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

<table>
<thead>
<tr>
<th>Plant size, MWₑlec</th>
<th>Coal sulphur content, %</th>
<th>FGD process</th>
<th>Fixed O &amp; M</th>
<th>Variable O &amp; M</th>
<th>Fixed capital charge</th>
<th>Total costs</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>2.6</td>
<td>Wet limestone scrubber*</td>
<td>79</td>
<td>90</td>
<td>183</td>
<td>352</td>
</tr>
<tr>
<td>200</td>
<td>2.6</td>
<td>Spray dry scrubber**</td>
<td>40</td>
<td>143</td>
<td>134</td>
<td>317</td>
</tr>
<tr>
<td>200</td>
<td>2.6</td>
<td>Lurgi CFB***</td>
<td>15</td>
<td>140</td>
<td>123</td>
<td>277</td>
</tr>
<tr>
<td>500</td>
<td>4.3</td>
<td>Wet limestone scrubber</td>
<td>20</td>
<td>76</td>
<td>83</td>
<td>178</td>
</tr>
<tr>
<td>500</td>
<td>4.3</td>
<td>Spray dry scrubber</td>
<td>11</td>
<td>131</td>
<td>69</td>
<td>211</td>
</tr>
<tr>
<td>500</td>
<td>4.3</td>
<td>Lurgi CFB</td>
<td>3</td>
<td>130</td>
<td>63</td>
<td>196</td>
</tr>
</tbody>
</table>

* 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, Chapter 2) is the option of *in-situ* SO₂ capture. The temperature level of 800 ~ 950°C 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 NOₓ 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

\[
\text{calcination, followed by sulphation} \\
\text{CaCO}_3 (s) \rightarrow \text{CaO} (s) + \text{CO}_2 \quad \text{(R3-49)} \\
\text{CaO} (s) + \frac{1}{2}\text{O}_2 + \text{SO}_2 \rightarrow \text{CaSO}_4 (s) \quad \text{(R3-46)}
\]

or

\[
\text{direct sulphation} \\
\text{CaCO}_3 (s) + \frac{1}{2}\text{O}_2 + \text{SO}_2 \rightarrow \text{CaSO}_4 (s) + \text{CO}_2 \quad \text{(R3-53)}
\]

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, 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

\[
\text{fully-calcined dolomite sulphation} \\
\text{CaCO}_3@\text{MgCO}_3 (s) \rightarrow \text{CaO} (s) + \text{MgO} (s) \
\text{CaO} (s) + \frac{1}{2}\text{O}_2 + \text{SO}_2 \rightarrow \text{CaSO}_4 (s) \quad \text{(R3-54)}
\]

or
half-calcined dolomite sulphation

\[
\begin{align*}
\text{CaCO}_3@ & \text{MgCO}_3 (s) \rightarrow \text{CaCO}_3 (s) + \text{MgO} (s) \\
\text{CaCO}_3 (s) + \frac{1}{2}\text{O}_2 + \text{SO}_2 & \rightarrow \text{CaSO}_4 (s) + \text{CO}_2
\end{align*}
\] (R3-55)

From the equilibrium of the calcium carbonate calcination reaction it can be deduced that for a CO\textsubscript{2} 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.

Pure CaCO\textsubscript{3} has a molar volume of 36.9 cm\textsuperscript{3}/mole, calcination gives CaO at 16.9 cm\textsuperscript{3}/mole and sulphation gives CaSO\textsubscript{4} at 46.0 cm\textsuperscript{3}/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 CaSO₄ 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, CaCO₃; the calcination process (reaction R3-49) in a way “opens up” the pore structure by the release of CO₂, 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 MgCO₃, 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 SO₂ 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 five limestones given in Table 3.7, at 15 bar, 850°C and 950°C.

