight as this affects the total mass circulated;
- (d) volatility: the absorbent should have a low vapour pressure to avoid its loss from the system;
- (e) corrosiveness: the absorbent should not require specialist materials to avoid corrosion problems;
- (f) cost: the quantity of absorbent used may be very large so its cost is a critical factor;
- (g) viscosity: low viscosity absorbents generally exhibit higher absorption rates for a given amount of absorbent and consequently reduce the power requirement of circulation pumps and also reduce an absorption tower's propensity for flooding;
- (h) chemical stability: the absorbent should either be chemically stable or be easily replaced as it degrades.

Of all of these factors the most critical for this application is the freezing point, since this must be sufficiently low to avoid the need for pressurizing the column. Studies have been conducted of many different binary mixtures between CO₂ and other substances, with many of these systems exhibiting low temperature eutectics [17, 18]. Eggeman and Chafin [19] describe the formation of solid CO₂ in cryogenic equipment and the different binary solutions used in industry to avoid this problem. There has also been renewed interest in the use of CO₂-based refrigerants where relatively small amounts of existing organic and fluoro-organic refrigerants are added to CO₂ [20]. By this means viable low temperature refrigerants are formed – again by eutectic formation.

Most of the literature on CO₂ binaries relates to those formed between CO₂ and organic compounds (the binary system CO₂/*n*-butane being used in the Ryan–Holmes process for example). In the case of a power station, however, due to cost constraints it is clearly desirable to avoid an additional feedstock. One way of doing this is to use a condensable constituent of the flue gas itself as the absorbent. Below is a list of the compounds contained in the flue gas that might be used in this way. These inorganic substances are either available directly or can be made from the constituents of the flue gas by some simple chemical steps as follows:

- (a) water;
- (b) sulphur dioxide;
- (c) nitrogen dioxide;
- (d) nitric oxide;
- (e) sulphuric acid;
- (f) nitric acid;
- (g) sulphur trioxide;

- (h) dinitrogen trioxide;
- (i) ammonia.

Examining this list, SO₂ appears to be a reasonable candidate for use as the absorbent due to its relative abundance in many flue gas streams and the fact that it can form and remain a liquid at the temperatures of interest. Does SO₂ meet the requirements for an absorbent detailed above?

3.1.1 Gas solubility

This subject will be discussed in detail in section 3.2.

3.1.2 Freezing point

The Smithsonian tables [21] give the temperature of a freezing mixture of dry ice in liquid SO₂ as –82 °C, but do not specify the composition of the resulting eutectic mixture. Thiel and Schulte [22] took measurements of the constant pressure equilibrium for a binary mixture of liquid CO₂ and SO₂ at –78.64 °C and critically specified the concentration in both liquid and vapour phases. These two references indicate that the freezing point of mixtures of CO₂ and SO₂ is relatively low.

3.1.3 Molecular weight

SO₂'s molecular weight (64.1 kg/kmol) is not low, but is of similar magnitude to CO₂'s (44.1 kg/kmol). As a result the inventory of circulating absorbent should be manageable.

3.1.4 Volatility

SO₂'s volatility is high at the temperatures likely to occur in the process. In consequence SO₂ is likely to boil-off into the flue gas stream. This problem can be resolved by the use of a 'lean oil' downstream of the scrubbing section to capture any SO₂. As will be shown later in the current paper, sulphuric acid (produced by the oxidation of SO₂ in the plant) can be used in this way in an additional precooling stream.

3.1.5 Corrosiveness

SO₂, being an acid gas, represents a potential corrosion problem, especially when damp. This will necessitate the use of materials of construction similar in places to those used by the sulphuric acid industry. Fortunately, corrosion rates are generally lower at cryogenic temperatures [23] and the low levels of water vapour present at these temperatures should also reduce corrosion rates.

3.1.6 Cost

SO₂ is freely available in many flue gases if medium to high sulphur fuels are being burned and can be condensed from the flue gas stream at low temperature.

3.1.7 Viscosity

A graph of the dynamic viscosity of liquid SO₂ and CO₂ is given in Fig. 3. This graph has been drawn using correlations from Yaws [24]. The dotted lines show an extrapolation of the formulae beyond their stated temperature range. As the graph shows, SO₂ and CO₂ have a very low viscosity.

