

3.10 Costs related to FGD

The costs related to the use of any of the above-mentioned FGD processes can be broken down into fixed and variable operation & maintenance (O & M) costs and fixed capital charge costs (see *e.g.* Coulson and Richardson, 1993). For a few commercial FGD process options, two plant sizes and two types of coal, a comparison is given in Table 3.6, based on 90 % SO₂ removal efficiency and 30 years levelised costs (Soud, 1995).

Table 3.6 Cost comparison for several FGD options, 1995 US\$/tonne SO₂

Plant size, MW _{elec}	Coal sulphur content, %	FGD process	Fixed O & M	Variable O & M	Fixed capital charge	Total costs
200	2.6	Wet limestone scrubber*	79	90	183	352
200	2.6	Spray dry scrubber**	40	143	134	317
200	2.6	Lurgi CFB***	15	140	123	277
500	4.3	Wet limestone scrubber	20	76	83	178
500	4.3	Spray dry scrubber	11	131	69	211
500	4.3	Lurgi CFB	3	130	63	196

* See section 3.6 ** See section 3.9 *** See section 3.8

The wet limestone scrubber becomes most economic for large plants, with relatively high fixed O&M costs due to equipment wear and pressure drop. For wet FGD the necessity of reheating the flue gas from the scrubber exit temperature of 50~60°C to 80~100°C stack temperature may cost ~1% of the furnace power.

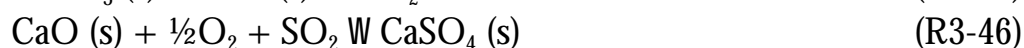
Several other aspects related to costs of FGD, power consumption, construction materials and by-products management are discussed in a report by Ciemat (1998).

3.11 High temperature SO₂ capture during fluidised bed combustion

One of the great benefits of fluidised bed combustion (FBC, 7 Chapter 2) is the option of *in-situ* SO₂ capture. The temperature level of 800 ~ 950EC is such that CaSO₄ is a stable compound, and by adding a calcium-based sorbent to the fuel/bed material mixture the SO₂ can be effectively captured immediately after it has formed. (Or maybe even earlier - H₂S is maybe also captured, forming CaS, before it can form SO₂, followed by oxidation of CaS to CaSO₄). This is one of the benefits of FBC, together with the relatively low NO_x emissions as a result, again, of the relatively low combustion temperature (L chapter 4). The principle is relatively simple: a calcium-based sorbent such as calcite (CaCO₃), dolomite (CaCO₃@MgCO₃), or dolomitic limestone is added to the bed. Sorbent size depends mainly on the densities of fuel and sorbent and the fuel particle size, optimising for fluidisation behaviour and contacting between sorbent particles and gas.

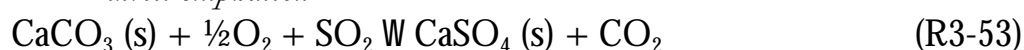
Depending on the partial pressure of carbon dioxide the calcium carbonate calcines to calcium oxide, or remains uncalcined. Thus, for calcined or uncalcined limestone, the reactions taking place are

calcination, followed by sulphation



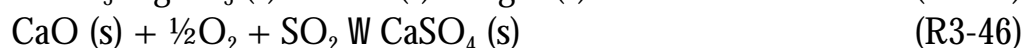
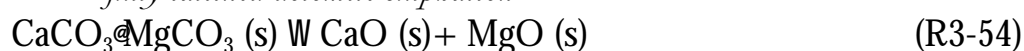
or

direct sulphation



When dolomite is used there are differences compared to the use of limestone. The magnesium carbonate in the dolomite calcines to magnesium oxide both under atmospheric and pressurised FBC (PFBC, 7 chapter 2) conditions, where it gives half-calcined dolomite. The magnesium oxide formed does not react with sulphur dioxide since MgSO₄ is not stable under these conditions, although CaSO₄@MgSO₄ was recently identified in sulphated calcareous sorbents from Estonia (Trikkel *et al.*, 1999). Thus, depending on whether or not the calcium carbonate fraction of the dolomite calcines, the chemical reactions taking place are

fully-calcined dolomite sulphation



or

half-calcined dolomite sulphation

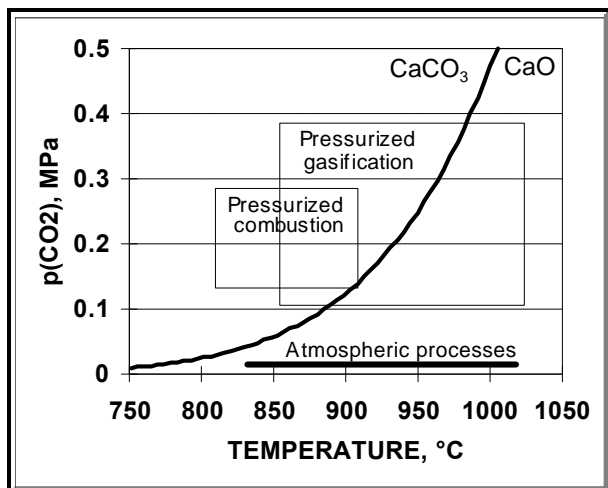
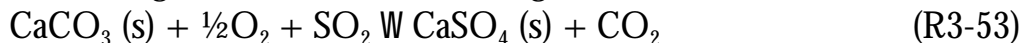


Figure 3.23 Sulphur capture in fluidised beds: the CaCO₃ calcination reaction equilibrium (picture from Iisa, 1992)

From the equilibrium of the calcium carbonate calcination reaction it can be deduced that for a CO₂ volume fraction of 15% in the gas, the calcination will not occur at pressures above 3.5 bar at 850°C or above 14 bar at 950°C as shown in Figure 3.23 (Iisa, 1992).

Depending on the sulphur content of the fuel, calcium-based sorbents are fed to FBC furnaces at Ca/S (molar) ratios of the order 2 ~ 4 - see Figure 3.24. Obviously this results in calcium

conversions of the order of 25-50%, which is basically the result of the blocking and plugging of the internal structure of the sorbent particle.

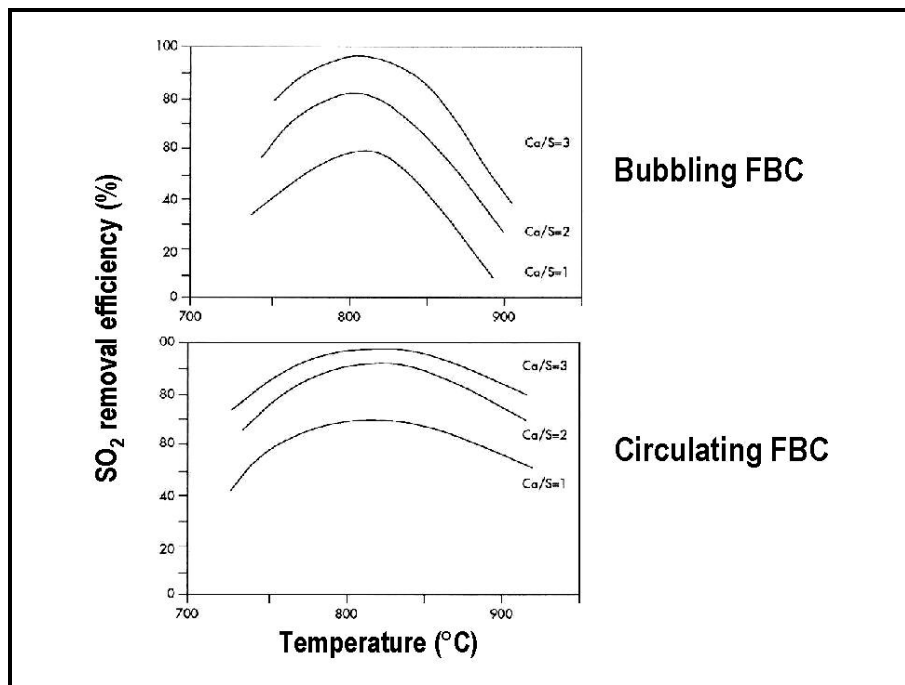


Figure 3.24 Sulphur dioxide capture with calcium-based sorbents in bubbling or circulating FBC at 1 bar: the influence of temperature and Ca/S ratio (after Iisa, 1995)

Pure CaCO₃ has a molar volume of 36.9 cm³/mole, calcination gives CaO at 16.9 cm³/mole and sulphation gives CaSO₄ at 46.0 cm³/mole.

Hence, although the natural calcareous materials that are used as sulphur capture sorbents contain impurities and have some porosity, it is clear that the formation of CaSO_4 will result in plugging and blocking of the pore structure that leads to the centermost part of the particle. This also explains why calcined limestone, CaO is more reactive than uncalcined limestone, CaCO_3 : the calcination process (reaction R3-49) in a way “opens up” the pore structure by the release of CO_2 , making pore diffusion faster and making the sorbent less vulnerable to pore plugging and blocking. Therefore the sulphur capture in pressurised FBC is, in general, accomplished with dolomite or dolomitic limestones. As a result of the decomposition of the MgCO_3 , reaction (R3-55) followed by (R3-53) in a dolomitic sorbent is often faster than reaction (R3-53) with a limestone.