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

<table>
<thead>
<tr>
<th>SORBENTS</th>
<th>CaCO₃* (%wt)</th>
<th>MgCO₃* (%wt)</th>
<th>Specific Surface ** (m²/g)</th>
<th>Particle Porosity (-)</th>
<th>Particle Density (kg/m³)</th>
<th>Average Pore Diameter *** (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limestone 1</td>
<td>98.4</td>
<td>0.90</td>
<td>2.25</td>
<td>0.178</td>
<td>1681</td>
<td>0.323</td>
</tr>
<tr>
<td>Limestone 2</td>
<td>97.9</td>
<td>0.65</td>
<td>1.49</td>
<td>0.075</td>
<td>2416</td>
<td>0.251</td>
</tr>
<tr>
<td>Limestone 3</td>
<td>98.6</td>
<td>0.61</td>
<td>4.63</td>
<td>0.324</td>
<td>1351</td>
<td>0.412</td>
</tr>
<tr>
<td>Limestone 4</td>
<td>88.9</td>
<td>1.15</td>
<td>2.94</td>
<td>0.077</td>
<td>1762</td>
<td>0.209</td>
</tr>
<tr>
<td>Limestone 5</td>
<td>90.4</td>
<td>2.87</td>
<td>3.74</td>
<td>0.063</td>
<td>2786</td>
<td>0.074</td>
</tr>
<tr>
<td>Dolomite 1</td>
<td>60.4</td>
<td>32.9</td>
<td>0.93</td>
<td>0.022</td>
<td>2727</td>
<td>0.112</td>
</tr>
<tr>
<td>Dolomite 2</td>
<td>47.4</td>
<td>26.0</td>
<td>0.060</td>
<td>0.010</td>
<td>2855</td>
<td>0.291</td>
</tr>
</tbody>
</table>

* Chemical composition taken from Yrjas et al. (1993)
** Found from N₂ BET surface measurement
*** Found from mercury penetration porosimetry
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 CaSO₄ 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 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).
Returning to atmospheric FBC: Figure 3.24 shows also that the best performance is obtained at 800-850°C, 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 850°C. It is nowadays accepted, however, that this is mainly related to the stability of the CaSO₄ 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 CaSO₄ is being reduced, by CO and/or H₂, to CaS, CaO or CaCO₃, depending on temperature, and partial pressures of the reactants.

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 SO₂, however, should be produced by oxidation of sulphur-containing gases (probably H₂S) that are released in the emulsion.
phase of the bed, and are then to react, as SO₂, again in the emulsion phase, with the sorbent - see Figure 3.28. At an overall stoichiometry \( \lambda_{\text{bed}} \), the stoichiometry in the emulsion phase is lower, \( i.e. \quad U_{\text{mf}} \lambda_{\text{bed}}/U < \lambda_{\text{emulsion}} < \lambda_{\text{bed}} \) (for gas velocity \( U \) and minimum fluidisation velocity \( U_{\text{mf}} \)), 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.

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 CaSO₄ that has been formed, via a complex chemistry that involves the following reactions (Yrjas and Hupa, 1997; Zevenhoven et al., 1999):

\[
\begin{align*}
\text{CaSO}_4(s) + \text{CO} &\rightarrow \text{CaO}(s) + \text{SO}_2 + \text{CO}_2 \quad \text{at 1 bar} \quad (R3-56) \\
\text{CaSO}_4(s) + \text{CO} &\rightarrow \text{CaCO}_3(s) + \text{SO}_2 \quad \text{at 15 bar} \quad (R3-57) \\
\text{CaSO}_4(s) + 4\text{CO} &\rightarrow \text{CaS}(s) + 4\text{CO}_2 \quad (R3-58) \\
\text{CaS}(s) + 2\text{O}_2 &\rightarrow \text{CaSO}_4(s) \quad (R3-59) \\
\text{CaO}(s) + \text{SO}_2 + 3\text{CO} &\rightarrow \text{CaS}(s) + 3\text{CO}_2 \quad \text{at 1 bar} \quad (R3-60) \\
\text{CaS}(s) + 1\frac{1}{2} \text{O}_2 &\rightarrow \text{CaO}(s) + \text{SO}_2 \quad \text{at 1 bar} \quad (R3-61) \\
\text{CaS} &\rightarrow 3\text{CaSO}_4(s) \quad 4\text{CaO}(s) + 4\text{SO}_2 \quad (R3-62) \\
\text{CaSO}_4(s) + \text{H}_2 &\rightarrow \text{CaO}(s) + \text{SO}_2 + \text{H}_2\text{O} \quad \text{at 1 bar} \quad (R3-63) \\
\text{CaSO}_4(s) + \text{H}_2 + \text{CO}_2 &\rightarrow \text{CaCO}_3(s) + \text{SO}_2 + \text{H}_2\text{O} \quad \text{at 15 bar} \quad (R3-64) \\
\text{CaSO}_4(s) + 4\text{H}_2 &\rightarrow \text{CaS}(s) + 4\text{H}_2\text{O} \quad (R3-65)
\end{align*}
\]

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 CaSO₄, \( i.e. \) CaS, CaO or CaCO₃, to CaSO₄ becomes slow when compared to the decomposition reactions themselves.
Or from a thermodynamic point of view: the equilibria for reactions (R3-56...58 and R3-63..65) shift more and more to the right. (The stability of CaSO₄ 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 SO₂ higher up in the riser).