3.1.8 Chemical stability

SO₂'s chemical stability is high, but an issue is the slow oxidation of SO₂ in the presence of NO₂ to sulphuric acid, this will necessitate the fuel having sufficient sulphur to maintain the quantity of SO₂ in the process.

Overall, SO₂ appears to meet many of the requirements for an absorbent and the following section details an analysis of an absorption column for CO₂ using liquid SO₂.

3.2 CO₂ absorption efficiency

The most important factor in selecting an absorbent is its ability to absorb CO₂. As a result, to analyse an absorption column using liquid SO₂, a model of the vapour liquid equilibrium (VLE) of the SO₂/CO₂ binary is required. The literature contains relatively little data on this binary and there is no specific

Fig. 3 Graph of the dynamic viscosity versus temperature of liquid SO₂ and CO₂ [24]

model for activity coefficients or an equation of state. Hence, a Gamma-Phi model of the VLE was constructed and this model is included in Appendix 2 for information.

Of interest at this stage is the efficacy of liquid SO₂ as an absorbent of CO₂ vapour in a realistic absorption column. A study of Fig. 2 shows that two critical areas exist if CO₂ is to be absorbed successfully in the proposed plant. First, the concentration of CO₂ in the absorbent stream at the top of the column, since this affects the residual concentration of CO₂ in the flue gas. Second, the concentration of CO₂ in the liquid SO₂ stream at the coldest part of the column. These two concentrations are important together since they affect the degree of separation needed in the CO₂ recovery columns and consequently influence the thermodynamic efficiency of the whole cycle.

A complete analysis of the absorption column at this stage is of limited use, since there are a number of complicating factors which have not been discussed. These include the boiling off of SO₂ from the absorbent stream and also the high solubility of both oxygen and nitrogen in liquid SO₂ [25]. Nonetheless, a simplified analysis is still seen as useful and this is made possible by a feature of an additional precooling stream to be introduced below. Due to the precooling stream, the system can be designed to ensure that the flue gas enters and leaves the scrubbing section at roughly the same, low temperature. Also, the quantity of CO₂ collected in the absorbent is relatively small. Thus, to a first approximation, even if the column is assumed to be adiabatic, the scrubbing section can be assumed to be isothermal. A further simplification is to assume that only CO₂ mass transfer occurs between the flue gas and absorbent. Souders and Brown [26] performed an analysis for absorption columns with similar assumptions, but they also stipulated that the VLE follows either Raoult's or Henry's law. They introduced the concept of the absorption factor, A

$$A = \frac{L_m}{mG_m}, \quad \text{where } m = \frac{y_{\text{CO}_2}}{x_{\text{CO}_2}} \quad (1)$$

where L_m is the molar flow per unit area of absorbent stream, G_m the molar flow per unit area of gas stream, and m is the volatility of CO₂ in the absorbent stream.

Using the assumptions above, the absorption factor is constant at a specified temperature, when the ratio between L_m and G_m is specified. This is because the value of m , the volatility, is constant for a given temperature, if Raoult's or Henry's law is assumed. Souders and Brown's analysis yielded a simple analytical solution to absorption problems by applying this constant absorption factor. The

analysis related the relative absorption, R , to the absorption factor, for ' n ' theoretical plates, where

$$R = \frac{y_{n+1} - y_1}{y_{n+1} - y_0} = \frac{A^{n+1} - A}{A^{n+1} - 1} \quad (2)$$

where $y_{n+1} - y_1$ is the actual change of gas composition and $y_{n+1} - y_0$ is the ideal change of gas composition with gas in equilibrium with absorbent.

Rearranging equation (2) yields the polynomial

$$A^{n+1}(R - 1) + A - R = 0 \quad (3)$$

Equation (3) can be solved to give values of absorption factor if the number of theoretical plates and relative absorption factor are specified, as shown in Fig. 4. Once the value of R is found from this graph, the required liquid gas ratio can be determined for a given value of m .

