

Chapter 3 Sulphur

3.1 Introduction

Sulphur is probably the “easiest” pollutant from a gas clean-up point of view. A first reason for that is certainly that the chemistry involved is relatively simple and (hence) well understood. In combustion plants sulphur in fuel will eventually be oxidised to sulphur dioxide SO_2 and some sulphur trioxide SO_3 , be it that small amounts may be bound by ash-forming minerals as sulphates. At the same time, a long history of SO_2 capture with limestone and other calcareous rocks exists, which is accomplished at relatively low costs due to the abundance of these materials in nature. Hence, it is no surprise that in response to stricter legislations introduced during the 1970-1980s, significant sulphur oxides (“ SO_x ”) emission reductions were rapidly implemented (Ponting, 1991). In Europe, sulphur emissions dropped by 53% since 1980 (Acid News, 2000a). This in contrast with the ongoing struggle to reduce nitrogen oxides (NO_x) emissions from the same facilities.

In gasification or pyrolysis plants hydrogen sulphide H_2S will be the most important sulphur compound. Methods for its control have been developed first by the petro-chemical industry, while later methods based on (regenerable) sorbents were specially developed for coal gasification units. Upon release to the environment, H_2S will be oxidised to SO_2 .

One fact remaining, though, is that sulphur must eventually be disposed of in some chemical form. Unlike fuel-related nitrogen, that without any environmental concern may be released partly as molecular nitrogen N_2 , there is no such “escape route” for sulphur. Fuel-related sulphur that is captured may end up as molecular sulphur, sulphuric acid, or bound in flue gas desulphurisation (FGD) residues like gypsum, and partly in bottom ashes and fly ashes. In other cases, such as cement kilns, the cement product may contain a significant amount of the sulphur from the fuels used (coals, petcoke, alternative fuels) without causing problems.

For utilities and power plants firing sulphur-containing solid fuels SO_2 capture can be implemented with guaranteed success, but a different situation exists for the fuels derived from oil. As a result of tight limits on sulphur contents of transport fuels like gasoline and light fuel oils, it is difficult for the petro-chemical industry to find an outlet for the sulphur that is obtained from oil refining. Currently much of that

sulphur is found in heavy fuel oils used on ships without emissions control, that is, at those seaways where high-sulphur fuels for shipping are accepted ("Cleaner Shipping", 1997) (L section 3.15).

Sulphur emissions to the environment may be divided in being the result of human activities, basically the combustion of fuels for heat and power or transport, plus a contribution from natural sources. Volcanoes emit significant amounts of sulphur as well. Emissions of sulphur dioxide are correlated with deposition of sulphur compounds, often in the form of dilute sulphuric acid, part of which is known as "acid rain". Figures 3.1 and 3.2 give an impression of the situation in Europe during the last decade. It is seen that the sulphur emissions result in deposition mainly in the densely populated and industrialised "band" from England via Germany to Central and South-East Europe. The countries in Scandinavia can be considered as importers of sulphur-related pollution, whilst countries like Spain, Portugal, Ireland and Russia appear to export most of their sulphurous pollutants.

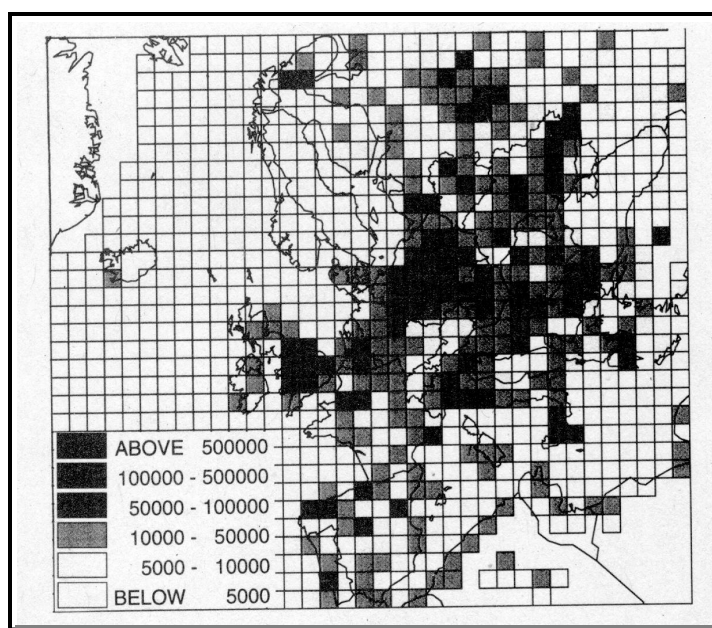


Figure 3.1 Annual emissions of SO_2 in Europe in 1994, in tonnes (picture from Ågren and Elvingson, 1997)

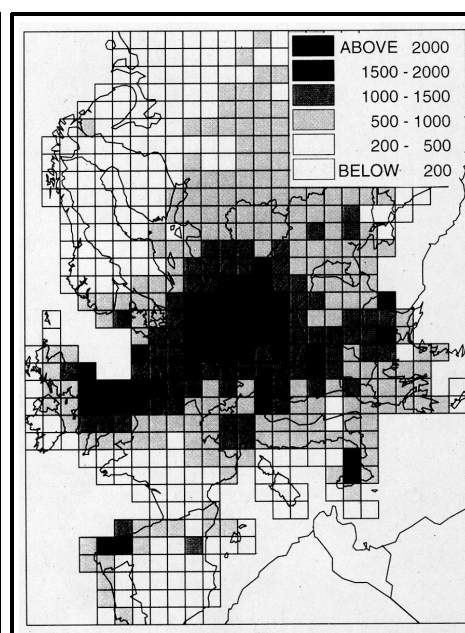


Figure 3.2 Annual depositions of sulphur in Europe in 1994, in mg S/m^2 (picture from Ågren and Elvingson, 1997)

Reasons for controlling SO_2 emissions are related to its contribution to acid rain, and more recently it was recognised that sulphate-containing aerosols form a health hazard as well, causing problems to the respiratory and cardio-vascular systems. With oil and gas processing, and gasification processes H_2S is the most important sulphur

species to be controlled, being not only highly poisonous and bad smelling, but also resulting in SO_2 after oxidation in the environment.

In this chapter, the routes from sulphur present in fuels to pollutants and methods to avoid these from being emitted to the atmosphere are discussed. After a short discussion on in what forms sulphur occurs in fuels, the essentials of the chemistry of sulphur during combustion and gasification are given. This is followed by some emission standards for SO_2 , for Finland and abroad. A general summary of approaches to sulphur control is given, which is followed by a rather extensive treatment of the most important technique: flue gas desulphurisation (FGD) for SO_2 . Wet, semi-dry and dry FGD with non-regenerable or regenerable sorbents are discussed. High temperature SO_2 capture is discussed addressing furnace sorbent injection and *in situ* SO_2 control during fluidised bed combustion (FBC). After this the point of focus switches to H_2S . First, low temperature processes for H_2S removal from gases are considered, followed by the famous Claus process. Methods based on H_2S capture with calcium-based and regenerable sorbents as used in relation to (coal) gasification, sometimes referred to as high temperature gas clean-up for sulphur, are discussed next. After that the control of sulphur compounds emissions from transport vehicles is addressed.

3.2 Sulphur in fuel

In solid fossil fuels, such as coals ranking from brown coals and lignites up to anthracite, peat, oil shales *etc.*, sulphur is present in two inorganic forms, being pyritic sulphur (FeS_2), and sulphates (Na_2SO_4 , CaSO_4 , FeSO_4) and as organic sulphur. Organic sulphur is bound in these fuels as sulphides, mercaptanes, bisulphides, thiophenes, thiopyrones *etc.*, see Figure 3.3. These organic compounds are also found in unrefined oil and heavy fuel oils. In natural gases as well as in raw fuel gases from gasification processes sulphur is generally present as hydrogen sulphide (H_2S) and carbonyl sulphide (COS).