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 % CO ~ λ = 0.997) as analysed by Yrjas and Hupa (1997) showed that the amount of CaCO₃ formed was not significant. Later work (Zevenhoven et al., 1999) with periodic strongly reducing conditions (1 % CO ~ λ = 0.97, and 4% CO or 4% CO+H₂ ~ λ = 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 CaSO₄ (reaction R3-65).

The oxidation of CaS to CaSO₄ with oxygen (reaction R3-59) is a relatively slow process that is competing with oxidation to CaO under release of SO₂ (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.
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 (Dₑ) when compared to a calcined sorbent particle. For longer conversion times this compensates slower chemical kinetics - see Figure 3.31.

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 \( \text{H}_2\text{S} \) control at low temperatures

Several processes for removing \( \text{H}_2\text{S} \) 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 \( \text{CO}_2 \) 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 \( \text{H}_2\text{S} \) removal from gases**

<table>
<thead>
<tr>
<th>Principle</th>
<th>Temperature range</th>
<th>Process names</th>
<th>Sorbent / catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical absorption</td>
<td>240 - 400 K</td>
<td>Selexol, Rectisol, Sulfinol, Purisol, CNG</td>
<td>Methanol (Rectisol), dimethyl ether of polyethylene glycol (Selexol), sulfolane (Sulfinol), carbon dioxide</td>
</tr>
<tr>
<td>product: ( \text{H}_2\text{S} )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical absorption</td>
<td>250 - 350 K</td>
<td>Alkanol amines, Girbotol, SNPA-DEA, ADIP, Econamine</td>
<td>Amines (MEA, DEA, MDEA, MGA, DIPA), potassium carbonate</td>
</tr>
<tr>
<td>product: ( \text{H}_2\text{S} )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxidation</td>
<td>300 - 400 K</td>
<td>Stretford, Takahax, Townsend</td>
<td>Solution of Na-salts of ( \text{H}_2\text{CO}_3 ), anthraquinone-2-sulphonic acid, .....</td>
</tr>
<tr>
<td>product: sulphur</td>
<td>~ 300 K</td>
<td>Iron sponge</td>
<td>Hydrated ( \text{Fe}_2\text{O}_3 )</td>
</tr>
</tbody>
</table>

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 \( T_{\text{abs}} \), pressure \( p_{\text{abs}} \), 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).
The choice for physisorption (or physical sorbent) or chemisorption (chemical sorbent) processes depends on the gases that are to be removed (H$_2$S 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$_2$S removal. Sorbents for physisorption are expensive. Chemisorption processes are mainly based on alkanolamines ("amines"), used in aqueous solutions (15 - 50%) to absorb H$_2$S and CO$_2$. Primary amines (RNH$_2$), secondary amines (R$_2$NH) and tertiary amines (R$_3$N), where organic groups “R” can be selected which react differently with H$_2$S and CO$_2$ (Bloemendal and Kerkhof, 2000):

with primary or secondary amines:

\[
\begin{align*}
\text{H}_2\text{S} + R_2\text{NH} \rightarrow & R_2\text{NH}_2^+ + \text{HS}^- \quad \text{(R3-66)} \\
\text{CO}_2 + 2 R_2\text{NH} \rightarrow & R_2\text{NH}_2^+ + R_2\text{NCOO}^- \quad \text{(R3-67)} \\
\text{CO}_2 + R_2\text{NH} + \text{H}_2\text{O} \rightarrow & R_2\text{NH}_2^+ + \text{HCO}_3^- \quad \text{(R3-68)}
\end{align*}
\]

with tertiary amines:

\[
\begin{align*}
\text{H}_2\text{S} + R_3\text{N} \rightarrow & R_3\text{NH}^+ + \text{HS}^- \quad \text{(R3-69)} \\
\text{CO}_2 + 2 R_3\text{N} \rightarrow & \text{no reaction} \quad \text{(R3-70)} \\
\text{CO}_2 + R_3\text{N} + \text{H}_2\text{O} \rightarrow & R_3\text{NH}^+ + \text{HCO}_3^- \quad \text{(R3-71)}
\end{align*}
\]

For H$_2$S 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$_2$S is not removed very well by amines, and it is therefore usually
catalytically hydrolysed to H$_2$S and CO$_2$ at low temperatures (reaction R3-6).