Since the calcareous materials used are taken from nature, large differences exist between chemical composition, impurities and texture. Examples for the purity and internal structure is given in Table 3.8 for five limestones and two dolomites that were tested (besides many others) for sulphur capture in atmospheric and pressurised FBC (Yrjas *et al.*, 1993, Zevenhoven *et al.*, 1998a). These differences lead to the large differences found in SO_2 uptake by different sorbents when these are tested at identical conditions - Figure 3.25 compares the direct sulphation (*i.e.* reaction R3-53) of the 5 five limestones given in Table 3.7, at 15 bar, 850EC and 950EC.

Table 3.7 Chemical and texture properties of several limestones and dolomites (taken from Zevenhoven *et al.*, 1998a)

SORBENTS	CaCO_3^* (%wt)	MgCO_3^* (%wt)	Specific Surface ** (m^2/g)	Particle Porosity (-)	Particle Density (kg/m^3)	Average Pore Diameter *** (μm)
Limestone 1	98.4	0.90	2.25	0.178	1681	0.323
Limestone 2	97.9	0.65	1.49	0.075	2416	0.251
Limestone 3	98.6	0.61	4.63	0.324	1351	0.412
Limestone 4	88.9	1.15	2.94	0.077	1762	0.209
Limestone 5	90.4	2.87	3.74	0.063	2786	0.074
Dolomite 1	60.4	32.9	0.93	0.022	2727	0.112
Dolomite 2	47.4	26.0	0.060	0.010	2855	0.291

* Chemical composition taken from Yrjas *et al.* (1993)

** Found from N_2 BET surface measurement

*** Found from mercury penetration porosimetry

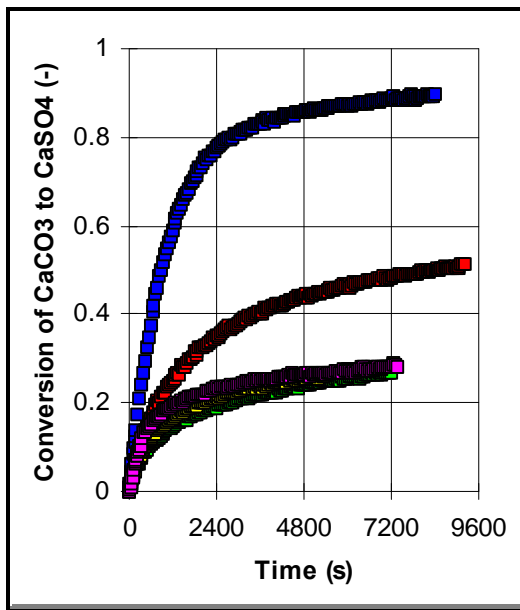


Figure 3.25a Direct sulphation of five limestones under PFBC conditions: 15 bar, 850EC. (data from Yrjas *et al.*, 1993)

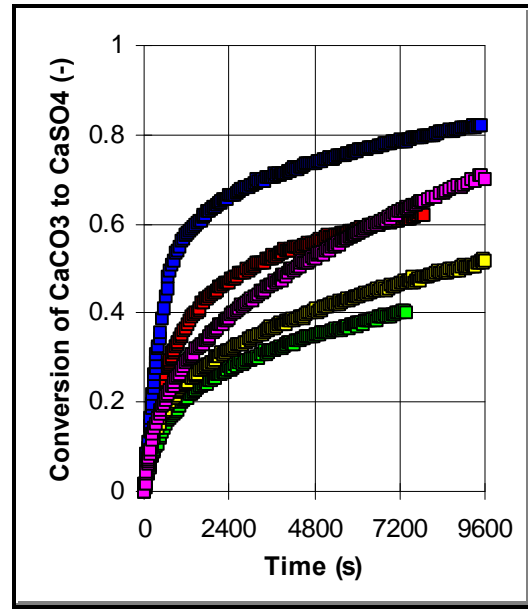


Figure 3.25b Direct sulphation of five limestones under PFBC conditions: 15 bar, 950EC. (data from Yrjas *et al.*, 1993)

An example of a sorbent particle that has been partly sulphated is shown in Figure 3.26. It clearly shows a white coating of product CaSO_4 on a greyish unreacted core. Most research on modelling and quantifying the sulphation of sorbent particles uses an unreacted shrinking core (USC) type approach (see *e.g.* Levenspiel, 1972). Several

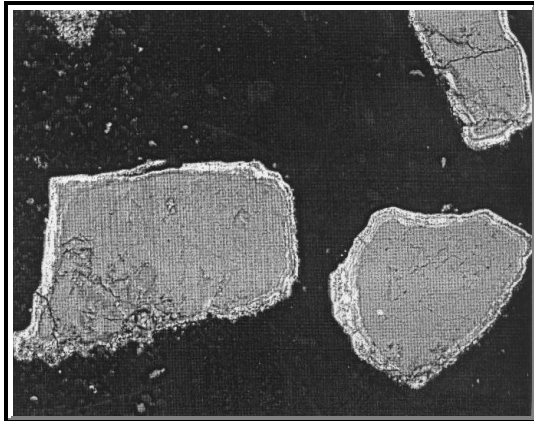


Figure 3.26 SEM photo of a cross-section of a partly sulphated dolomite particle (picture from Yrjas, 1992)

improvements to that approach have been suggested in the huge literature on this subject, such as pore model and grain model descriptions, as illustrated by Figure 3.27. A complicating factor is the changing intra-particle structure of the particle during the sulphation process, which can be taken into account by a variable effective diffusivity of the gases inside the sorbent particle, based on a characterisation of the initial texture of the particles (Zevenhoven *et al.*, 1998a). Moreover, the thickness of the product layer that separates the gases (in the pores) from

the unreacted solid is probably much thinner than what USC-based modelling predicts. This can be shown when taking into account the changing internal pore surface of the sorbent particle during the conversion (Zevenhoven *et al.*, 1998b), based on, *e.g.*, a random pore model description (Bhatia and Perlmutter, 1980, 1983).

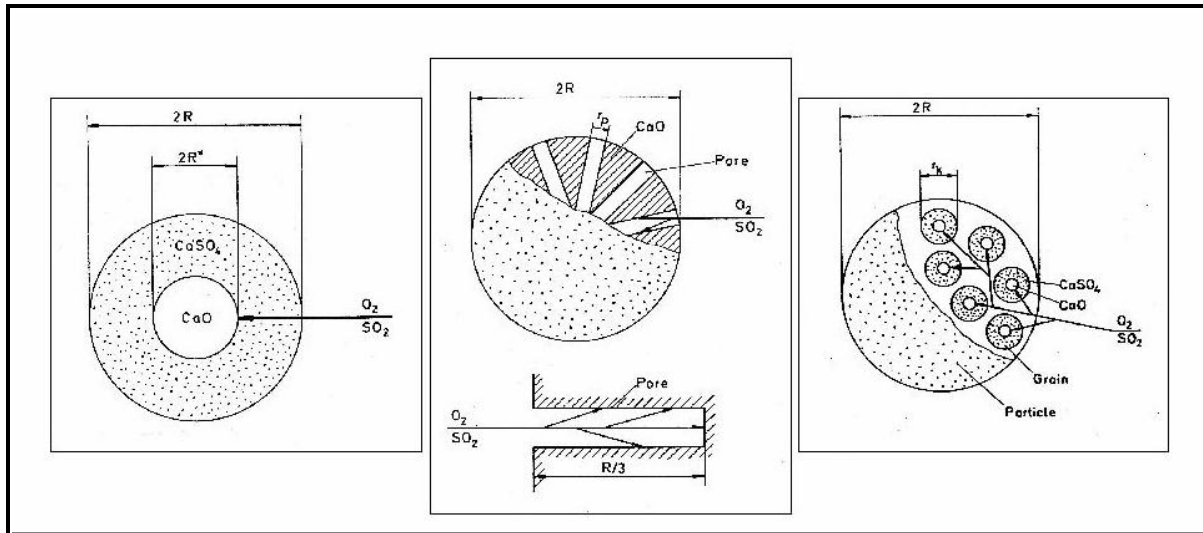


Figure 3.27 Physical models for lime particle sulphation. *Left* : Unreacted shrinking core model. *Centre*: Pore model. *Right*: Grain model. (pictures from Staudinger, 1986)

Returning to atmospheric FBC : Figure 3.24 shows also that the best performance is obtained at 800-850EC, which is more sensitive for BFBC than CFBC. Initially this maximum was believed to be the result of sintering of the sorbent at temperatures above 850EC. It is nowadays accepted, however, that this is mainly related to the stability of the CaSO_4 product at elevated temperatures, and the fact that in the fluidised bed the sorbent particles are exposed to periodically changing oxidising and reducing conditions (e.g. Lyngfelt and Leckner, 1989, 1998, Lyngfelt *et al.*, 1995, Hansen *et al.*, 1993). The CaSO_4 is being reduced, by CO and/or H_2 , to CaS, CaO or CaCO_3 , depending on temperature, and partial pressures of the reactants.