Biomass fuels such as waste wood, straw, bagasse (residual from sugar cane processing) and energy crops (*Salix*, *Miscanthus*, *etc.*) contain very small amounts of sulphur. The relatively large amount of sulphur in bark is apparently correlated with the exposure of this part of the tree to the surrounding atmosphere and occasional acid rain and other downfall. In waste-derived fuels, sulphur can be found in car-tyre scrap and electronic scrap as a vulcaniser, in food-derived wastes (onions and garlic)

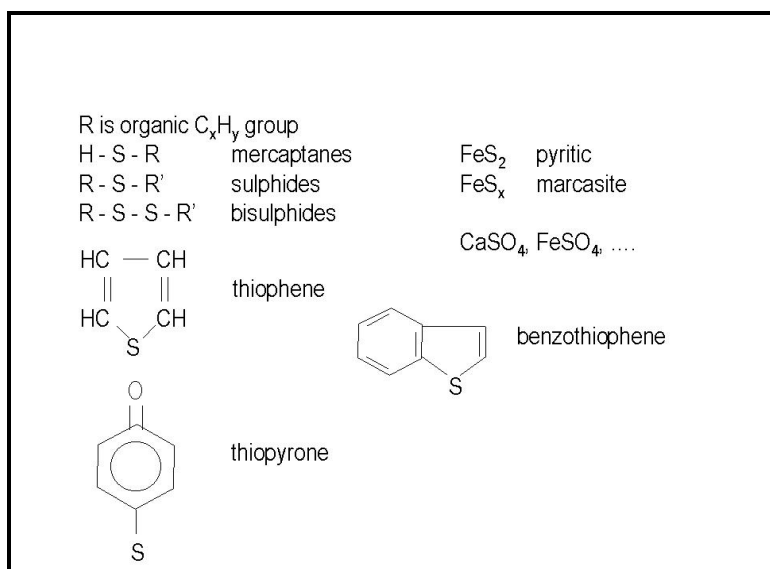


Figure 3.3 Typical sulphur compounds found in fuels

etc. Specific for pulp and paper processing is black liquor, for which the large sulphur content, mainly as Na₂SO₄, is recovered in reduced form as Na₂S in so-called recovery boilers (Hupa, 1993). Typical values for the sulphur content of various fuels are given in Table 3.1.

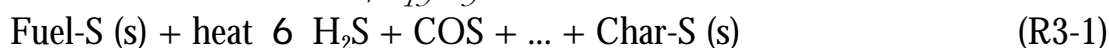
Table 3.1 Typical values for the sulphur content of fuels (%-wt, dry)

Fossil fuels		Biomasses & waste derived fuels	
Coal	0.2 - 5	Wood	< 0.1
		Bark	< 2
Oil	1 - 4	Straw	~ 0.2
Natural gas	0 - 10		
Light fuel oil	< 0.5	Sewage sludge	~ 0.2
Heavy fuel oil	< 5	Car tyre scrap	~ 2
		Municipal solid waste (MSW)	0.1 - 1
		Refuse derived fuel (RDF)	0.1 - 1
Peat	< 1	Packaging derived fuel (PDF)	~ 0.2
		Auto shredder residue (ASR)	~ 0.3
Petroleum coke, "petcoke"	~ 5	Leather waste	1 - 2
Estonian oil shale	~ 2		
Orimulsion™	~ 4	Black liquor solids	~ 5

3.3 Formation of sulphur compounds during combustion and gasification

In short, the formation of sulphuric pollutants during combustion and gasification can be described by the following chemistry :

Fuel devolatilisation / "pyrolysis"



Char oxidation



Gas phase reactions



Sulphuric oxide formation



The reactions involving O_2 lead to the major sulphuric product during combustion, SO_2 via (R3-2) and (R3-5). Although the thermodynamics of (R3-10) are in favour of SO_3 , the oxidation of SO_2 to SO_3 is a slow chemical reaction. It requires temperatures above 1100EC if it is to proceed as a gas phase reaction, or a catalyst such as oxides of vanadium, nickel and iron for the reaction to become important already at temperatures as low as 500EC.

This catalytic effect explains why during the early 20th century when oil-derived transport fuels were introduced corrosion problems arose that were not seen that strongly with coal. The sulphur in the transport fuels was oxidised to SO_2 and further to SO_3 , catalysed by traces of metallic elements in the fuel, which did not occur that strongly with coal. Upon cooling, this SO_3 which had bound with water to form H_2SO_4 , formed highly corrosive liquid sulphuric acid. The "dew point" of H_2SO_4 , *i.e.* the temperature at which condensate is formed is determined by the concentrations of water and SO_3 in the gas. Figure 3.4 (Backman *et al.*, 1983) gives the dewpoint of sulphuric acid.

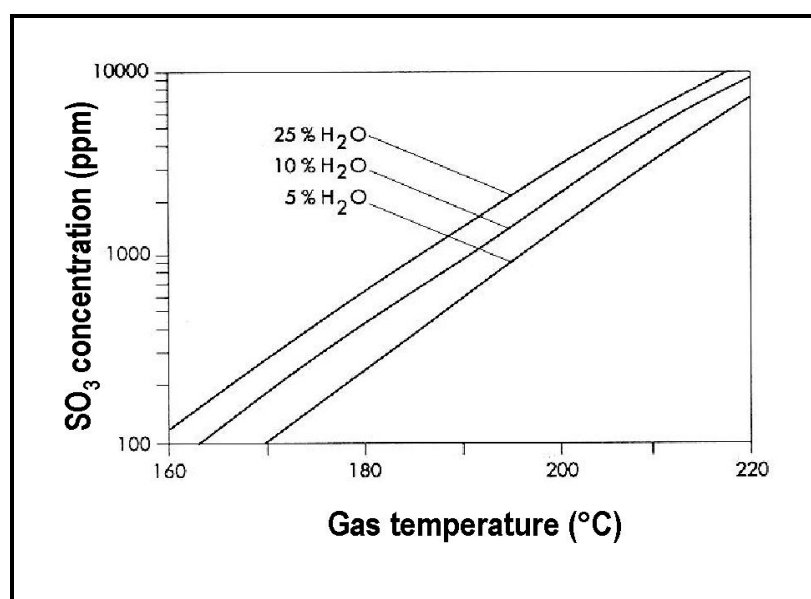


Figure 3.4 The temperature at which sulphuric acid condensation occurs in flue gas as function of SO_3 and water concentration (after Backman *et al.*, 1983)

For gasification processes the situation is more complicated. The most important sulphur species will be H_2S , which is in equilibrium with certain amounts of COS

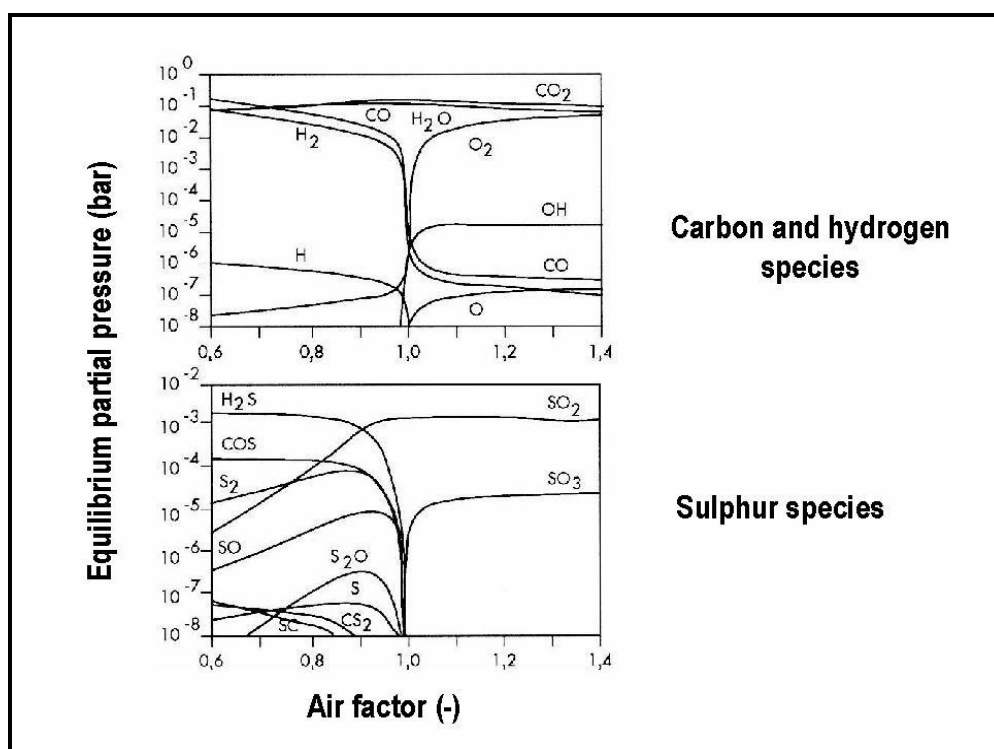


Figure 3.5 Carbon, hydrogen and sulphur species from combustion (air factor >1) and gasification (air factor <1) according to thermodynamic equilibrium calculations (after Iisa, 1992, 1995)

(carbonyl sulphide), CS₂ and elemental sulphur S_x (with S₈ as a common form) via reactions (R3-6,7,8,9). H₂S control is one option here, besides removing the sulphur as SO₂ after an oxidation if that occurs downstream in the process, via reaction (R3-5). Figure 3.5 gives some results of thermodynamic equilibrium calculations for sulphur compounds in combustion (air factor=1) and gasification (0<air factor<1) reactors (Iisa, 1992, 1995). As mentioned above, the SO₃ levels shown generally do not occur due to slow SO₂ oxidation kinetics, leading to slightly higher SO₂ levels than what thermodynamics indicate.