Figure 3.35 gives guidelines for a first selection of a process for physisorption or chemisorption of H$_2$S, together with CO$_2$ or selectively.

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.

### 3.13 H$_2$S control by the Claus process

In the Claus process H$_2$S is oxidised to sulphur and water. It is a very important process for the treatment of the concentrated H$_2$S streams (preferably > 50..60%) that result from oil (section 3.5.2) and natural gas processing, i.e. typically from amine sorption (section 3.12). The Claus reaction is

\[ 2\text{H}_2\text{S} + \text{O}_2 \xrightarrow{\text{W}2/\text{x}} \text{S}_x\ (s) + 2\text{H}_2\text{O} \] (R3-72)
The same result is obtained by oxidation of $\frac{1}{3}$ of the incoming H$_2$S, and mixing it with the rest:

\[
2 \text{H}_2\text{S} + \text{O}_2 \xrightarrow{W} \text{SO}_2 + 2 \text{H}_2\text{O} \quad \text{(R3-5)}
\]
\[
2 \text{H}_2\text{S} + \text{SO}_2 \xrightarrow{W} \frac{3}{x} S_x (s) + 2 \text{H}_2\text{O} \quad \text{(R3-73)}
\]

Other reactions taking place, depending on the presence of CO$_2$ and NH$_3$ are

\[
\text{H}_2\text{S} \xrightarrow{W} \text{H}_2 + \frac{1}{x} S_x (s) \quad \text{(R3-74)}
\]
\[
\text{H}_2\text{S} + \text{CO}_2 \xrightarrow{W} \text{H}_2\text{O} + \text{COS} \quad \text{(R3-6)}
\]
\[
\text{COS} + \text{H}_2\text{S} \xrightarrow{W} \text{H}_2\text{O} + \text{CS}_2 \quad \text{(R3-8)}
\]
\[
2 \text{NH}_3 + 3 \text{O}_2 \xrightarrow{W} 2 \text{NO} + 3 \text{H}_2\text{O} \quad \text{(R3-75)}
\]

Depending on the concentration of the H$_2$S, 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$_2$S in the gas  
   Straight-through Claus process

II. $15...50 \%$ H$_2$S in the gas  
   Split-flow Claus process

III. $< 15 \%$ H$_2$S in the gas  
   Direct oxidation Claus process

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$_x$ oligomers into monoatamtic 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 - 1400°C, followed by cooling in a waste heat boiler where also liquid sulphur product is obtained. After cooling to 200 - 350°C the gas is led to the catalytic Claus reactor. Since a single Claus stage does not give sufficient H$_2$S
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 ~ 1500°C.

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 H$_2$S control by regenerable sorbents

Mainly as a result of developments on IGCC processes for coal a need was generated for the removal of H$_2$S from gasification product gas at temperatures and pressures typical for the inlet of a gas turbine combustion chamber (section 2), say, above 500°C, 20 bar. For a typical IGCC coal gasification process, H$_2$S (+ COS + CS$_2$ + ...) concentrations are of the order of 1%-%. This would produce SO$_2$ emissions of several 1000 ppm-vol SO$_2$ 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 500°C.

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 H$_2$S sorbents and some performance characteristics.

\begin{center}
\textbf{Table 3.9 Qualities of sorbents for high temperature H$_2$S removal (taken from Konttinen and Mojtahedi, 1993)}
\end{center}

\begin{tabular}{|l|c|c|c|}
\hline
\textbf{Sorbent} & \textbf{Chemical formula} & \textbf{Theor.\% cap.} & \textbf{Equil.\% H$_2$S, ppm} & \textbf{Temp. Range, °C} \\
\hline
Zinc ferrite & ZnFe$_2$O$_4$ & 39.83 & 10 & 540–650 \\
Zinc copper ferrite & 0.86ZnO·0.14CuO·Fe$_2$O$_3$ & 38.90 & 1 & 540–650 \\
Zinc titanate & 0.8ZnO·TiO$_2$ & 17.68 & 8 & 540–730 \\
Copper ferrite aluminate & $3\text{CuO}·\text{Fe}_2\text{O}_3·\text{Al}_2\text{O}_3$ & 22.31 & 1 & 540–620 \\
Copper aluminate & CuO·Al$_2$O$_3$ & 8.79 & 2 & 540–590 \\
Copper managanese oxide & CuMn$_2$O$_4$ & 53.78 & 1 & 510–650 \\
Nickel supported on alumina & Al$_2$O$_3$·20%Ni & 10.90 & 0.02 & 500–700 \\
Zinc oxide & ZnO & 39.51 & 7 & 450–650 \\
Iron oxide & Fe$_3$O$_4$ & 41.38 & 560 & 450–700 \\
Copper & Cu & 25.00 & 70 & 540–700 \\
Copper oxide & Cu$_2$O & 22.38 & 1 & 540–700 \\
Limestone & CaCO$_3$ & 32.00 & 100 & 815–980 \\
Lime & CaO & 57.14 & 150 & 815–980 \\
\hline
\end{tabular}