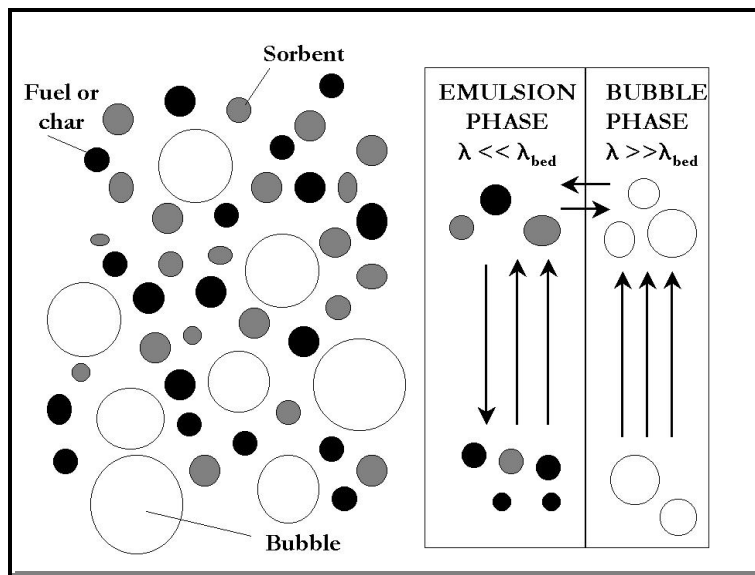


Figure 3.28 Gas by-pass of air via bubbles in BFBC.

For bubbling FBC this can be readily accepted when it one realises that a significant portion of the gas passes the bed as bubbles - in fact it is roughly the gas volume that exceeds the flow needed for minimum fluidisation that follows this route. The SO_2 , however, should be produced by oxidation of sulphur-containing gases (probably H_2S) that are

released in the emulsion phase of the bed, and are then to react, as SO_2 , again in the emulsion phase, with the sorbent - see Figure 3.28. At an overall stoichiometry λ_{bed} , the stoichiometry in the emulsion phase is lower, *i.e.*

$U_{\text{mf}} \lambda_{\text{bed}} / U < \lambda_{\text{emulsion}} < \lambda_{\text{bed}}$, (for gas velocity U and minimum fluidisation velocity U_{mf}), whilst in the bubble phase the actual stoichiometry is much higher.

For circulating FBC, Hansen *et al.* (1993) reported the CO concentration profile shown in Figure 3.29.

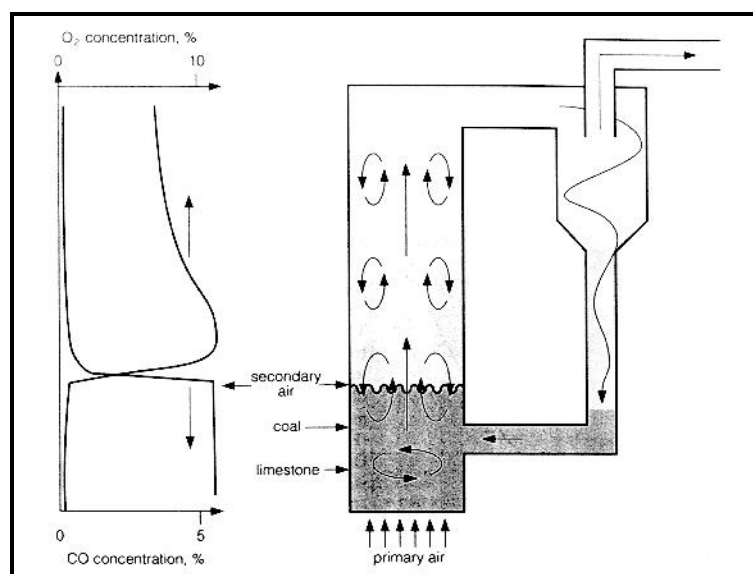
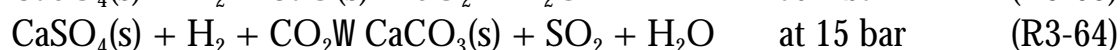
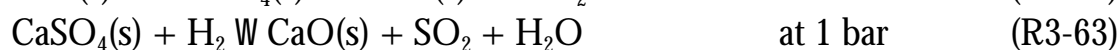
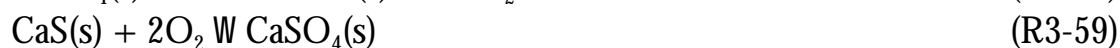


Figure 3.29 CO concentration profile inside a CFBC furnace (picture from Hansen *et al.*, 1993)

This “by-pass” of oxygen via the bubbles and the presence of a significant amount of CO has a double effect on the sulphur capture process:

1. without oxygen reaction (R3-53) cannot proceed, and
2. reducing gases will be able to decompose the CaSO_4 that has been formed, via a complex chemistry that involves the following reactions (Yrjas and Hupa, 1997; Zevenhoven *et al.*, 1999):



Based on this the maxima in the curves in Figure 3.24 can be explained: the oxidation or re-sulphation of the decomposition products of CaSO_4 , *i.e.* CaS , CaO or CaCO_3 , to CaSO_4 becomes slow when compared to the decomposition reactions themselves.

Or from a thermodynamic point of view: the equilibria for reactions (R3-56...58 and 63..65) shift more and more to the right. (The stability of CaSO_4 at high temperatures was already mentioned in section 3.9). That BFBC shows a sharper maximum in Figure 3.24 than CFBC is due to the much smaller bed in the latter, making it less likely for sorbent particles to be exposed to reducing conditions. (Less of the sorbent is in the bottom bed, more recapture of SO_2 higher up).

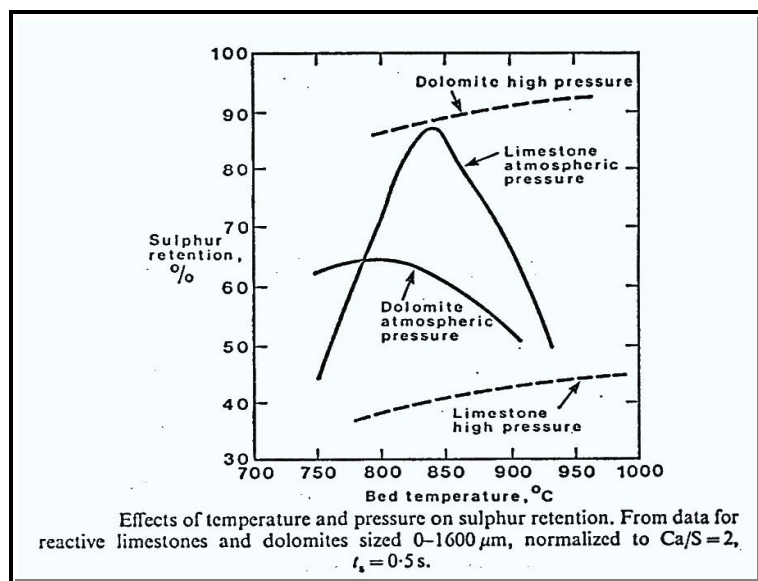


Figure 3.30 Sulphur capture in with limestone or dolomite in fluidised bed combustion: the effect of pressure (picture from Stanton, 1983)

that the amount of CaCO_3 formed was not significant. Later work (Zevenhoven *et al.*, 1999) with periodic strongly reducing conditions (1 % $\text{CO} \sim \lambda = 0.97$, and 4% CO or 4% $\text{CO}+\text{H}_2 \sim \lambda = 0.90$) showed rapid formation of CaS , especially at temperatures above 900°C (reaction R3-58). With water, the CaS formed can be oxidized back to CaSO_4 (reaction R3-65).

The oxidation of CaS to CaSO_4 with oxygen (reaction R3-59) is a relatively slow process that is competing with oxidation to CaO under release of SO_2 (reaction R3-61) - see Yrjas *et al.* (1996).

Further illustration of the differences between sulphation under atmospheric and pressurised FBC is given by Figure 3.31. Although direct sulphation (reaction R3-53) is slower than sulphation of calcined limestone, higher conversions are obtained at longer retention times. Since time scales of several hours are not exceptional for FBC this would allow for more efficient use of sorbent in PFBC.

For PFBC conditions the maximum in the efficiency curves are not found: sulphur capture efficiency increases with temperature as shown in Figure 3.30. Apparently, under pressurised conditions the reactions (R3-57..58 and R3-64..65) do not take place at temperatures below 950 ~ 1000°C (Lyngfelt, 2001). Sulphation at 15 bar with periodically slightly reducing conditions (0.2 % $\text{CO} \sim \lambda = 0.997$) as analysed by Yrjas and Hupa (1997) showed

An explanation is given by Figure 3.32: the release of CO₂ during the direct sulphation of CaCO₃ gives a CaSO₄ product layer that is less porous than that from CaO. This is quantified by a higher value, by 2-3 orders of magnitude, for the effective diffusivity inside a directly sulphated sorbent particle (D_{eff}) when compared to a calcined sorbent particle. For longer conversion times this compensates slower chemical kinetics - see Figure 3.31.