3.4 Emission standards for SO₂

The maximum allowable SO₂ emissions are dependent on the location, the type of fuel and the size and type of the facility from which they arise. Tabled data is presented and frequently updated by various authorities, following changes which, in general, show lower allowable emissions with each update. Typically, new and existing facilities are distinguished in order to reduce economic burden on older facilities. For coal (and peat), SO₂ emission standards for Finland (1995) and the European Community (1988) are given in Tables 3.2 and 3.3. The World Bank suggests a worldwide emission limit for all new coal-fired units of 2000 mg/m³_{STP} (dry) @ 6 % O₂, or 500 tonnes SO₂ /day (Soud, 1991, McConville, 1997).

For waste firing, the SO₂ emission standard for Finland (as of 1.8.1994) is 50 mg/m³_{STP} (dry) @ 10 % O₂ (Finland, 1994). The same value recently came into force for the EU15 countries for waste firing as well as cement plants.

Table 3.2 SO₂ emission standards for Finland (1995)

Type of plant	New / Existing	Plant size (MW _{th})	Emission standard (mg/m ³ _{STP} dry 6% O ₂)	Comments
Combustor, peat	New	> 300	378	
Utility, hard coal	New	< 50	2150	
Utility, hard coal	New	50 -150	620	
Utility, hard coal	New	> 150	380	
Combustor, hard coal	New and Existing	all	sulphur content # 1 %	plant without de-sulphurisation equipm.
Utility, hard coal	Existing	< 200	2105	lifetime > 15000 hours after 1.1.1994
Utility, hard coal	Existing	> 200	620	ibid.

Table 3.3 *SO₂ emission standards for the European Community (1988)*

Type of plant	New / Existing	Plant size (MW _{th})	Emission standard (mg/m ³ _{STP} dry 6% O ₂)	Comments
Combustion, coal	New *	50-100	2000	
Combustion, coal	New *	100-500	2400 - 4×P	P = plant size in MW _{th}
Combustion, coal	New *	> 500	400	
Combustion, coal	New *	≤ 400	800	operation < 2200 h/yr
Combustion, coal	New *	100 - 166	40 % removal	domestic high or variable sulphur coal
Combustion, coal	New *	167 - 500	(15+0.15×P) % removal	P = plant size in MW _{th} domestic high or variable sulphur coal
Combustion, coal	New *	> 500	90 % removal	domestic high or variable sulphur coal

* construction licence after July 1 1988

3.5 Options for sulphur emissions control

Several routes are open for reducing the sulphur emissions from thermal processes that fire or treat sulphur-containing fuels or materials.

1. **Substitute the fuel.**

It is obvious that replacing a high-sulphur fuel with a low-sulphur or sulphur-free fuel is an option that should never be forgotten. This depends on the fuel-flexibility of the unit, the economics of operation with another fuel and the adjustments that may be needed, and the contracts with the fuel (or whatever is thermally treated) supplier. It must be noted that a fuel switch may have more benefits, for instance less ash formation or lower taxation when *e.g.* a renewable fuel is chosen. At the same time, it should not be forgotten that sulphur may have positive effects on ash behaviour in boilers and furnaces, and on the performance of an electrostatic precipitator (ESP) for dust emissions control (L Chapter 5). In some cases, fuel substitutions may also be enforced by local authorities.

2. **Fuel cleaning.**

A second method that prevents the sulphur from entering the facility is to apply fuel pre-treatment. Inorganic fuel sulphur, especially pyritic sulphur, FeS₂, can be relatively easily removed to up to 90% by physical methods based on gravity, flotation,

agglomeration or flocculation. Chemical methods may be able to remove organic fuel sulphur as well, involving treatment with alkaline or caustic solutions, oxidative leaching or chlorinolysis with chlorine-based chemicals. The price for these chemical methods is that part of the material is oxidised, which reduces its potential for use as a fuel. A third method is biological treatment, capable of removing inorganic as well as organic sulphur. It was found that *Thiobacillus ferrooxidans* converts FeS_2 into water-soluble FeSO_4 , whilst a mutant of *Pseudomonas*, called CB1 (coal bug 1) consumes organic sulphur in thiophene groups. These techniques may require very small particles, are time-consuming, and may need close process control. All methods mentioned are quite expensive and still may have a limited effect. On the other hand many low-grade coals are “washed” in order to reduce their mineral content which results in some level of sulphur removal as well. A discussion on coal desulphurisation was given by Celik and Somasundran (1994). In a recent paper by Rubiera *et al.* (1999) it was argued that biological treatment does not have a substantial effect on the combustion behaviour of coal.

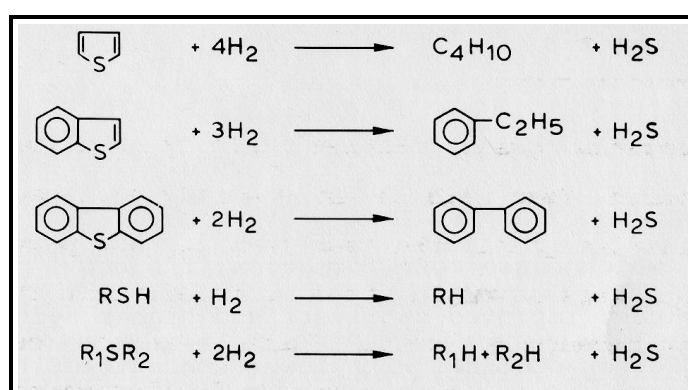


Figure 3.6 Cracking reactions during hydro-desulphurisation (picture from van den Berg and de Jong, 1980)

Desulphurisation of petroleum fractions has been successfully applied for a long time in the field of petro-chemicals. Using H_2 and a Co/Mo catalyst, sulphur is removed from petroleum fractions by conversion to H_2S . Examples of “hydrocracking” reactions are given in Figure 3.6 (van den Berg and de Jong, 1980).

3. Abatement techniques.

Since eventually the sulphur that enters the facility will come out in some form, these methods are based on lowering the sulphur input, with the fuel, to the process. This implies increasing the thermal efficiency of the fuel conversion process by increasing the steam parameters (supercritical or ultra-supercritical steam). Alternatively, the facility can be upgraded by “repowering” - examples are: transforming a pulverised coal fired unit to a (pressurised) fluidised bed unit, implementing combined-cycle technology or even the use of fuel cells (7 Chapter 2). In practically all cases this implies rather expensive changes with many risks.

4. **End-of-pipe control technologies.**

The last but most widespread option is to remove the sulphur as SO_2 or H_2S after it has been formed in the process. In fluidised bed reactors, sulphur can be captured *in situ* in the bed by a calcium-based sorbent (L section 3.11) - for older plants existing flue gas desulphurisation equipment may become obsolete after repowering to a fluidised bed furnace. The rest of this chapter will concentrate on techniques that accomplish that. In all cases this brings with it the production of significant amounts of by-products, such as spent lime and dolomite, gypsum, elemental sulphur or sulphuric acid.

3.6 Flue Gas Desulphurisation (FGD) 1: Non-regenerable processes

Worldwide, at those power utilities that have sulphur emissions control equipment installed, in more than 80% of the cases the sulphur is removed from the flue gas using FGD with a non-regenerable (“throwaway”) sorbent based on calcium. In general lime (CaO), limestone (CaCO_3) and ashes with a high calcium+magnesium content are used, in an aqueous solution. The product is then an FGD gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) that finds large-scale application as a building or filling material. Typically FGD can be applied to processes involving sulphur contents up to ~ 10 %-wt in the fuel or input material. The most important FGD processes as listed by IEA Coal Research (Soud, 1995) are given in Table 3.4.