By way of example, for 90 per cent carbon capture from flue gas with an initial CO₂ mole fraction of 12 per cent $y_1 = 0.012$. y_0 is the equilibrium level of CO₂ vapour above the absorbent feed stream. This feed stream will have been stripped of CO₂ by the side columns, so to a first approximation y_0 can be set to zero. Using these values gives a relative absorption of

$$\frac{y_{n+1} - y_1}{y_{n+1} - y_0} = \frac{0.12 - 0.012}{0.12} = 0.90 = R$$

Souders and Brown intended Raoult's or Henry's law to be used to evaluate the value of m , but for

Fig. 4 Graph of relative absorption versus absorption factor for different numbers of theoretical plates

their analysis to hold, all that is required is that the value of m remains essentially constant, regardless of the composition. Since the concentration of CO₂ in the SO₂ is always low in this case, the activity coefficient can be assumed to remain close to the value at infinite dilution. Further, since the absorption column is largely isothermal the temperature dependence of the infinite dilution activity coefficient and vapour pressure need not be considered. This enables a constant value of m to be defined, thus

$$m = \frac{y}{x} = \frac{\gamma_{CO_2}^\infty P_{CO_2}^0}{P_{Gas}} \quad (4)$$

$$\Rightarrow A = \frac{P_{Gas} L_m}{\gamma_{CO_2}^\infty P_{CO_2}^0 G_m} \quad (5)$$

Inserting into equation (5) the vapour pressure for CO₂ calculated using a Wagner equation [27], the infinite dilution activity coefficients evaluated in Appendix 2 and assuming the column operates at atmospheric pressure ($P_{Gas} = 1.013$ bara), the necessary liquid–gas ratio for different numbers of theoretical plates can be plotted against temperature (Fig. 5). This graph can now be used to estimate the required temperature of the liquid SO₂ stream if the initial liquid–gas ratio and number of plates are specified. By way of example, for a column with four theoretical plates and a liquid–gas ratio of two, the column needs to operate at -73.7°C . This is well within the range of operating temperature possible

Fig. 5 Graph of required liquid/gas ratio versus temperature when absorbing CO₂ vapour using liquid SO₂ for different numbers of theoretical plates and an absorption factor of 0.90

with the SO_2/CO_2 binary mixture if freezing is to be avoided.

4 PRECOOLING STREAM

4.1 The need for a precooling stream

The brief analysis above has indicated that low temperatures are essential if adequate carbon capture is to be achieved when using liquid SO_2 as an absorbent. As Fig. 2 shows, in the proposed process, the hot flue gas passes directly into packing drowned in liquid SO_2 . This would be impractical even without the need to augment the absorption of CO_2 by the use of low temperatures, since the hot flue gas would proceed to boil off much of the SO_2 into the flue gas stream. For this reason a precooling stream needs to be used to reduce the temperature of the flue gas to a level

where the liquid SO_2 absorbent can function properly without all being evaporated.

Figure 6 shows a slightly more advanced schematic to that of Fig. 2 with an additional precooling stream. As can be seen, the precoolant is made to follow a similar closed circuit to the liquid SO_2 circuit, first cooling and then reheating the flue gas regeneratively. A secondary purpose of the precoolant is to recover any SO_2 that is lost from the absorption section; the precooling stream is designed to absorb SO_2 vapour and prevent it exiting the main column and thus passing to the atmosphere. The precooling stream therefore needs to be a reasonable solvent for SO_2 vapour. The SO_2 recovered in this way is evaporated in a flash vessel, compressed, condensed and then returned to the liquid SO_2 stream. This SO_2 recovery system also acts to refrigerate the precoolant stream.

Fig. 6 Schematic diagram of the proposed absorption column including precooling stream

Fig. 7 Graph of the melting point of an aqueous solution of sulphuric acid versus concentration

4.2 Choice of aqueous H₂SO₄ as precooling stream

In choosing the fluid for the precooling stream the philosophy outlined earlier in the current paper has been adopted – that is, only using fluids obtainable from the flue gas. This led to the adoption of a solution of sulphuric acid as the precoolant.

Sulphuric acid can be generated from the constituents of the flue gas by reactions similar to those used by the sulphuric acid industry in the nineteenth and early twentieth centuries in the lead-chamber process. Use of a modified lead-chamber process (described as a ‘nitrogen oxide sulphuric acid process’) for scrubbing of SO₂ lean flue gas has been developed by Ciba Geigy [28] and uses identical reactions.