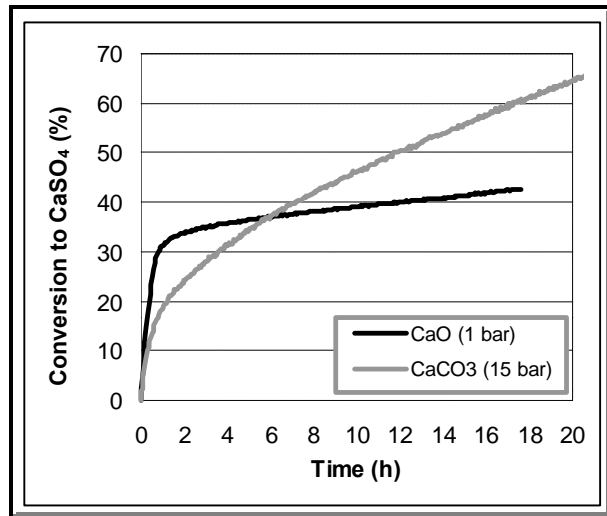


Figure 3.31 Sulphation at 850EC of CaO (1 bar) and CaCO₃ (15 bar) (picture from Yrjas *et al.*, 1998)

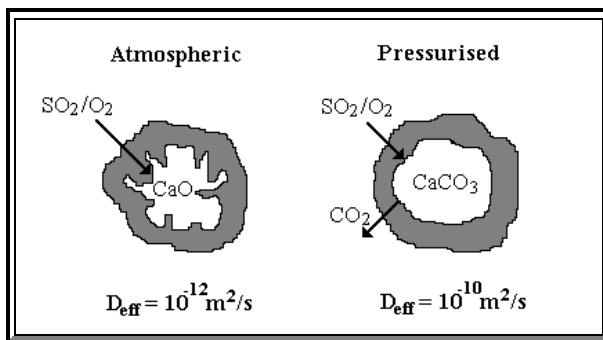


Figure 3.32 Sulphation of calcined (*left*) and uncalcined (*right*) limestone and the effect of intra-particle diffusion (picture from Iisa and Hupa, 1992)

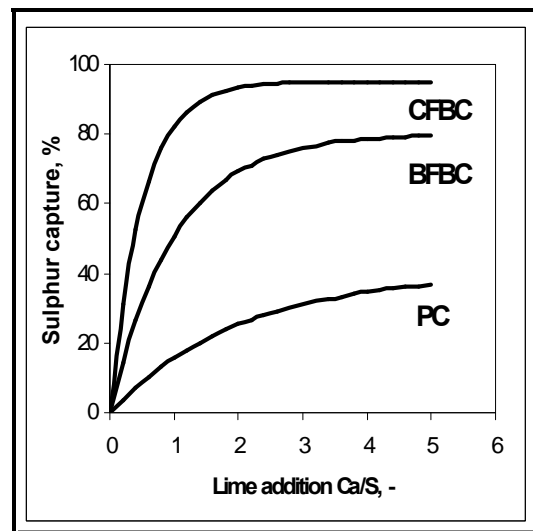


Figure 3.33 *In-situ* sulphur capture in CFBC and BFBC furnace sorbent injection for pulverised coal furnaces (picture from Yrjas, 1997)

Finalising, Figure 3.33 compares the use of *in-situ* sulphur capture in CBFC and BFBC with furnace sorbent injection for pulverised coal (PC) firing (7 section 3.9).

One disadvantage of *in-situ* sulphur capture in FBC is that the solid residues find limited use. Due to a high lime content CFBC residues cannot be used in concrete or cement. PFBC residues have better properties unless dolomite is used instead of limestone - the magnesium oxide in it limits the use of these residues. Only small-scale applications are found for the residues from FBC of sulphur containing fuels (coal, peat) with *in-situ* sulphur capture, in contrast to the use of ashes from pulverised coal combustion (Sloss, 1996).

3.12 H₂S control at low temperatures

Several processes for removing H₂S from gas streams at relatively low temperatures were developed within the chemical and petro-chemical industry, often referred to as "sour gas stripping", which may include CO₂ removal. The most important application is to clean natural gases. In general this is the first of two process steps, the second being the Claus process (L 3.13).

A summary of some important processes is given in Table 3.8 (van den Berg and de Jong, 1980; van Yperen, 1994; Bloemendal and Kerkhof, 2000).

Table 3.8 Low temperature methods for H₂S removal from gases

Principle	Temperature range	Process names	Sorbent / catalyst
Physical absorption product: H ₂ S	240 - 400 K	Selexol, Rectisol, Sulfinol, Purisol, CNG	Methanol (Rectisol), dimethyl ether of polyethylene glycol (Selexol), sulfolane (Sulfinol), carbon dioxide
Chemical absorption product: H ₂ S	250 - 350 K	Alkanol amines, Girbotol, SNPA-DEA, ADIP, Econamine	Amines (MEA, DEA, MDEA, MGA, DIPA), potassium carbonate
Oxidation product: sulphur	300 - 400 K	Stretford, Takahax, Townsend	Solution of Na-salts of H ₂ CO ₃ , anthraquinone-2-sulphonic acid,
Dry bed process product: sulphur	~ 300 K	Iron sponge	Hydrated Fe ₂ O ₃

Physical and chemical absorption ("physisorption" and "chemisorption") involve the reversible binding, by physical or chemical bonds, to a sorbent. Basically, the pollutant is absorbed at a temperature T_{abs} , pressure p_{abs} , and released ("desorbed") from it in a more concentrated form at temperature $T_{\text{des}} > T_{\text{abs}}$, pressure $p_{\text{des}} < p_{\text{abs}}$, after which the sorbent can be re-used. Schematic process diagrams for chemisorption and physisorption are given in Figure 3.34. More details can be found in texts on separation processes design and unit operations (*e.g.*, Coulson and Richardson, 1978).

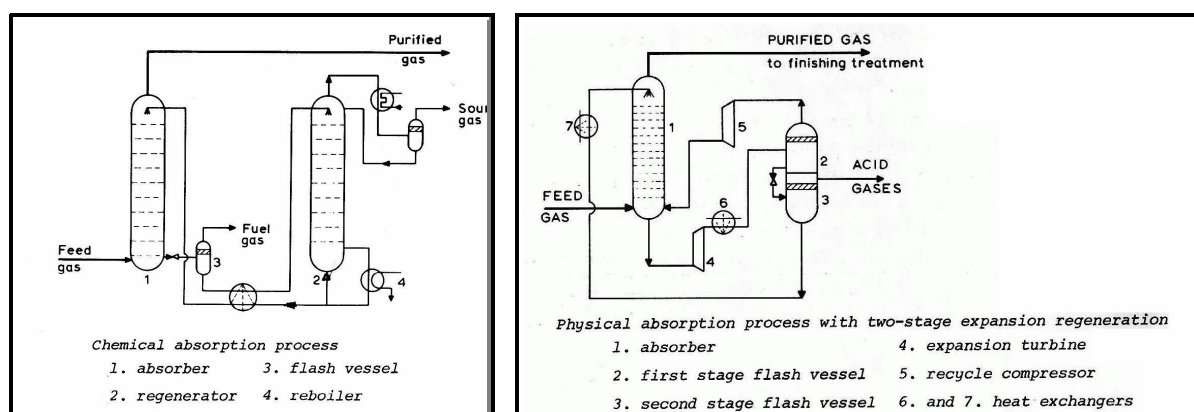
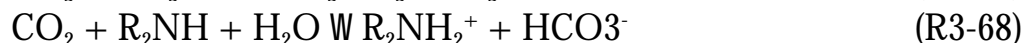


Figure 3.34 Typical process lay-out for a chemisorption (*left*) and physisorption process (*right*) (pictures from van den Berg and de Jong, 1980)

The choice for physisorption (or physical sorbent) or chemisorption (chemical sorbent) processes depends on the gases that are to be removed (H_2S and/or CO_2 plus others, such as NH_3 , HCN , water), the required selectivity and the allowable energy input. Chemical sorption involves a stronger bond between the species that may require more energy (*i.e.* steam) during the regeneration step.

The most common use of physisorption processes is for bulk removal of carbon dioxide or selective H_2S removal. Sorbents for physisorption are expensive. Chemisorption processes are mainly based on alkanolamines (“amines”), used in aqueous solutions (15 - 50%) to absorb H_2S and CO_2 . Primary amines (RNH_2), secondary amines (R_2NH) and tertiary amines (R_3N), where organic groups “R” can be selected which react differently with H_2S and CO_2 (Bloemendal and Kerkhof, 2000):

with primary or secondary amines:



with tertiary amines:



For H_2S the reactions with all amines are very fast; for CO_2 the reactions are much slower: reaction (R3-70) does not occur at all. Carbonyl sulphide (COS), which often accompanies H_2S is not removed very well by amines, and it is therefore usually

catalytically hydrolysed to H₂S and CO₂ at low temperatures (reaction R3-6).

Figure 3.35 gives guidelines for a first selection of a process for physisorption or chemisorption of H₂S, together with CO₂ or selectively.