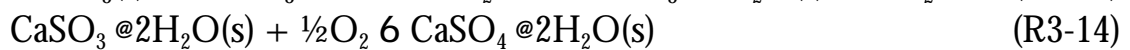
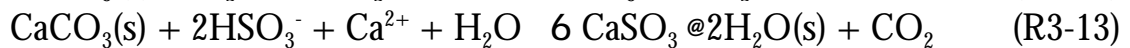
Table 3.4 The most important FGD systems with non-regenerable sorbents

Process	Sorbent	End/by - product
Wet scrubbers	Lime / Limestone Lime / Fly ash	Gypsum, Calcium sulphate/sulphite Calcium sulphate/sulphite/fly ash
Spray-dry scrubbers	Lime	Calcium sulphate/sulphite
Dual - alkali	Primary: sodium hydroxide Secondary: lime	Calcium sulphate/sulphite
Seawater	Primary: seawater Secondary: lime	Waste seawater
Walther	Ammonia	Ammonia sulphate

Lime, CaO , is produced by limestone burning, *i.e.* “calcining” the CaCO_3 at temperatures above 800EC under release of CO_2 .

Limestone/lime scrubbing of SO_2 is based on the following chemistry, at temperatures of the order of 70-90°C:

limestone scrubbing



lime scrubbing

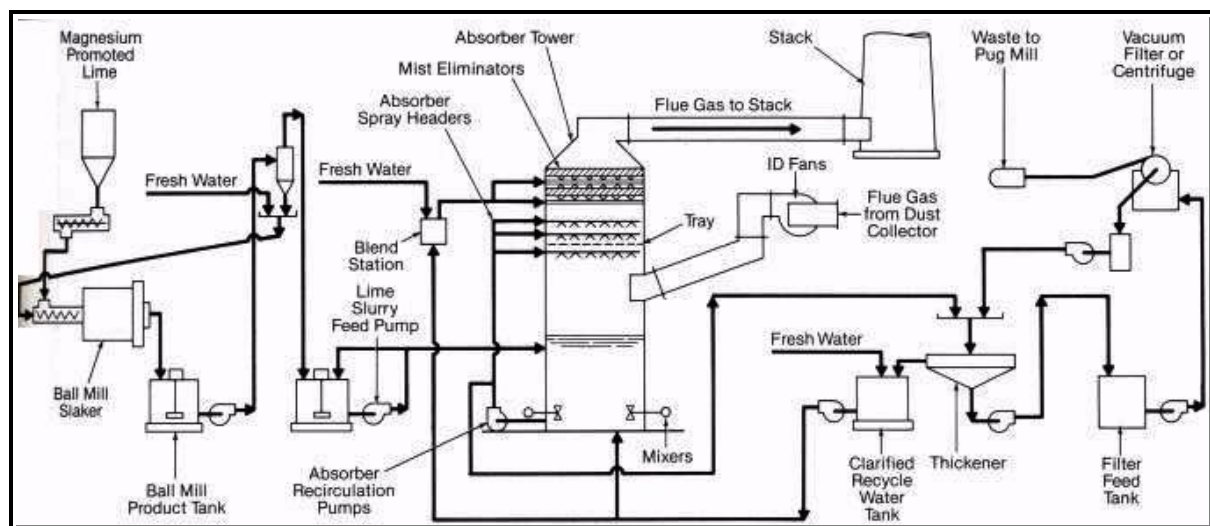
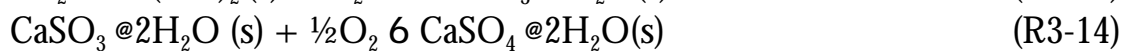
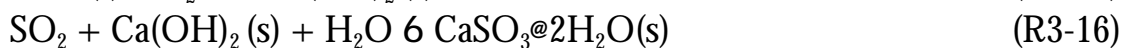


Figure 3.7 Process scheme for a typical wet flue gas desulphurisation process (picture from Stultz and Kito, 1992)

A typical process scheme of FGD for a combustion flue gas is shown in Figure 3.7. The flue gas is confronted with the aqueous lime (or limestone) solution in a scrubber; the liquid collected by the scrubber is partly recycled and partly fed to the thickener where calcium sulphite is further oxidised to calcium sulphate (reaction R3-14). This can be applied with or without air added to the thickener, which are referred to as natural or forced oxidation, respectively. The latter gives higher gypsum quality that finds wider application, whilst the larger crystals produced make de-watering easier.

Figure 3.8 shows a flue gas desulphurisation absorber for a 600 MW power plant.

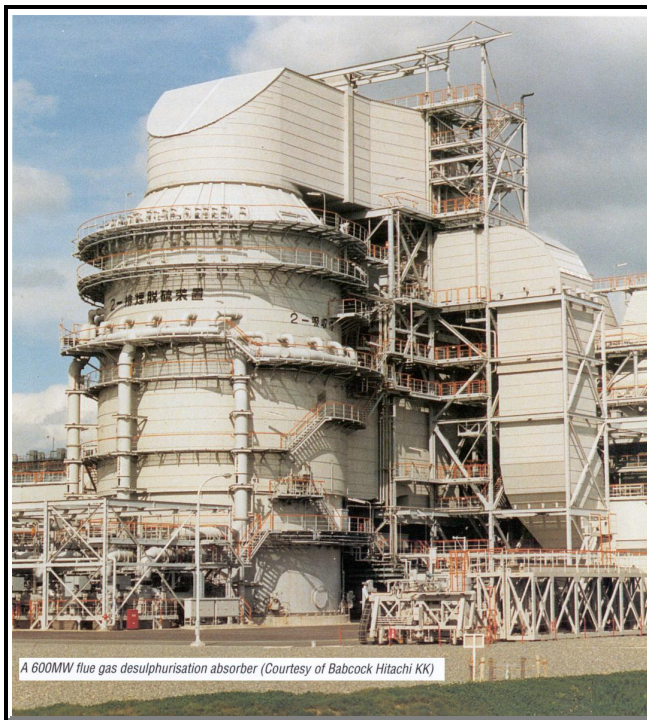


Figure 3.8 Flue gas desulphurisation absorber (picture from OECD/IEA&ETSU, 1993)

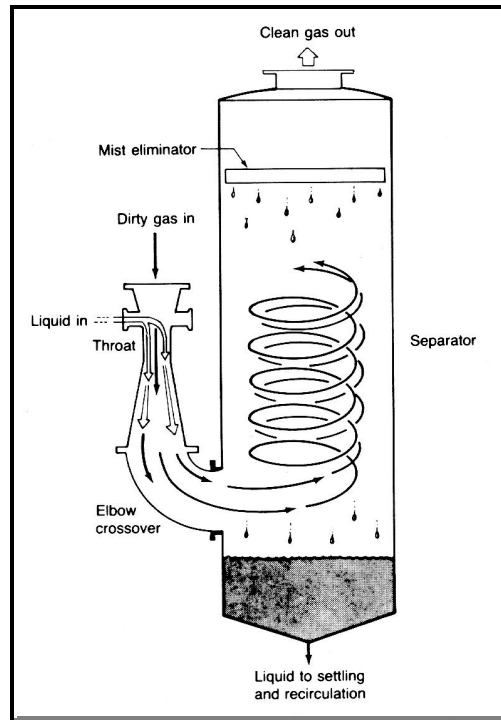


Figure 3.9 A venturi scrubber (picture from Cooper and Alley, 1994)

As an illustration a venturi scrubber is given in Figure 3.9. In principle it is very well suited for the removal of other gases and dust particles at the same time.

Recently, the integration of the FGD scrubber process into the off-gas stack was presented by Klitzke and Bengtsson (1999).

An FGD process that can be applied in coastal regions is scrubbing with seawater as illustrated by Figure 3.10. Seawater, that is claimed to possess sufficient natural alkalinity for SO₂ removal is preheated in the condenser of the steam cycle of the power plant shown in the Figure, and is used to scrub fly ash particles as well as SO₂.