The precoolant stream is expected to pass through a wide temperature range and specifically down to cryogenic temperatures. It is necessary, therefore, that freezing of the solution is avoided. Figure 7 shows a graph adapted from Gable *et al.* [29] on which the freezing point of aqueous sulphuric acid at different acid concentrations is plotted. The lowest temperature achievable without supercooling is -61°C at a concentration of 36 per cent H₂SO₄ by weight (4.01 M). The corresponding boiling point for this concentration is 110.9°C [30].

Although the precoolant is primarily intended to perform heat transfer duties it also needs to absorb SO₂ that boils off from the absorption section. Govindarao and Gopalakrishna [31] reviewed the large amount of solubility data available for mixtures of H₂SO₄ and SO₂ and Appendix 3 details an analysis of the likely SO₂ emissions from a cycle running at

Fig. 8 Psychrometric chart showing the mixing line of limiting atmospheric humidity to avoid chimney plume condensation

typical conditions using a simplified model for the vapour–liquid equilibrium. This analysis shows that SO₂ levels would be well below the 200 mg/nm³ limit stipulated by the 2015 European Large Combustion Plant Directive (LCPD).

An additional benefit of the cycle is that flue gas reheating can be avoided. This is normally specified in power stations with a flue gas scrubbing system which reduces the flue gas temperature considerably. Without reheating, a large, dense chimney plume is often formed by condensation*, and condensation can also occur downstream of the scrubber resulting in corrosion of the chimney lining and associated ductwork [32]. Reheating is unnecessary in the present case due to the hygroscopic nature of the sulphuric acid used in the scrubbing column.

As an example, assuming a chimney outlet temperature of 30°C and an acid concentration of 45 per cent at the top of the main column, the vapour pressure of water in the presence of the acid is 1.96 kPa, as opposed to 4.24 kPa at saturation (equivalent to RH: 46.2 per cent), data from [30]. Figure 8 shows a psychrometric chart with a mixing line drawn tangent to the saturation line and crossing through this initial humidity. To the left of the point of tangency (0.5°C for the values specified) this line represents the limit of atmospheric humidity if condensation is to be avoided. To the right of the tangent condensation cannot occur whatever the atmospheric humidity, indeed the chimney plume would ‘cut holes’ in any clouds or fog in its vicinity above this temperature.

*London’s Battersea power station had this problem, producing dense clouds of steam commonly mistaken for smoke. Battersea had the world’s first large-scale flue gas desulphurization (FGD) plant and remarkably low sulphur emissions for a coal burner in the 1930s. Pointedly, the station did not have flue gas reheating.

5 CONCLUSION

The current paper has proposed the use of a liquid SO₂ stream, as the primary CO₂ absorbent in a new postcombustion carbon capture process. An analysis of a simplified absorption column is conducted that demonstrates that liquid SO₂ is an excellent absorbent of CO₂ vapour at low partial pressures as long as temperatures are also low.

The paper goes on to propose an extension to the process with an additional stream designed to pre-cool the flue gas. By this means the flue gas is able to enter (and leave) the liquid SO₂ stage of the absorption column at a temperature more appropriate for this absorption process. Any SO₂ that boils off from the scrubbing section is absorbed in this precooling stream thus avoiding a pollution problem.

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APPENDIX 1

Notation

A	absorption factor
CCS	carbon capture and storage
CNG	consolidated natural gas (process)
f_i^o	standard state fugacity
f_{iV}	vapour phase fugacity
f_{iL}	liquid phase fugacity
G	molar flow per unit area of gas stream
H	Henry's law coefficient
L	molar flow per unit area of absorbent stream
LCPD	European Large Combustion Plant Directive
m	volatility of CO ₂ in absorbent stream
p_i	partial pressure
P	pressure
P_i	pressure of stream
P_i^{sat}	saturation pressure
$(PF)_i$	Poynting factor
R	relative absorption
T	thermodynamic temperature
V_i^L	molar volume of liquid
VLE	vapour/liquid equilibrium
x_i	liquid phase mole fraction
y_i	vapour phase mole fraction
y_n	vapour phase mole fraction for stage number n
z	liquid phase coordination number
β_i	proportionality constant in Wilson equation
γ_i	activity coefficient
γ_i^∞	infinite dilution activity coefficient
$\Delta h_{\text{vap},i}$	enthalpy of vapourisation
λ_{ii}	pure component interaction energy for species i
λ_{ij}	pair interaction energy between species i and j

Λ_{ij}	Wilson coefficient, species i relative to species j
$\hat{\phi}_{iL}$	liquid phase fugacity coefficient
$\hat{\phi}_{iV}$	vapour phase fugacity coefficient
ϕ_i^{sat}	standard state liquid phase fugacity coefficient
R	universal gas constant

Subscripts

i or j	generic chemical species
n	stage number counted from gas entry point
sat	saturation condition
o	sink condition: -25°C , 1.01 bara.