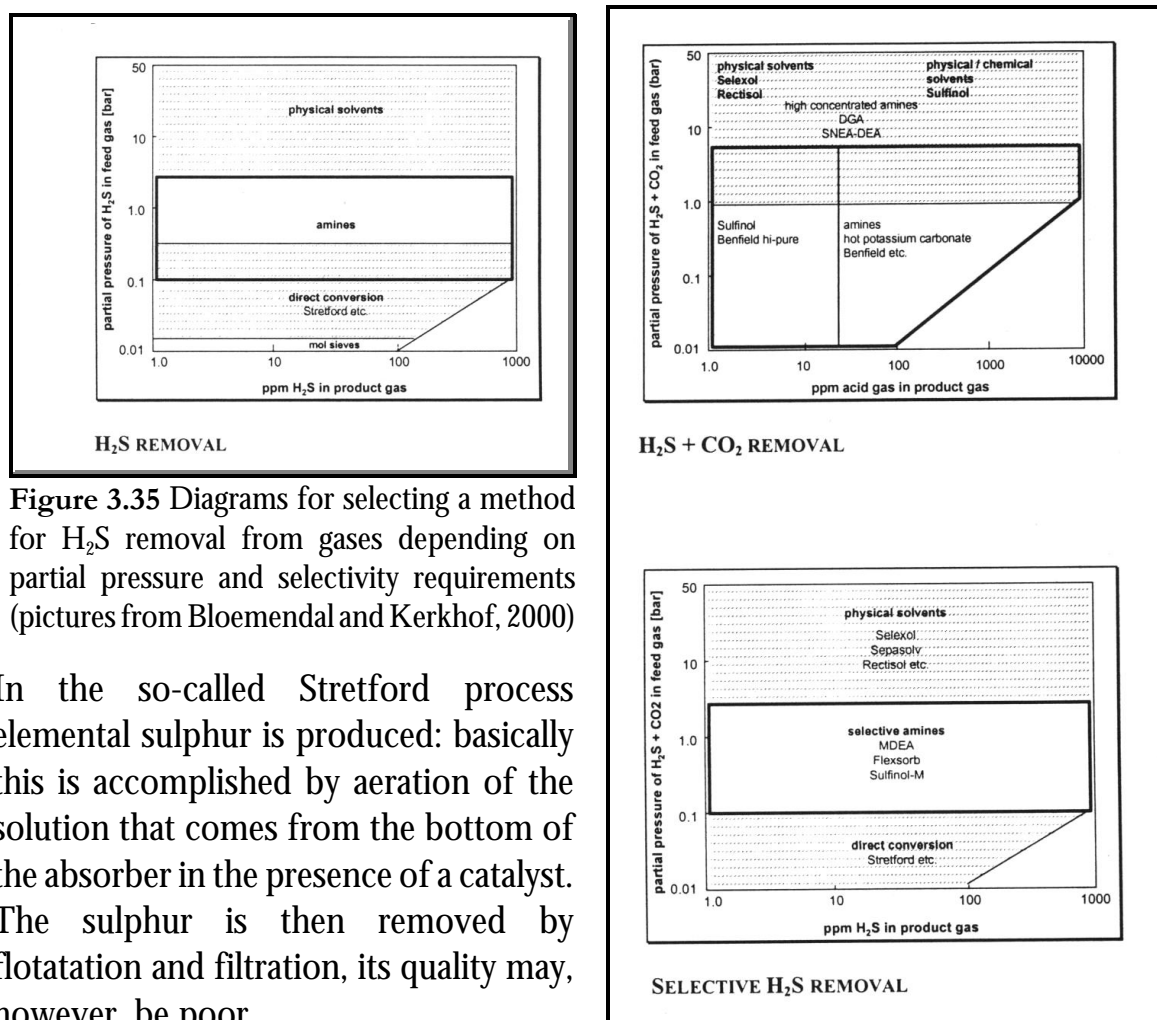


Figure 3.35 Diagrams for selecting a method for H₂S removal from gases depending on partial pressure and selectivity requirements (pictures from Bloemendal and Kerkhof, 2000)

In the so-called Stretford process elemental sulphur is produced: basically this is accomplished by aeration of the solution that comes from the bottom of the absorber in the presence of a catalyst. The sulphur is then removed by flotation and filtration, its quality may, however, be poor.

3.12 H₂S control by the Claus process

In the Claus process H₂S is oxidised to sulphur and water. It is a very important process for the treatment of the concentrated H₂S streams (preferably > 50..60%) that result from oil (7 section 3.5.2) and natural gas processing, *i.e.* typically from amine sorption (7 section 3.11). The Claus reaction is



The same result is obtained by oxidation of $\frac{1}{3}$ of the incoming H_2S , and mixing it with the rest:



Other reactions taking place, depending on the presence of CO_2 and NH_3 are



Depending on the concentration of the H_2S , three types of Claus processes can be distinguished (van den Berg and de Jong, 1980; McIntyre and Lyddon, 1997) - see also Figure 3.37:

- | | | |
|------|-------------------------------------------|--------------------------------|
| I. | > 50 % H_2S in the gas | Straight-through Claus process |
| II. | 15...50 % H_2S in the gas | Split-flow Claus process |
| III. | < 15 % H_2S in the gas | Direct oxidation Claus process |

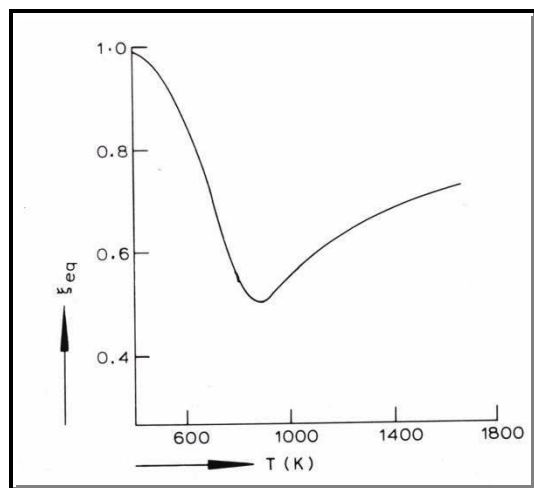


Figure 3.36 Equilibrium conversion for the Claus reaction *vs.* temperature (picture from van den Berg and de Jong, 1980)

The Claus reaction (R3-71) is exothermic and in fact the straight-through Claus process is a net producer of steam. Hence, the reaction equilibrium for the Claus reaction shown in Figure 3.36 first decreases with temperature. It rises again at high temperatures due to the dissociation of S_x polymers into monoatomic S.

A catalyst is used to reach high conversions with sufficient speed: typically an activated alumina, activated bauxite or cobalt-molybdenum hydrogenation catalyst are used.

The process involves a partial oxidation step with air at 1000 - 1400EC, followed by cooling in a waste heat boiler where also liquid sulphur product is obtained. After cooling to 200 - 350EC the gas is led to the catalytic Claus reactor. Since a single Claus stage does not give sufficient H_2S

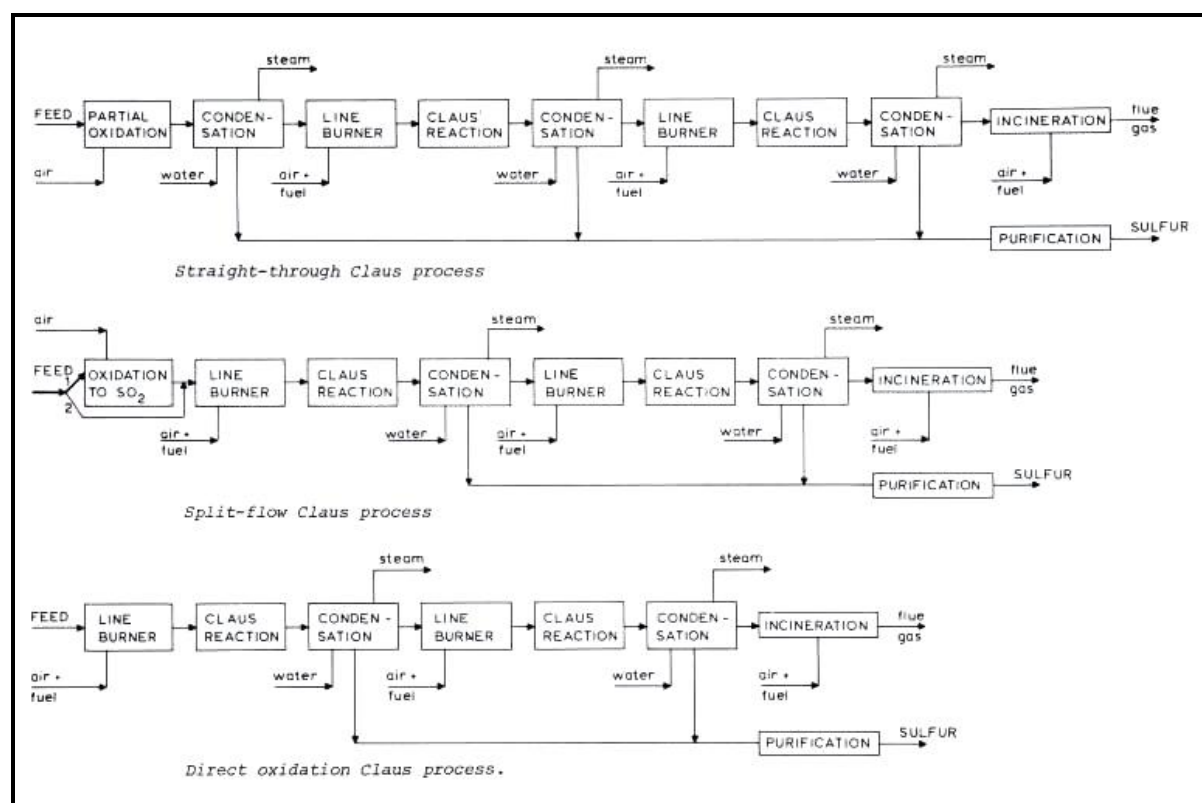


Figure 3.37 Three configurations for the Claus process. *Top:* Straight-through, *Centre:* Split-flow and *Bottom:* Direct oxidation (picture from van den Berg and de Jong, 1980)

conversion, two- or three-stage processes are used which give conversions of ~ 95 % and ~97 %, respectively. Several improvements give conversions higher than that: the Superclaus 99 and 99.5 process give corresponding %-conversions by using special catalysts (preventing the formation of SO₂) and a separate hydrogenation reactor between the second and third stage. Oxygen enrichment of the air to the burner in the final Claus stage improves flame stability and reduces soot formation and poisoning of the catalyst beds.