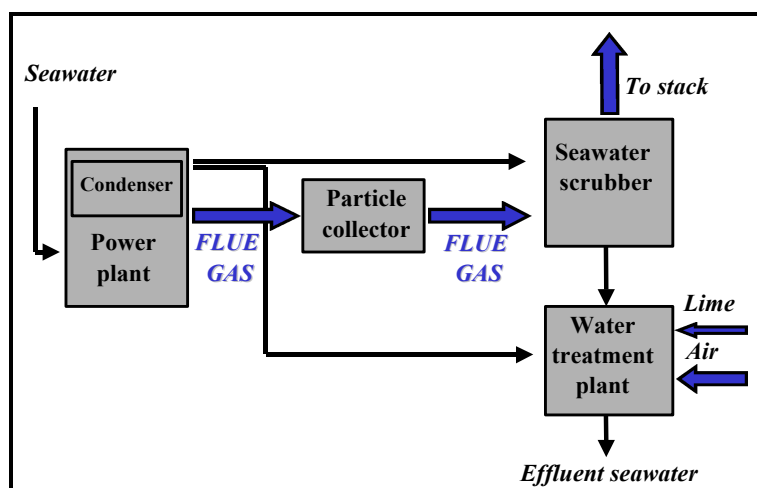
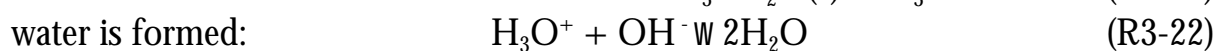
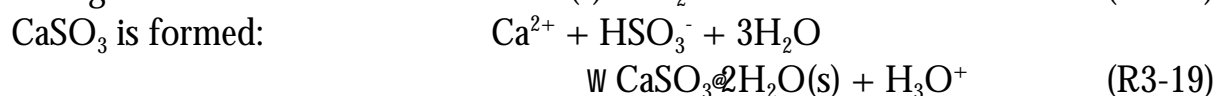
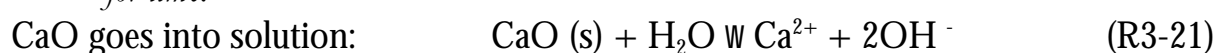
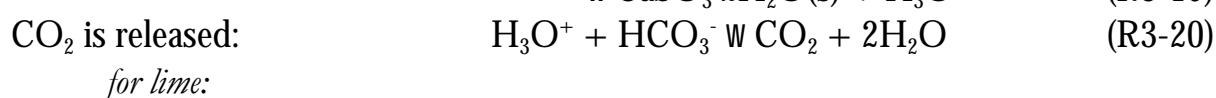
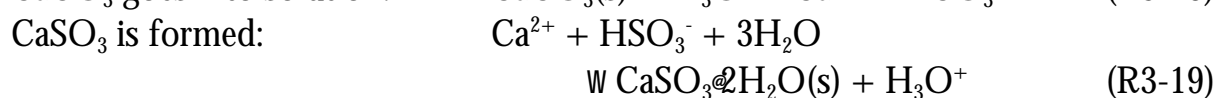
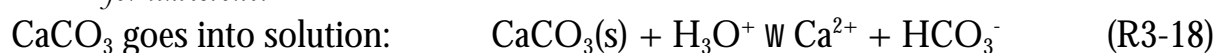
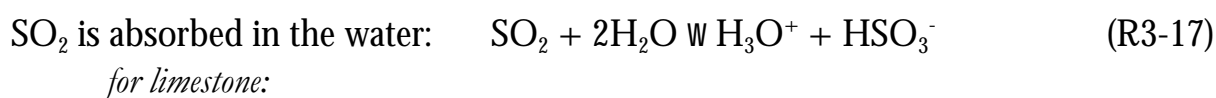


Figure 3.10 Principle of an FGD system based on seawater scrubbing, using the natural alkalinity of seawater (after Soud, 1995)

In the water treatment plant the pH of the scrubbing liquid is adjusted before disposal back into the sea (Soud, 1995). A seawater scrubbing plant with *in situ* oxidation (in the bottom part of the absorber) is operating in Indonesia (Scheuch, 2000)

An important issue in limestone / lime scrubbing is the pH ($= -\log [H_3O^+]$) of the solution. For lime scrubbing the optimum value is pH~8, for limestone scrubbing pH~6. This difference is illustrated by the following gas/solid/water equilibrium chemistry (Flagan and Seinfeld, 1988):



The excess H_3O^+ concentration with limestone scrubbing explains the slightly acidic solution, the excess OH^- concentration with lime scrubbing explains the slightly alkaline solution. In both cases, a sulphite product is formed that has to be further oxidised, for which the oxygen is available in the flue gas that is cleaned (natural oxidation). Alternatively the calcium sulphite can be further oxidised in a separate reactor to which air is fed (forced oxidation). From a product quality point of view a calcium sulphite concentration of 0.25 %-wt besides 90-95 %-wt calcium sulphate is considered acceptable: gypsum quality specifications for its use in wallboard are given in Figure 3.11 for several countries (Carpenter, 1998).

As argued by Sandelin *et al.* (1997), HF can interact with Al that may be present in an FGD unit (as impurity of the lime(stone) or from fly ash) to form aluminium fluoride complexes that hinder the dissolution of the lime(stone) (R3-18 or R3-21).

It is clear that limestone/lime FGD is very sensitive to other strongly acidic or alkaline other components in the flue gas. For example HCl present in the flue gas

		Germany	Japan	Netherlands		UK*	USA†
				A	B		
CaSO ₄ ·2H ₂ O (gypsum)	min %	95	95	95	95	95	90-95
CaSO ₃	max %	0.25	0.25	0.25	0.25		0.5-2
MgO (soluble)	max ppm	1000		500	500	1000	50-250
Na ₂ O	max ppm	600		500	400	1000	75-250
K ₂ O	max ppm			600	1000		
Soluble salts (total)	max ppm		1000				600
Cl ⁻	max ppm	100		200	100	200-300	120-400
SiO ₂	max %	2.5		2.5	1.0		
Al ₂ O ₃	max %	0.3					
Fe ₂ O ₃	max %	0.15		0.5	1.5		
CaCO ₃	max %			2.5		1.6	
Ash/inert components	max %					1	1-3
Free moisture	max %	10	10	10	8	5	1-10
pH		5-9	6.5-8	5-8	5.5-7.5	7.5	3-9
Colour (whiteness‡)	%	80		75	70		
Odour		neutral					
Toxic constituents		none					

* typical purity guidelines issued by gypsum users in the UK
 † range of specifications for commercial grade gypsum given by three companies
 ‡ relative to BaSO₄ reference = 100%

Figure 3.11 Several national quality specifications for wallboard gypsum (taken from Carpenter, 1998)

reduces the pH, changes the equilibrium chemistry given above and consumes part of the calcium by forming CaCl₂. A pre-scrubber that operates at low pH (~1) can be applied for the removal of HCl and HF (and fly ash and mercury, Hg), improving gypsum quality. Alternatively, organic buffers can be applied that maintain a nearly constant pH of the solution. This results also in smaller absorber size and less pumping power needed.

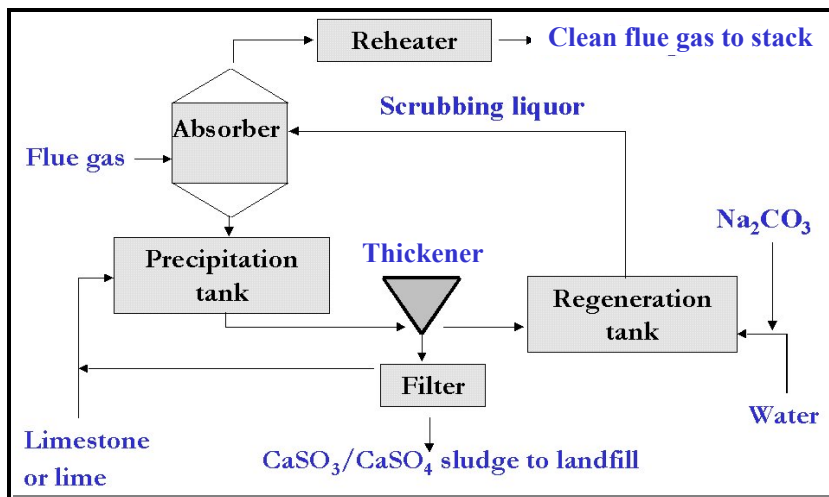


Figure 3.12 Principle of the dual-alkali process (after Cooper and Alley, 1994)

The development of the so-called dual-alkali process was initiated by the low solubility of lime and limestone in water and gypsum scaling problems in wet FGD. Several commercial-scale units have been applied in the USA. The solubility of sodium salts is much better, which led to this concept based on a

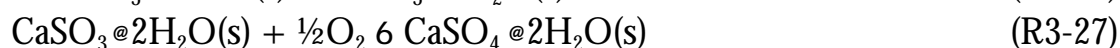
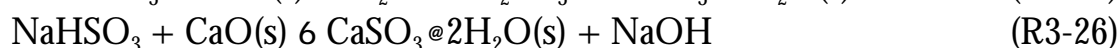
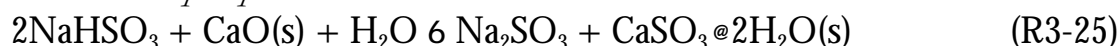
scrubbing liquor with NaHCO₃ and Na₂SO₃ as the SO₂-binding compounds. The principle of the process is given in Figure 3.12.