\footnotesize{\textsuperscript{a} g sulfur/100 g fresh sorbent \textsuperscript{b} H$_2$O/H$_2$ = 25:20 mol \% \textsuperscript{c} at 600 °C \textsuperscript{d} 565 °C \textsuperscript{e} at 650 °C \textsuperscript{f} ppmv at 500 °C \textsuperscript{g} at 15 bar, 6 mol-% H$_2$O, 11 mol-% CO$_2$, 980 °C \textsuperscript{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 H$_2$S 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. This shows that the most interesting candidates are the oxides of Mn, Mo, Fe, Co, Cu and Zn for temperatures below, say, 600 °C, whilst Ca is an option for temperatures above 600 °C. Apart from single oxides such as MeₓOᵧ, the use of mixed oxides such as Me₁Me₂O₄ is very much limited by the formation of highly stable spinels of the type Me₁Me₂O₄, e.g., ZnCrO₄, which are non-reactive towards H₂S.

The desulphurisation reaction can be written as

\[ y\text{H}_2\text{S} + \text{Me}_x\text{O}_y \rightarrow \text{Me}_x\text{S}_y + y\text{H}_2\text{O} \]  

(R3-76)

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 550-650 °C. The latter has a higher capacity but suffers from stability (reduction of the iron oxide to unreactive iron at above 500 °C) in gasifier product gas and self-poisoning by catalysing the soot-forming Boudouard reaction (Konttinen and Mojtahedi, 1993):

\[ 2\text{CO} \rightarrow \text{CO}_2 + \text{C}(s) \]  

(R3-77)

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 Fe₂O₃ are very fast reacting sorbents for H₂S, 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.

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 H₂S is fed further to a Claus unit (7 section 3.13) at >10%-vol H₂S.

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 H₂O and CO₂ in the coal gas it will be very difficult to reduce H₂S + COS concentrations below the objective level of 20 ppmv.
It was found that between 500 and 700°C the kinetics of the reaction

$$\text{CaO (s) + H}_2\text{S} \rightarrow \text{CaS (s) + H}_2\text{O} \quad (R3-78)$$

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

$$\text{CaO (s) + COS} \rightarrow \text{CaCO}_3 (s) + \text{CS}_2 \quad (R3-79)$$

and that the sorbent tends to prefer to react with CO$_2$, giving CaCO$_3$ (reaction R3-49) rather than reacting with H$_2$S. Considering regeneration, only dolomite gave complete regeneration within reasonable time:

$$\text{MgO/CaS (s) + O}_2/\text{H}_2\text{O} \rightarrow \text{MgO/CaO (s) + H}_2\text{S/SO}_2 \quad (R3-80)$$

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$_{\text{elec}}$ 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 ~980°C. 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 CaSO$_4$ (reaction R3-59) which can then be landfilled. High levels of CaS-containing solids cannot be disposed of as such, since it will release H$_2$S when exposed to the open air, via

$$\text{CaS (s) + H}_2\text{O} \rightarrow \text{CaO (s) + H}_2\text{S} \quad (R3-81)$$
One disadvantage with a fluidised bed gasifier when compared to an entrained flow gasifier (chapter 2) is the relatively large particle size ~1 mm, which makes the stabilisation of CaS more difficult.

CaS stabilisation, i.e. oxidation to CaSO₄ is not a straightforward issue: it is highly exothermic and has several undesirable side-routes that yield SO₂ (Yrjas et al., 1996; García-Calzada et al., 2000):

\[
\begin{align*}
\text{CaS} + 2\text{O}_2 &\rightarrow \text{CaSO}_4 & \Delta H_{298}^\circ &= -961 \text{ kJ/mol} \\
\text{CaS} + 1\frac{1}{2}\text{O}_2 &\rightarrow \text{CaO} + \text{SO}_2 & \Delta H_{298}^\circ &= -459 \text{ kJ/mol} \\
\text{CaS} + 3\text{CaSO}_4 &\rightarrow 4\text{CaO} + 4\text{SO}_2 & \Delta H_{298}^\circ &= 1048 \text{ kJ/mol}
\end{align*}
\]

Best results are obtained at temperatures of the order 800~900°C, higher temperatures give significant SO₂ release.