For gases containing ammonia, burner modifications and/or air enrichment with oxygen are applied to prevent the formation of ammonium salts, *e.g.* the Oxyclaus process. In general this gives higher burner temperatures of ~ 1500EC.

For the tail-gas cleanup, the SCOT (Shell Claus Off-gas Treatment) process is often used, which is based on oxidation of all remaining sulphur to SO₂ and returning that to the inlet of the Claus unit.

More detail on the various Claus processes is given by McIntyre and Lyddon (1997).

3.14 High temperature H₂S control by regenerable sorbents

Mainly as a result of developments on IGCC processes for coal a need was generated for the removal of H₂S from gasification product gas at temperatures and pressures typical for the inlet of a gas turbine combustion chamber (7 chapter 2), say, above 500EC, 20 bar. For a typical IGCC coal gasification process, H₂S (+ COS+ CS₂ +...) concentrations are of the order of 1 %-v. This would produce SO₂ emissions of several 1000 ppm-vol SO₂ after combustion in a gas turbine, regardless of other harmful effects between gasifier and off-gas stack. Clearly, a process is needed that provides at least 90% removal efficiency - which for reasons of overall thermal power efficiency of the plant is to be carried out at temperatures above 500EC.

Based on costs and experiences with calcium-based minerals these were the first candidates as sorbents for desulphurisation, followed by a wide range of metal oxides - see Table 3.9 for a list of potential H₂S sorbents and some performance characteristics.

Table 3.9 Qualities of sorbents for high temperature H₂S removal (taken from Konttinen and Mojtahedi, 1993)

Sorbent	Chemical formula	Theor. ^a cap.%	Equil. ^b H ₂ S, ppm	Temp. Range, °C
Zinc ferrite	ZnFe ₂ O ₄	39.83	10 ^c	540-650
Zinc copper ferrite	0.86ZnO·0.14CuO·Fe ₂ O ₃	38.90	1 ^c	540-680
Zinc titanate	0.8ZnO·TiO ₂	17.68	8 ^c	540-730
Copper ferrite aluminate	3CuO·Fe ₂ O ₃ ·Al ₂ O ₃	22.31	1 ^d	540-620
Copper aluminate	CuO·Al ₂ O ₃	8.79	2 ^d	540-590
Copper managanese oxide	CuMn ₂ O ₄	53.78	1 ^e	510-650
Nickel supported on alumina	Al ₂ O ₃ +20% Ni	10.90	0.02 ^f	500-700
Zinc oxide	ZnO	39.51	7 ^c	450-650
Iron oxide	Fe ₃ O ₄	41.38	560 ^c	450-700
Copper	Cu	25.00	70 ^c	540-700
Copper oxide	Cu ₂ O	22.38	1 ^c	540-700
Limestone	CaCO ₃	32.00	100 ^g	815-980
Lime	CaO	57.14	150 ^h	815-980

^a g sulfur/100 g fresh sorbent

^b H₂O/H₂ = 25:20 mol %

^c at 600 °C

^d 565 °C

^e at 650 °C

^f ppbv at 500 °C

^g at 15 bar, 6 mol-% H₂O, 11 mol-% CO₂, 980 °C

^h at 980 °C

This table shows two major differences between lime or limestone and the other sorbents: apart from a lower cost Ca-based sorbents can be used at higher temperatures, but at much higher equilibrium concentrations for the H₂S in the "cleaned" gas. In practically all cases a better performance is required which is

accomplished by (regenerative) metal oxide sorbents or a combination of calcium-based and metal oxide sorbents in subsequent processes. Working temperature ranges of desulphurisation sorbents based on several elements are shown in Figure 3.38.

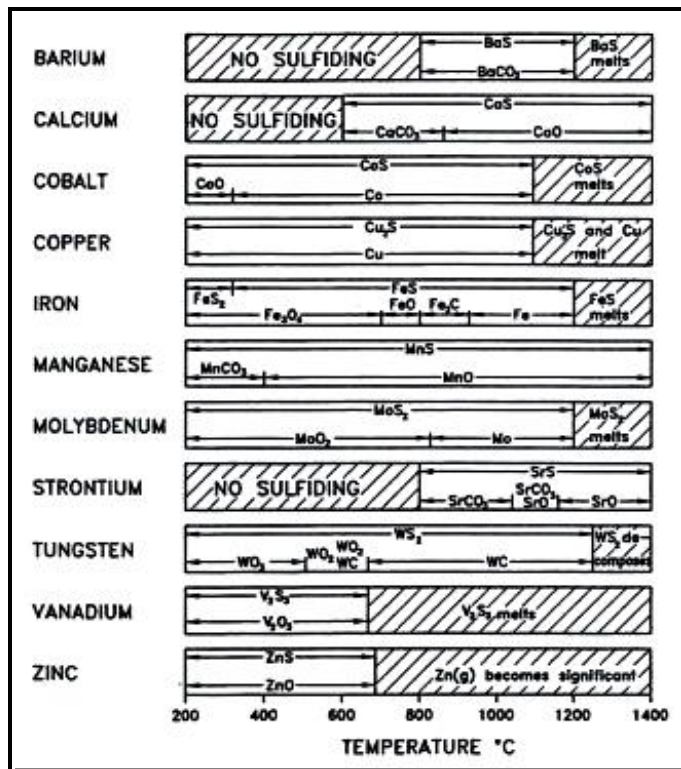
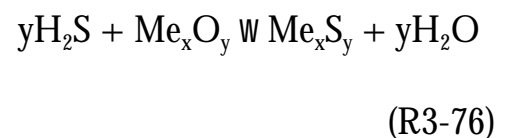


Figure 3.38 Temperature ranges for sorbents for H₂S removal (picture from Westmoreland and Harrison, 1976)

This shows that the most interesting candidates are the oxides of Mn, Mo, Fe, Co, Cu and Zn for temperatures below, say, 600 EC, whilst Ca is an option for temperatures above 600EC. Apart from single oxides such as Me_xO_y, the use of mixed oxides such as Me₁xMe₂zO_y is very much limited by the formation of highly stable spinels of the type Me₁Me₂zO₄, e.g. ZnCrO₄, which are non-reactive towards H₂S.

The desulphurisation reaction can be written as



The reversibility of reaction (R3-76) makes practically all sorbents regenerable, making sorbent stability under repeated operation the subject of optimisation.

The most versatile sorbents for desulphurisation were found to be zinc titanates (ZnO.xTiO₂) and zinc ferrites (ZnO.xFe₂O₃), for the temperature range 550-650EC. The latter has a higher capacity but suffers from stability (reduction of the iron oxide to unreactive iron at above 500EC) in gasifier product gas and self-poisoning by catalysing the soot-forming Boudouard reaction (Konttinen and Mojtahedi, 1993):



In zinc titanate, with Zn/Ti at ratios 0.5~2, the ZnO is stabilised against reduction to elemental Zn by the TiO₂. After sulphidation to ZnS.xTiO₂ it can be regenerated back to ZnO.xTiO₂ by oxidation with oxygen (or air) plus steam.

Manganese based sorbents have been studied by Wakker (1992). MnO and Fe_2O_3 are very fast reacting sorbents for H_2S , probably as a result of favourable texture.

A typical layout for a regenerative sorbent process for desulphurisation is shown in Figure 3.39 for a fixed bed arrangement. Here the gas will pass the reactor in plug flow, with a reaction zone profile moving through the reactor in the same direction. Alternatively a fluidised bed reactor can be used (7 chapter 2), in which' case the solids can be assumed perfectly mixed.

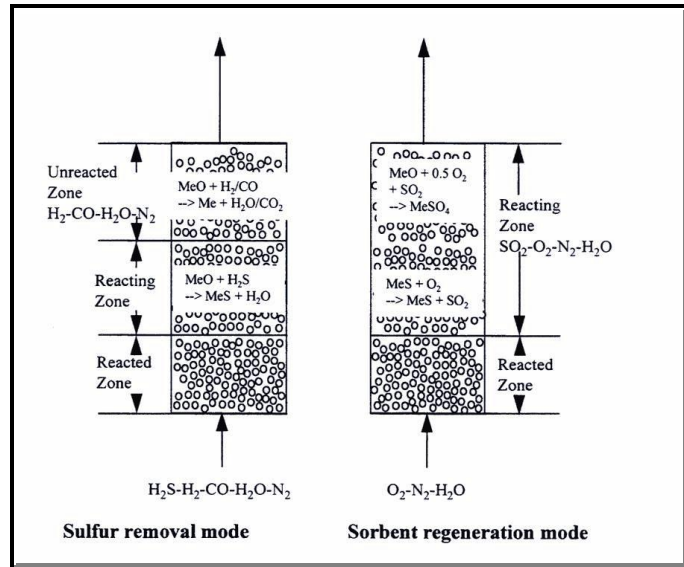


Figure 3.39 Typical arrangement for regenerative H_2S capture using fixed bed reactors (picture from Kontinen, 1998)

A regenerative desulphurisation process for coal gasifier product gas based on calcium-based sorbents (limestone or dolomites) in a fluidised bed reactor, was analysed by Heesink (1994), as shown in Figure 3.40. After the generation the concentrated H_2S is fed further to a Claus unit (7 section 3.13) at $>10\%$ -vol H_2S .