The chemistry of the process, again with FGD gypsum as the by-product, can be summarised as follows:

in the scrubber:



in the precipitation tank:



in the regeneration tank:



Since some sodium is lost from the system with the $\text{CaSO}_3/\text{CaSO}_4$ product, some make-up Na_2CO_3 (soda) or $\text{Na}_2\text{CO}_3 + \text{NaHCO}_3$ (trona) is continuously added to the regeneration tank. The actual SO_2 capture is accomplished with a more concentrated sodium-based washing liquid with limestone/lime scrubbers, combined with precipitation and regeneration in separate devices.

The Walther process is based on scrubbing with ammonia water: sulphur is obtained mainly as $(\text{NH}_4)_2\text{SO}_4$. Due to the risk of formation of ammonium sulphate aerosols a fuel sulphur content below 2%-wt is required. One installation in Germany operates at efficiencies ~90%. The technology is nowadays owned by the German LLB (Lurgi Lentjes Bischoff) who changed the concept to a two-stage scrubber and an electrostatic precipitator for aerosol particle removal (Scheuch, 2000).

3.7 Flue Gas Desulphurisation (FGD) 2: Regenerable processes

One important disadvantage of FGD with throwaway sorbents is that large amounts of (by-)products and spent sorbents are being generated. Although this is driven by economics (abundance of limestone and other calcareous rock), wet FGD methods have been developed using a regenerable sorbent as well. Production of a valuable sulphur-based product, reducing gypsum scaling problems or the possibility to combine SO_2 control with the control of other pollutants provide the basis for these processes. The most important FGD processes using regenerable sorbents, as listed by IEA Coal Research (Soud, 1995) are given in Table 3.5.

Table 3.5 The most important FGD systems with regenerable sorbents

Process	Sorbent / principle	End/by - product
Wellman - Lord	Sodium sulphite (Na_2SO_3)	Concentrated SO_2
Bergbau Forschung / Uhde	Activated carbon	Concentrated SO_2
Linde SOLINOX	Physical absorption (amine)	Concentrated SO_2
Spray-dry scrubbing	Sodium carbonate (Na_2CO_3)	Elemental sulphur
MgO process	Magnesium oxide (MgO)	Concentrated SO_2

The Wellman-Lord process (the most widely used wet, renewable sorbent FGD process) has similarities to the dual alkali process mentioned above. A simplified process scheme is given in Figure 3.13. Also here, sodium sulphite, Na_2SO_3 is the actual sorbent, binding sulphur as NaHSO_3 . However, the sulphur is not passed on to calcium, but it is released again as SO_2 , which is extracted as a concentrated

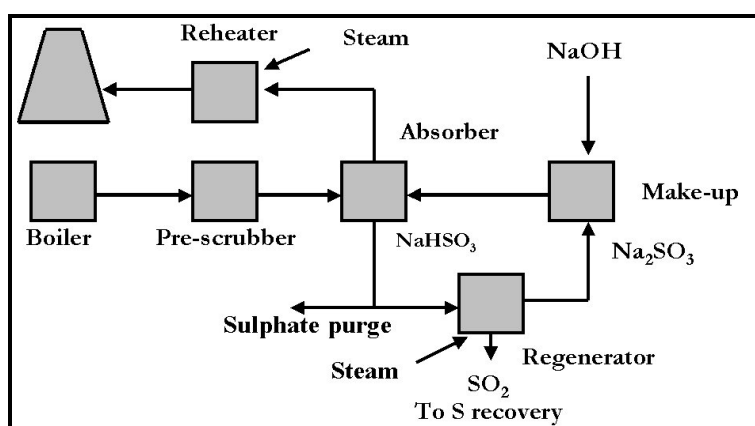


Figure 3.13 Principle of the Wellman-Lord process (after Soud, 1995)

mixture with water (~85% SO_2 , 15% water) for further processing to sulphuric acid. Some sodium sulphite/sulphate is formed as a by-product: make-up soda or trona is needed to balance this. Pre-scrubbing for HCl *etc.* prevents sorbent deactivation. Process chemistry can be summarised as follows:

in the scrubber:



in the regenerator:



make-up soda or lime:



in the gaseous product:



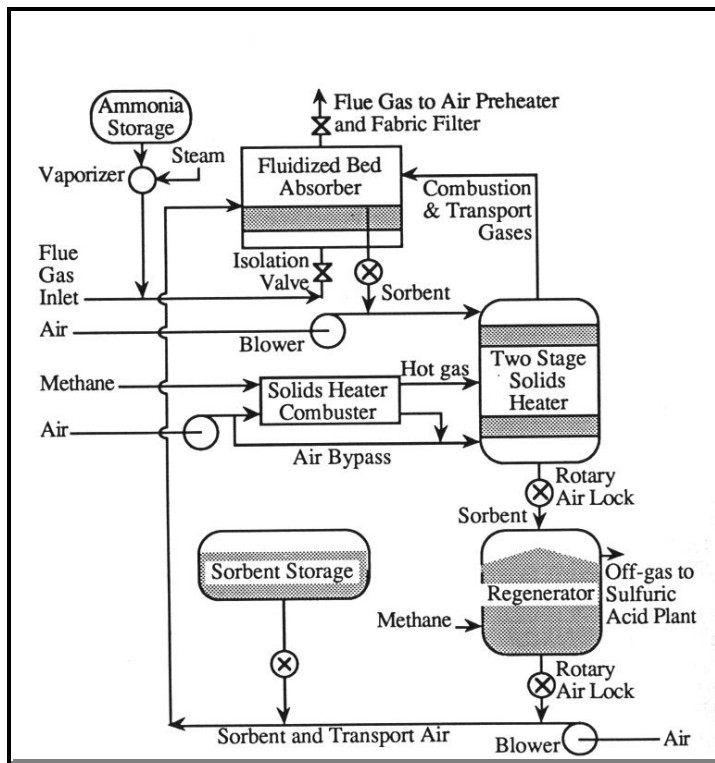


Figure 3.14 The fluidised bed copper oxide process (picture from Frey, 1993)

~500EC. A simplified process scheme is shown in Figure 3.14. In short, the chemistry involved here is as follows:

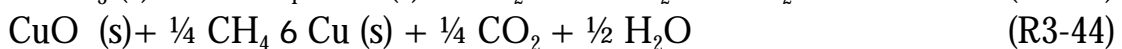
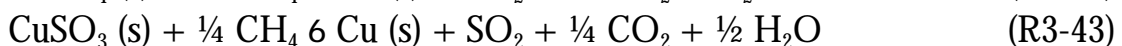
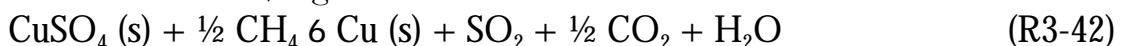
in the absorber:



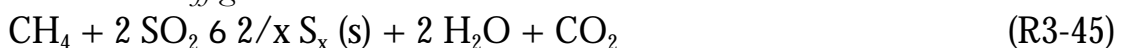
in the transport section:



in the heater / regenerator:



in the off-gas treatment:



A process that allows for the control of SOx and NOx (nitrogen oxides NO and NO₂, Chapter 4) at the same time is the fluidised bed copper oxide process (Frey, 1993). This process needs methane, CH₄ as well as ammonia, NH₃. In a fluidised bed absorber, SO₂ is captured by copper oxide CuO at ~400EC. At the same time, NO is reduced by ammonia to nitrogen, for which copper oxide is a very good catalyst. The copper sulphate CuSO₄ product is transported to the two-stage heater/regenerator section where it is reduced to Cu at the expense of methane at

The sulphur is released as concentrated SO₂ that can be used to produce sulphuric acid, similar to the Wellman-Lord process. The Cu sorbent is transported back to the fluidised bed using air, during which it is oxidised to CuO. The SO₂ product gas may contain some methane that is converted via reaction (R3-45). Currently the FB copper oxide is receiving more attention from an NO_x control point of view (*e.g.* Jeong and Kim, 2000) whilst earlier SO₂ was the main target pollutant.