APPENDIX 2

Vapour–liquid equilibrium of CO₂/SO₂ binary mixture

To perform process design calculations, the VLE between SO₂ and CO₂ needs to be established. The governing relationship for equilibrium in terms of partial fugacities is given by

$$\hat{f}_V = \hat{f}_L \quad (6)$$

If fugacity coefficients are substituted equation (6) becomes

$$y_i \hat{\phi}_V P = x_i \hat{\phi}_L P \quad (7)$$

The liquid phase fugacity coefficient is often difficult to determine so the standard state fugacity can be introduced using an activity coefficient model, thus

$$\hat{\phi}_L P = \gamma_i f_i^o \quad (8)$$

Using a standard state of saturation conditions the standard state fugacity is given by

$$f_i^o = \phi_i^{\text{sat}} P_i^{\text{sat}} (PF)_i \quad (9)$$

Combining equations (7) to (9) gives

$$y_i \hat{\phi}_V P = x_i \gamma_i \phi_i^{\text{sat}} P_i^{\text{sat}} (PF)_i \quad (10)$$

Where the Poynting factor is a correction for effect of pressure on the liquid fugacity and is given by

$$(PF)_i = \exp \int_{P_i^o}^P \left(\frac{\bar{V}_{iL}}{RT} \right) \cdot dP \quad (11)$$

Hence

$$\Rightarrow y_i = \frac{x_i \gamma_i \phi_i^{\text{sat}} P_i^{\text{sat}} (PF)_i}{\hat{\phi}_V P} \quad (12)$$

This equation is often simplified at low reduced pressures by assuming the two fugacity coefficients, along with the Poynting factor, are equal to unity [33]. With these simplifications to equation (12), the equilibrium can be expressed as follows

$$y_i = \frac{x_i \gamma_i P_i^{\text{sat}}}{P} \quad (13)$$

If the system pressure and pure component saturation pressure are known, the only term that needs to be established is the activity coefficient. This coefficient is specific to the mixture and is a function of composition (and weakly of temperature). If this coefficient is also assumed to be unity, equation (13) can be further simplified to Raoult's law when the mixture is said to be an ideal solution, thus

$$y_i = \frac{x_i P_i^{\text{sat}}}{P} \quad (14)$$

To establish if Raoult's law can be assumed for an SO₂/CO₂ binary, values for the activity coefficients are normally estimated from experimental data. There is a paucity of data for the CO₂/SO₂ binary and much of it dates from the nineteenth or early twentieth centuries: references [34] to [36] give VLE data, whereas references [17], [21], [36], and [37] give limited data on the solid-liquid equilibrium. The data from Blümcke [34] appears the most reliable and Gerrard plotted his VLE data for -10°C on a graph of CO₂ partial pressure versus mole fraction [38]. He compared the experimental data to a straight reference line. Gerrard described these as 'R-lines', but they represent Raoult's law. Figure 9 shows a more complete set of 'R-lines' for different temperatures plotted against Blümcke's data. These plots indicate a noticeable departure from Raoult's law so activity coefficients cannot be assumed to be unity for this binary.

Activity coefficients are normally correlated from experimental data using a thermodynamically consistent empirical correlation. Examples include the van Laar, Margules, and Wilson equations [33]. The Wilson equation has been used here due to its relative simplicity, but also because it can be applied more easily to the limited data set available for the present mixture. For binary mixtures, the Wilson equation

Fig. 9 Graph of the solubility of CO₂ in liquid SO₂ versus partial pressure of CO₂ at different temperatures

reduces to

$$\ln \gamma_i = -\ln(x_i + \Lambda_{ij}x_j) + x_j \left(\frac{\Lambda_{ij}}{x_i + \Lambda_{ij}x_j} - \frac{\Lambda_{ji}}{x_j + \Lambda_{ji}x_i} \right) \quad (15)$$

where the temperature-dependent constants are given by

$$\Lambda_{ij} = \frac{V_j^L}{V_i^L} \exp \left(-\frac{\lambda_{ij} - \lambda_{ii}}{RT} \right) \quad (16)$$

where V_i^L and V_j^L is the molar volume of pure liquid i and j , at the temperature of the system, T , λ_{ij} , and λ_{ji} is the pair interaction energy between species i and j , and λ_{ii} , and λ_{jj} is the pure component interaction energy for species i and j .