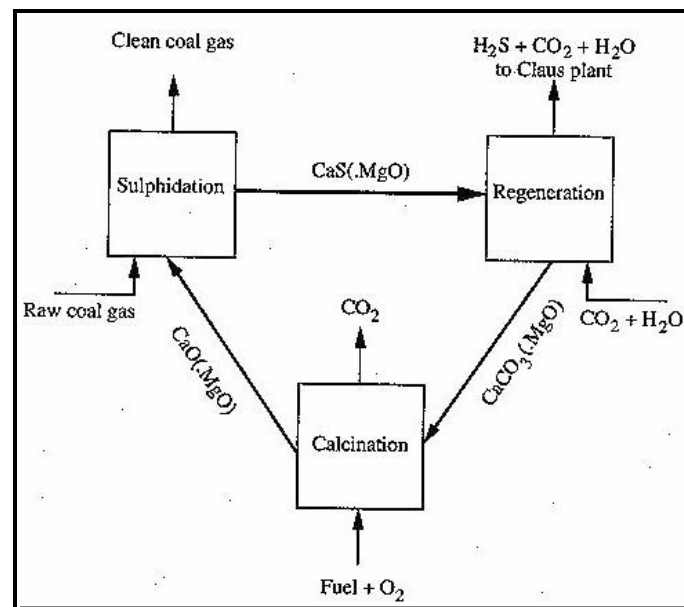


Figure 3.40 Coal gas desulphurisation process based on calcium-based sorbents (picture from Heesink, 1994)

Apart from being economically unfeasible (at a sorbent cost of ~ 25 US\$/tonne, compared to ~ 5000 US\$/tonne for a typical zinc titanate, disposal of spent sorbent is the most economic option), the process suffers from unfavourable thermodynamics, as illustrated by Figures 3.41. For typical concentrations of several % of H_2O and CO_2 in the coal gas it will be very difficult to reduce $H_2S + COS$ concentrations below the objective level of 20 ppmv.

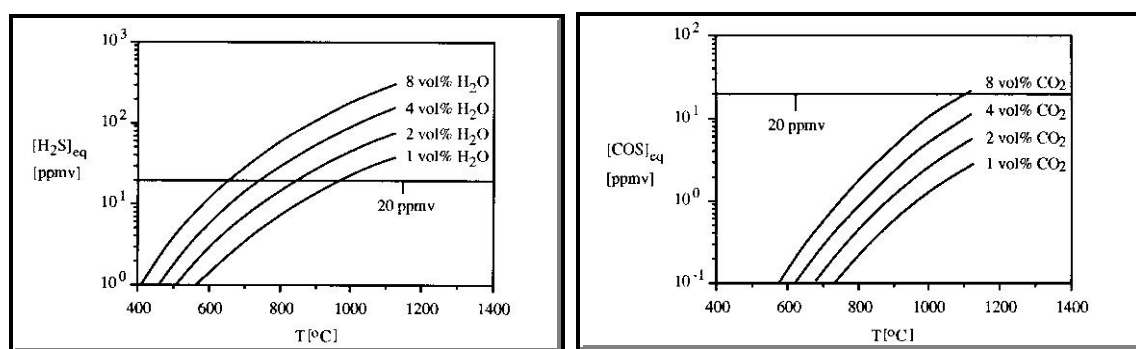


Figure 3.41 Equilibrium partial pressures for H₂S (*left*) and COS (*right*) vs. temperature for typical gasification product gases for removal with CaO (pictures from Heesink, 1994)

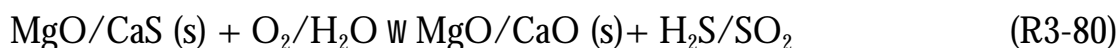
It was found that between 500 and 700EC the kinetics of the reaction



were too slow for practical applications. Another problem was the side-reaction



and that the sorbent tends to prefer to react with CO₂, giving CaCO₃ (reaction R3-49) rather than with H₂S. Considering regeneration, only dolomite gave complete regeneration within reasonable time:



Due to the low cost of calcareous minerals it is an interesting option, though, to remove part of the sulphur *in-situ* in the gasifier, where it forms CaS, followed by a deeper desulphurisation of the gas using regenerable sorbents. One typical example is the fluidised bed coal gasification project at Piñon Pine (NV), a demonstration project on a 100 MW_{elec} test facility (US DOE, 1996) - see Figure 3.42. In a spouted bed gasifier, coal (sulphur content ~0.4%-wt) is gasified with steam and air at ~980EC. About 50% of the sulphur is bound by CaO to form CaS (reaction R3-78). The CaS is then fed to a “sulfator” where it is further oxidised to CaSO₄ (reaction R3-59) which can then be landfilled. High levels of CaS-containing solids cannot be disposed of as such, since it will release H₂S when exposed to the open air, via



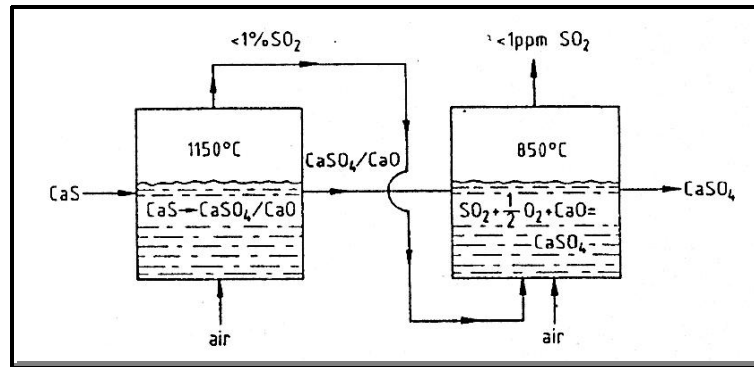


Figure 3.43 Two-reactor process for CaS stabilisation (picture from Schwerdtfeger and Barin, 1993)

The thermodynamics of CaS stabilisation is depending on the partial pressures of O₂ and SO₂ and temperature as shown in Figure 3.44 for 1100 K and 1300 K.

The problem with CaS stabilisation is similar to the reduction of CaSO₄ during *in-situ* sulphur capture in FBC (7 section 3.11): CaS is rather stable under reactor conditions and the (re-)oxidation of CaS to CaSO₄ is a complicating factor in these processes.

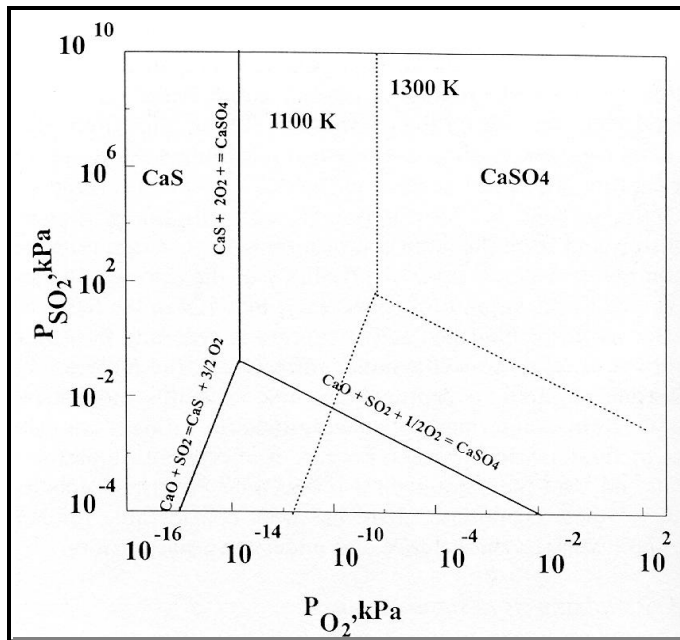
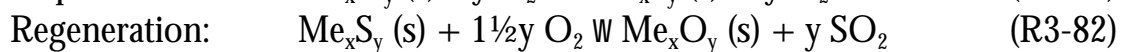


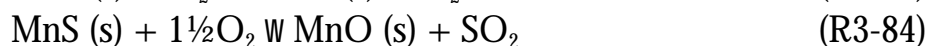
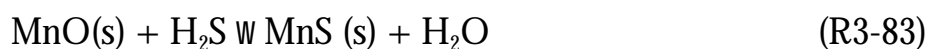
Figure 3.44 Phase diagram for the system Ca-S-O at 1100 and 1300 K (picture from Grace *et al.*, 1997)

With or without a pre-removal with Ca-based sorbents in the gasifier itself, the general approach to gasifier product gas desulphurisation to ppm-level concentrations of H₂S is to use a regenerable metal oxide sorbent. The chemistry can be summarised as:



In general, the regeneration takes place at a slightly higher temperature, and reaction stoichiometry for reaction (R3-82) favours regeneration at elevated pressures.

Examples of sulphidation/regeneration reactions are



with, for ZnO, the following side-reactions :



The loss of Zn due to reduction is suppressed by stabilising the ZnO in zinc titanate, $\text{ZnO} \cdot x\text{TiO}_2$. The production of $\text{ZnSO}_4\text{(s)}$ can be a serious problem during ZnS regeneration. Apart from partial deactivation of zinc it also leads to effectivity loss due to pore plugging and blocking in the sorbent, owing to the larger molecular volume of ZnSO_4 . (Similar to CaSO_4 in comparison with CaO : 7 section 3.11).