3.8 In-duct sorbent injection at low temperatures

As alternatives for the wet FGD methods discussed above, dry or semi-dry in-duct sorbent injection methods can be used more upstream in the flue gas channel, at temperatures of the order of 150-400°C. For a combustion plant this means between the air pre-heater and the cold-side (electro-) filter system for dust control (L Chapter 5). In dry systems a dry sorbent powder, usually lime, is dispersed in the flue gas channel, where it reacts with the SO₂ via the overall reaction

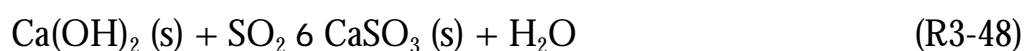


The CaSO₄ particles are then removed from the flue gas by the (electro-) filter for fly ash emissions control further downstream. This approach is relatively cheap and can easily be applied to older facilities with dust control but without proper sulphur control, such as can be found in Eastern Europe and in large parts of Asia.

In general, the sorbent used is lime which needs additional humidification, which is not needed when a (more reactive) sodium-based sorbent is used, such as sodium bicarbonate NaHCO₃. With semi-dry methods, a calcium-based sorbent is sprayed into the flue gas duct as a water slurry, which, after the water has been vaporised renders a more reactive sorbent when compared to dry methods. Similar activation of the sorbent can be obtained by feeding water to the dust a little downstream of the point where the actual sorbent is fed. The unreacted lime will be converted to calcium hydroxide :



which is more reactive to SO₂, giving calcium sulphite



that will be (partly) oxidised to calcium sulphate. A drawback of the semi-dry methods is the corrosion of the humidification duct.

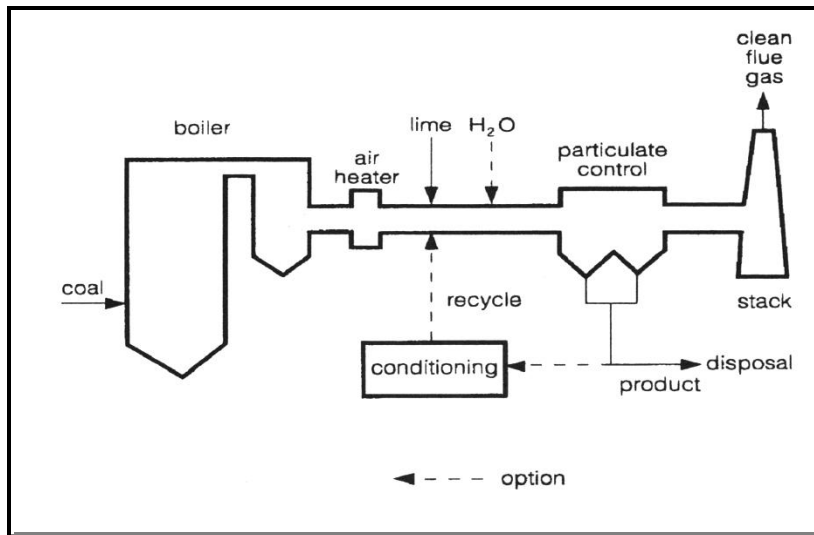


Figure 3.15 Principle of in-duct sorbent injection (picture from Ciemat, 1998)

Typically these processes are operated at Ca/S ratios near 2, with typical SO₂ concentrations of a few 1000 ppmv from coal combustion. Another very important process parameter is the so-called approach temperature, which is how far the gas temperature is above the saturation temperature for the water in the gas.

With a lower approach temperature more time is needed for water evaporation, resulting in a higher sulphur uptake by the sorbent (Ciemat, 1998).

A simplified process scheme for this is shown in Figure 3.15. Often the performance when it comes to conversion of lime is rather poor (50 ~ 70%) even after spent sorbent recycle, and better results are obtained with high-temperature sorbent injection methods (L section 3.9).

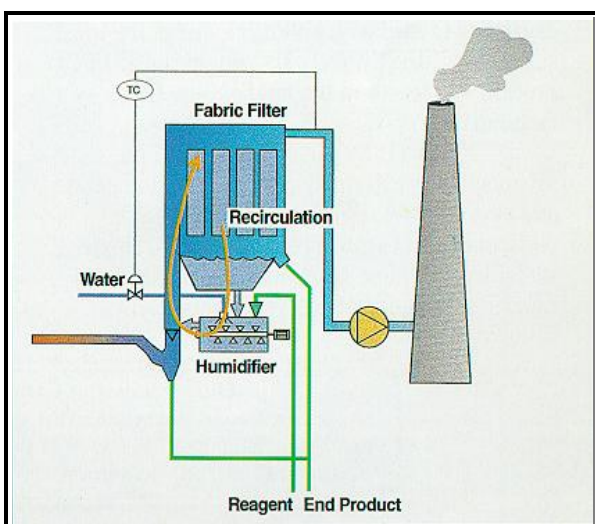


Figure 3.16a Main features of the NID process (picture from MPS, 1997)

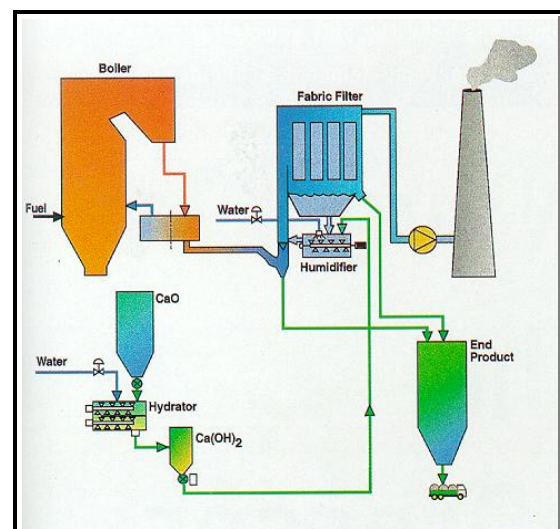


Figure 3.16b NID process at Laziska power plant in Poland (picture from MPS, 1997)

A recent low temperature process is the Alstom Power (earlier ABB Fläkt) NID (New Integrated Desulphurisation) process. The principle is illustrated in Figure 3.16. After hydration to $\text{Ca}(\text{OH})_2$, lime is mixed with some more water and part of the dust cake from a fabric filter. This wet solid is fed to the flue gas, by which it is rapidly transported to the fabric filter. In the filter the solids form a cake that is reactive to SO_2 , which is periodically removed by pressure pulses (see chapter 5 for more detail on fabric filters). One NID unit is operated at a 120 MW pulverised coal-fired boiler in Poland (Figure 3.16b), removing 90-95% of the SO_2 at 600-1200 ppm (MPS, 1997). Other facilities are operated in Germany and the UK (Åhman and Wiktorsson, 2000).

CFB-FGD technology (Baeye and Sauer, 2000) is FGD technology based on absorption on hydrated lime at $\sim 70^\circ\text{C}$ in a circulating fluidised bed. Also HF and HCl are removed from the flue gas. The process operates at Ca/S (molar) ratios in the range 1.1~1.5, depending on the SO_2 concentration *etc.* In order to cut the costs of the lime an alternative is to inject limestone into the upper zone of the boiler at 850-1000°C for calcination. Upon entering the CFB reactor the lime is reactivated by water injection.