Another process option for CaS stabilisation is shown in Figure 3.43, based on two fluidised bed reactors operating at 1150°C and 850°C, respectively. SO₂ that is released during the first stage is recaptured in the second reactor.
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 (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.

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:

Sulphidation: \[ \text{Me}_x\text{O}_y (s) + y \text{H}_2\text{S} \xrightarrow{\text{W}} \text{Me}_x\text{S}_y (s) + y \text{H}_2\text{O} \] \hspace{1cm} (R3-76)

Regeneration: \[ \text{Me}_x\text{S}_y (s) + 1\frac{1}{2}y \text{O}_2 \xrightarrow{\text{W}} \text{Me}_x\text{O}_y (s) + y \text{SO}_2 \] \hspace{1cm} (R3-82)

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:

\[
\begin{align*}
\text{MnO(s) + H}_2\text{S} & \rightarrow \text{MnS (s) + H}_2\text{O} & \text{(R3-83)} \\
\text{MnS (s) + } \frac{1}{2}\text{O}_2 & \rightarrow \text{MnO (s) + SO}_2 & \text{(R3-84)} \\
\text{ZnO(s) + H}_2\text{S} & \rightarrow \text{ZnS (s) + H}_2\text{O} & \text{(R3-85)} \\
\text{ZnS (s) + } \frac{1}{2}\text{O}_2 & \rightarrow \text{ZnO (s) + SO}_2 & \text{(R3-86)}
\end{align*}
\]

with, for ZnO, the following side-reactions:

\[
\begin{align*}
\text{Sulphidation : } & \quad \text{ZnO (s) + H}_2/\text{CO} \rightarrow \text{Zn + H}_2\text{O/CO}_2 & \text{(R3-87)} \\
\text{Regeneration : } & \quad \text{ZnS (s) + 2 O}_2 \rightarrow \text{ZnSO}_4 (s) & \text{(R3-88)}
\end{align*}
\]

The loss of Zn due to reduction is suppressed by stabilising the ZnO in zinc titanate, ZnO\text{xTiO}_2. The production of ZnSO_4(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, \textit{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.

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, \sim 550\text{EC}; the sulphided sorbent is regenerated with an oxygen/steam mixture at the same pressure as the sulphider reactor but at a higher temperature: 625-650\text{EC}. The stability of a commercial sorbent should be such that it can be sulphided/regenerated for periods of the order of a year (\textit{i.e.} hundreds to thousands of cycles) before replacement.
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 100°C, to as low as 475°C (Jothimurugesan and Gangwal, 1998).

Finalising, Figure 3.47 gives the pro’s and contra’s of various reactor types that can be selected for a regenerative sorbent-based H₂S removal process.

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

Figure 3.47 Comparison of reactor types for regenerative sorbent-based H₂S removal (picture from Konttinen and Mojtahedi, 1993)
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 SO₂ in the engine followed by further oxidation to SO₃ due to the presence of various catalytically active metals either in the fuel or in the engine itself. Upon cooling below ~550°C, sulphuric acid H₂SO₄ is formed which condensates, resulting in corrosion at temperatures below ~150°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 NOₓ, CO, unburned hydrocarbons and (for diesel driven vehicles) particulate emissions.

An exception are shipping fuels. Increasingly tight legislation for land-based SO₂ emissions within the 15 EU member states may exclude shipping, with the result that against 10% in 1990, 30% of the SO₂ 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).

![Figure 3.48 Development of SO₂ and NOₓ emissions from land-based sources and shipping assuming the later to stay outside stricter regulations (picture from “Cleaner Shipping”, 1997)
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:

\[
\text{Ce}(s) + \text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow 6 \text{Ce(SO}_4)_2 (s) \quad \text{(R3-89)}
\]

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

\[
\text{Ce(SO}_4)_2 (s) + 8 \text{H}_2 \rightarrow 6 \text{CeO}_2 (s) + 2\text{H}_2\text{S} + 6 \text{H}_2\text{O} \quad \text{(R3-90)}
\]

\[
\text{CeO}_2 (s) + 2 \text{H}_2 \rightarrow 6 \text{Ce} (s) + 2 \text{H}_2\text{O} \quad \text{(R3-91)}
\]

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

3.16 References


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