Work by Konttinen *et al.* (1997) has shown that this can be avoided when the partial pressure of oxygen is distributed along the reactor axis such that ZnSO_4 is not thermodynamically stable at the outlet, *i.e.* where the regenerated sorbent is returned to the sulphidation reactor. This is illustrated by Figure 3.45, in analogy with the previous picture.

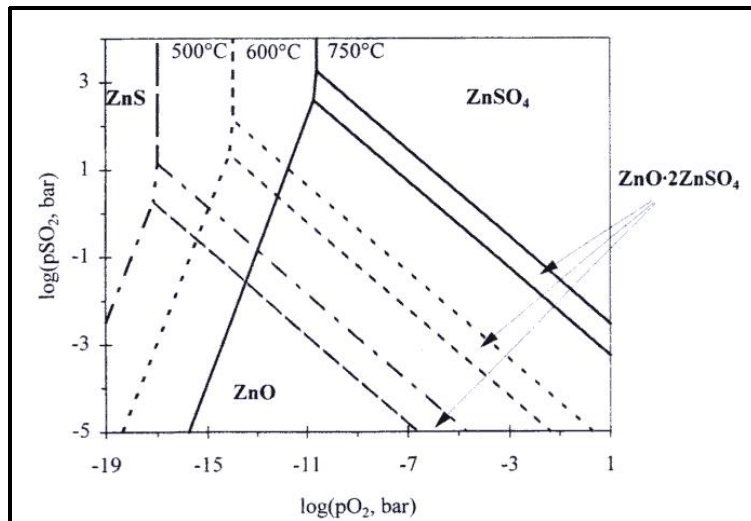


Figure 3.45 Phase diagram for the system Zn-S-O at 500, 600 and 750EC (picture from Konttinen *et al.*, 1997)

A typical process set-up for regenerative desulphurisation with a zinc titanate sorbent is shown in Figure 3.46. Coal gasifier gas is cleaned at 10-20 bar, ~550EC; the sulphided sorbent is regenerated with an oxygen/steam mixture at the same pressure as the sulphider reactor but at a higher temperature: 625-650EC. The stability of a commercial sorbent should be such that it can be sulphided/regenerated for periods of the order of a year (*i.e.* hundreds to thousands of cycles) before replacement.

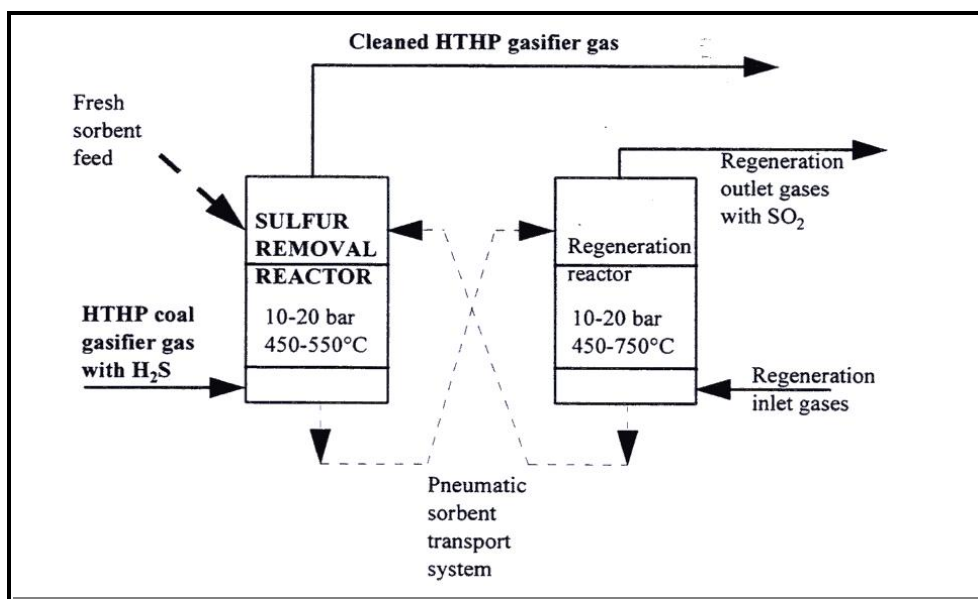


Figure 3.46 Process scheme for coal gasifier desulphurisation with a regenerable sorbent (zinc titanate) (picture from Konttinen, 1998)

Many developments are still going on to optimise this process, especially sorbent formulations. Adding carbon, for example as a pore structure modifier during zinc titanate pellet production gave a clear improvement of sorbent efficiency (Pineda *et al.*, 1998). Or, the addition of 5% Ni and/or Co to another zinc titanate, to be used

at Piñon Pine may allow for lowering the regeneration temperature by more than 100EC, to as low as 475EC (Jothimurugesan and Gangwal, 1998).

Fixed-bed with pellets	Moving-bed	Fluidized-bed
poor heat transfer, resulting in temperature gradients ("hot spots") inside the reactor resulting in undesirable reactions	heat transfer limitations lead to undesirable side-reactions	efficient heat transfer means that bed can be assumed isothermal
poor mass transfer due to large particles ($d_p = 10 - 15$ mm), results in poor solid utilization, slow reactions due to pore diffusion	mass transfer limitations due to large particles ($d_p = 2 - 3$ mm), resulting in poor sorbent utilization, slow reactions	efficient mass transfer ($d_p = 200 - 500 \mu\text{m}$) results in good gas-solid contact, fast reactions
low throughputs		high throughputs possible
reactors easy to scale-up (experience in chemical industry)	scale-up uncertain	scale-up includes uncertainties
steady-state operation very difficult due to sulfidation/regeneration cycling	steady-state operation has not yet been achieved	continuous, steady-state operation possible due to sorbent circulation
no need for gas filtering after reactors	gas filtering after reactors might be needed	gas filtering after reactors due to sorbent elutriation
requires many high temperature and pressure mechanical parts (valves)	requires HTHP valves for operation	number of moving, mechanical parts (valves) can be minimized
Demonstration		
long-term pilot-scale operation has not been demonstrated	demonstration going on at pilot-scale in USA	demonstration at pilot-scale going on in Japan and in Finland

Figure 4.47 Comparison of reactor types for regenerative sorbent-based H₂S removal (picture from Konttinen and Mojtahedi, 1993)

Finalising, Figure 4.47 gives the pro's and contra's of various reactor types that can be selected for a regenerative sorbent-based H₂S removal process.

3.15 Sulphur emission control for transport vehicles

The control of sulphur emissions from transport vehicles is largely determined by legislation considering maximum sulphur levels in transport fuels. Vehicles have the potential to cover a large area with pollution, that may even cross national boundaries. Within EU borders, the amount of sulphur in petrol and diesel fuel is 150 and 350 ppm, respectively (as of 2000), aiming at a new limit of 50 ppm for both fuels in 2005. In the USA the situation is very similar (Acid News, 2000b).

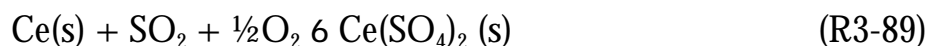
Gasoline and diesel fuel-fired cars, trucks, busses, motorcycles not too long ago generated sulphate emissions of the order of 20 mg/km to the direct environment (Heywood, 1988). Sulphur in the fuel is oxidised to SO_2 in the engine followed by further oxidation to SO_3 due to the presence of various catalytically active metals either in the fuel or in the engine itself. Upon cooling below $\sim 550^\circ\text{C}$, sulphuric acid H_2SO_4 is formed which condensates, resulting in corrosion at temperatures below $\sim 150^\circ\text{C}$. Within most of Western Europe transport fuels contain less than 0.05 %-wt sulphur, with levels below 0.01 %-wt in typical Finnish gasoline. Therefore, sulphur emissions from cars, trucks *etc.* are not a point of concern when compared to NO_x , CO, unburned hydrocarbons and (for diesel driven vehicles) particulate emissions.



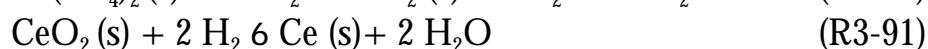
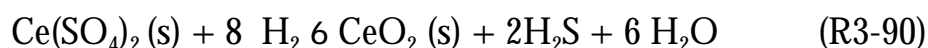
Figure 3.48 Development of SO_2 and NO_x emissions from land-based sources and shipping assuming the later to stay outside stricter regulations (picture from "Cleaner Shipping", 1997)

An exception are shipping fuels. Increasingly tight legislation for land-based SO_2 emissions within the 15 EU member states may exclude shipping, with the result that against 10% in 1990, 30% of the SO_2 emissions within the EU-15 area will be produced by shipping in 2010 - see Figure 3.48 (Cleaner shipping, 1997). Typical sulphur contents in bunker oils fired on ships on the North Sea are 2.5 - 3.5 % (Acid News, 2000b).

A contemporary issue are occasional H₂S emissions from cars, trucks *etc.* for which the human nose is much more sensitive than for SO₂. A study by Yrjas (1996) goes into the chemistry of this. The metal Ce, for example in modern car exhaust gas cleaning catalysts absorbs the SO₂ :



which is released as H₂S during reducing conditions, as they occur during vehicle deceleration :



which may explain the occasional smell of H₂S in city traffic.

3.16 References

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