The Wilson equation requires a minimum of two experimental points to evaluate the two constants. (Nonetheless large data sets are desirable not least to account for the variation of activity coefficients with temperature.) It is convenient to use the infinite dilution activity coefficients to evaluate the constants since equation (15) can be simplified at infinite dilution, thus

$$\ln \gamma_i^\infty = 1 - \ln \Lambda_{ij} + \Lambda_{ji} \quad (17)$$

A weakness of Blümcke's data is that it is limited to dilute solutions of CO₂ in SO₂ only. This severely limits the ability to correlate the activity coefficients

since only one infinite dilution activity coefficient can be evaluated. To reduce the Wilson equation so that it can be used with just one infinite dilution activity coefficient Wong and Eckert [39] and Shreiber and Eckert [40] assumed that both of the pair interaction energies were identical and that the pure component interaction energies can be calculated using the following equation

$$\lambda_{ii} = -\beta_i(\Delta h_{\text{vap},i} - RT) \quad (18)$$

where $\Delta h_{\text{vap},i}$ is the enthalpy of vapourization of species i and β_i is the proportionality constant.

Ladurelli *et al.* [41] suggested the following equations for β

$$\beta_i = \left(\frac{2}{z} \right) \left(\frac{V_j^L}{V_i^L} \right) \quad (19)$$

$$\beta_j = \frac{2}{z} \quad (20)$$

where species j is that with the smaller molar volume and ' z ' is the liquid phase coordination number assumed by Ladurelli *et al.* to be 10.

To calculate values of the Wilson coefficients, suitable values for pure component properties are entered into equations (18) to (20). The resulting parameters are then substituted into equation (17) to calculate the pure component interaction energies.

Values of molar volumes of both CO₂ and SO₂ have been calculated from correlations in Daubert *et al.* [42]. Heats of vapourization have been calculated using correlations from Yaws [43]. The vapour pressure of SO₂ has been calculated using an Antoine equation from Poling *et al.* [44]. While the vapour pressure of CO₂, has been calculated using a 'Wagner' equation with coefficients from McGarry [27]. The pair interaction energy is then selected so that a best fit is achieved to the experimental data, thus

$$\lambda_{\text{SO}_2, \text{CO}_2} = \lambda_{\text{CO}_2, \text{SO}_2} = -2768 \text{ kJ/kmol}$$

Figure 10 shows a graph of the infinite dilution activity coefficient calculated using the model. The experimental points of Blümcke are included for comparison. As can be seen from Fig. 10, the activity coefficient shows significant temperature dependence. However, most of the available data for the mixture, including Blümcke's, was recorded at relatively high temperatures. The Smithsonian tables [21] give the temperature of a freezing mixture of dry ice in liquid SO₂ as -82°C , but do not specify the composition of the resulting eutectic mixture. Thiel and Schulte [22] took measurements of the

Fig. 10. Graph of the predicted infinite dilution activity coefficient of CO₂ in liquid SO₂ with data of Blümcke [34] versus temperature

constant pressure equilibrium for a binary mixture of liquid CO₂ and SO₂ at -78.64°C . The mole fractions are given for each species in both vapour and liquid phases. This single data point can be used to validate the extrapolation of the activity coefficient model to low temperature.

Figure 11 shows a graph of the activity coefficients versus composition at different temperatures calculated using the value of pair interaction energy already established. This graph shows the remarkably close agreement between the model, (extrapolated to low temperature) and the single data point from Thiel and Schulte [22]. (Only the value of $\ln\gamma$ for CO₂ from Thiel and Schulte [22] has been plotted. This is due to the very low concentration of SO₂ in the vapour at the measured conditions, which is in turn due to the large volatility difference between CO₂ and SO₂; even the slightest error in the measurement of SO₂ vapour pressure would lead to significant changes in the calculated activity coefficient.)

APPENDIX 3

SO₂ emission control

Section 4.1 indicated that the precooling stream will need to absorb any SO₂ which boils-off from the SO₂/CO₂ circuit if atmospheric pollution it to be avoided. A considerable amount of research has been conducted on the solubility of SO₂ in sulphuric acid solutions and the following reviews should be studied for further information: references [31], [45], and [46]. Govindarao and Gopalakrishna [31]

Fig. 11 Graph of the predicted activity coefficients for CO₂/SO₂ binary versus mole fraction of CO₂ at three different temperatures and comparison with data point from Thiel and Schulte [22]

give a thermodynamically derived equation for the solubility of SO₂ in dilute H₂SO₄. Zhang *et al.* [47] extended this model to include concentrated solutions and showed that at concentrations greater than 22 wt per cent, the model could be simplified to Henry's law, due to the lack of hydrolysis of SO₂

$$N_{\text{SO}_2} \cong \frac{P_{\text{SO}_2}}{H} \quad (21)$$

where H is the Henry's law coefficient and N refers to the mole fraction of dissolved vapour. The reference goes on to use a van't Hoff type-equation to fit experimental data for the temperature dependence of the Henry's law coefficient, thus

$$\ln H = \ln a_d - \frac{\Delta H_d}{RT} = 27.92 - \frac{3785.9}{T} \quad (22)$$

This equation was shown by Zhang *et al.* [47] to represent well, data in the literature for a temperature interval of 0 to 90 °C.

The emissions of SO₂ with the chimney plume of the cycle detailed in the current paper would be determined by the concentration of SO₂ in the acid liquor as it returns to the top of the main column. This is because the emissions will relate directly to the partial pressure of SO₂ above the acid stream at this point. At the top of the main column the acid liquor is at, or around, ambient temperature, so equations (21) and (22) can be used as long as the SO₂ concentration in the acid is known. However, the concentration of SO₂ in the acid stream at the top of the column is identical to that at the bottom. The only difference is the temperature of the stream is much higher, but equations (21) and (22) can be applied as before if equation (22) is extrapolated to 110 °C. This assumption was seen as reasonable for the rough calculation performed below.

By the year 2015 the European LCPD will limit the maximum permissible concentration of SO₂ in the flue gas to 200 mg/m³ for all new build and existing power stations. This is equivalent to a partial pressure of SO₂ of 7.55 Pa for flue gas at ambient temperature [44]. To achieve this partial pressure with a recirculated acid temperature of 30 °C requires a residual SO₂ mole fraction in the acid of

$$N_{\text{SO}_2} \cong \frac{P_{\text{SO}_2}}{H_{30^\circ\text{C}}} = \frac{7.55}{6.12 \times 10^6} = 1.510 \times 10^{-6} \quad (23)$$

Thus, a concentration of SO₂ no greater than this value can be allowed in the recirculated acid if compliance with the LCPD is to be achieved. To calculate the concentration of SO₂ reached in the acid at the bottom of the column, an estimate is required of the initial partial pressure of SO₂ in the flue gas. The mole fraction of SO₂ in the recirculated acid is then equal to that which produces the same partial pressure of SO₂ as that of the flue gas.

Assuming a standard bituminous coal is burnt in the power station with 1.5 per cent sulphur concentration and also assuming all of this sulphur appears as SO₂ in the flue gas, this gives an initial SO₂ partial pressure in terms of molalities of

$$P_{\text{SO}_2} = \left(\frac{m_{\text{SO}_2} P_{\text{FlueGas}}}{m_{\text{N}_2} + m_{\text{O}_2} + m_{\text{H}_2\text{O}} + m_{\text{CO}_2} + m_{\text{SO}_2}} \right) \quad (24)$$

$$\begin{aligned} P_{\text{SO}_2} &= \frac{0.0469 \times 105\,000}{44.45 + 1.64 + 4.80 + 6.96 + 0.05} \\ &= 85.014 \text{ Pa} \end{aligned}$$

which gives a maximum mole fraction of SO₂ in the acid stream at 110 °C of

$$N_{\text{SO}_2} \cong \frac{P_{\text{SO}_2}}{H_{110^\circ\text{C}}} = \frac{85.01}{68.00 \times 10^6} = 1.252 \times 10^{-6}$$

As can be seen by comparison with equation (23) this is less than the residual mole fraction required by the LCPD.