3.9 High temperature SO_2 capture by furnace sorbent injection

A second method that is attractive for older boilers with a relatively short remaining lifetime is to inject a sorbent for SO_2 into the furnace or the hot part of the flue gas

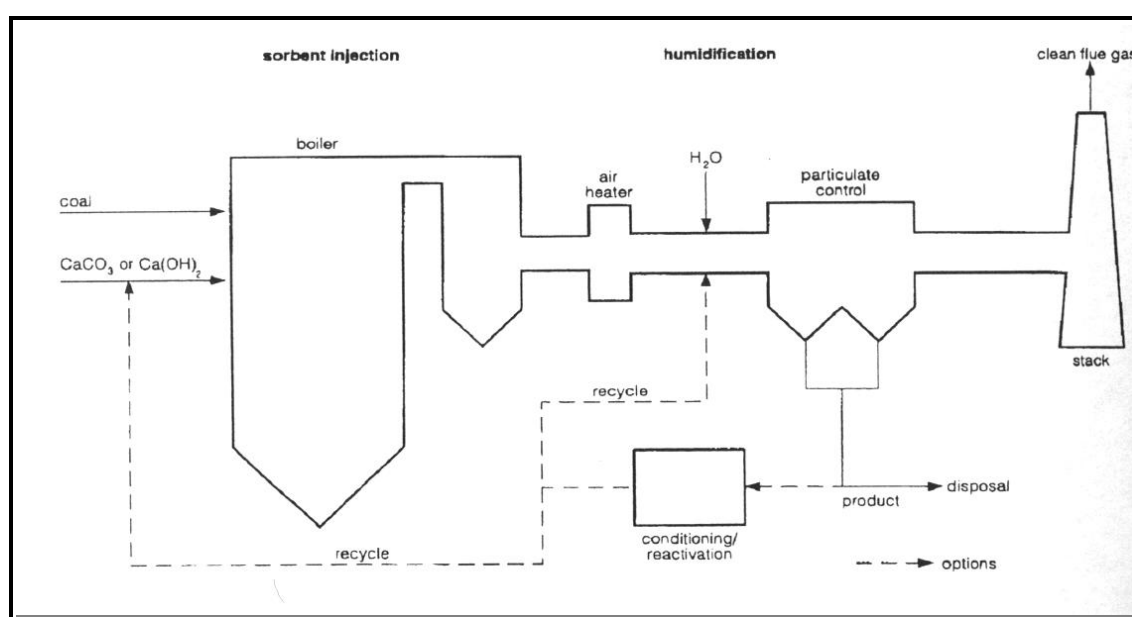


Figure 3.17 A typical furnace sorbent injection process (picture from Ciemat, 1998)

channel. The principle of furnace sorbent injection is shown in Figure 3.17. As with in-duct sorbent injection at lower temperatures this approach involves relatively low capital costs, achieving sulphur removal efficiencies of the order of 60-75 % with Ca/S ratios 2-4. Higher efficiencies can be reached when water is sprayed into the flue gas duct before the dust filter (which reactivates the unreacted sorbent for SO₂ that is still in the flue gas), by spent sorbent recycling and by careful optimisation of the position of sorbent injection with respect to the temperature.

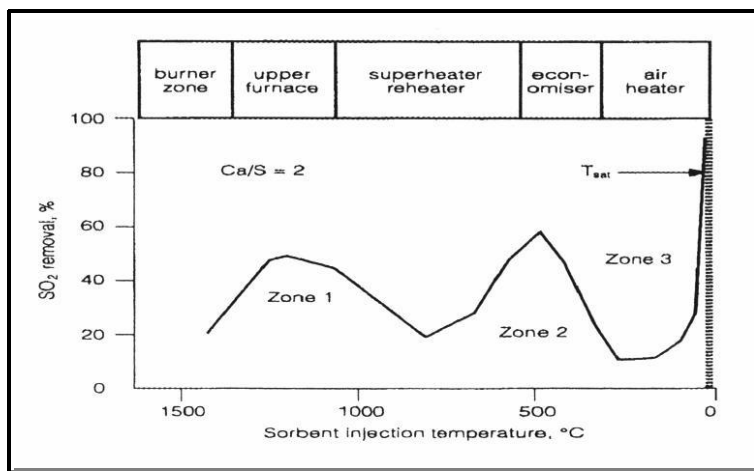


Figure 3.18 SO₂ removal efficiency *versus* temperature for lime sorbent injection (picture from Ciemat, 1998)

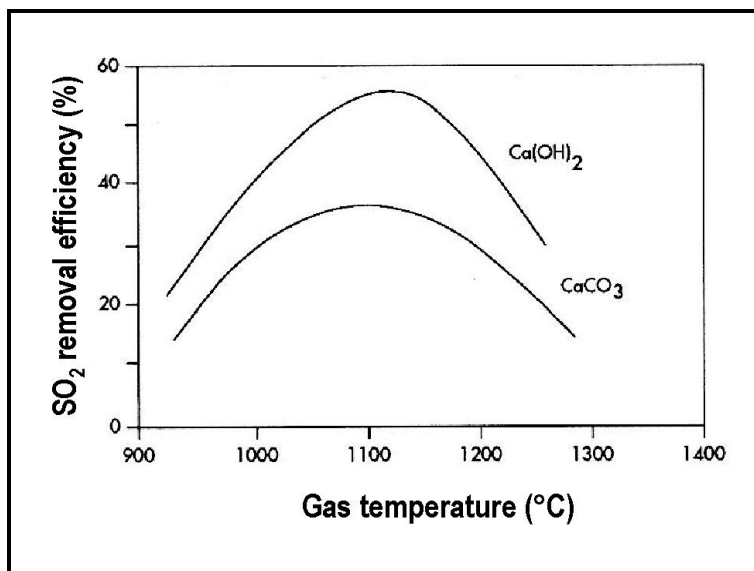


Figure 3.19 Sulphur uptake efficiency for limestone and hydrated lime *versus* temperature (picture from Iisa, 1995)

The relation between temperature and the SO₂ removal that can be obtained is shown in Figure 3.18 for a sorbent such as limestone or hydrated lime. The temperature maximum at around 1200°C is related to the kinetics of CaSO₄ formation on one hand and its thermodynamic stability on the other: CaSO₄ is not stable above around 1250°C in typical flue gases from coal-firing, containing up to 5000 ppm SO₂.

The difference between the use of CaCO₃ and Ca(OH)₂ is illustrated by Figure 3.19, corresponding to Zone 1 in Figure 3.18.

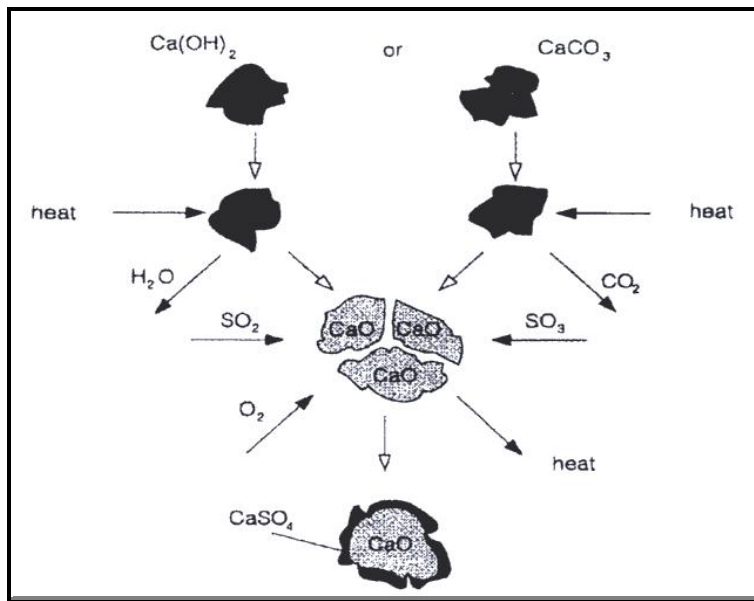
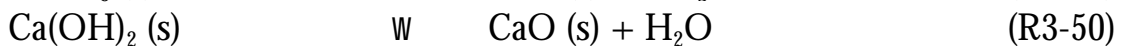
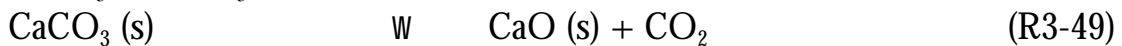


Figure 3.20 Chemical processes during in-duct sorbent injection for SO₂ removal (picture from Ciemat, 1998)

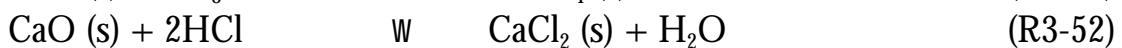
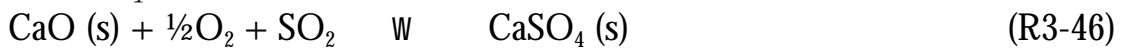
A simplified view on the chemistry of SO₂ capture by hydrated lime or limestone is shown in Figure 3.20. As shown, particle size - related effects such as fragmentation play a major role.

An advantage of furnace (and also in-duct) sorbent injection is that it more efficiently removes SO₃ than a wet FGD scrubber does, and that HCl and HF are captured as well:

formation of CaO:



sorption reactions:



Furnace sorbent injection may require some additional soot-blowing to remove solids accumulated on boiler tubes, which is not problematic, though (Ciemat, 1998).

One typical example is the LIFAC (Limestone Injection into the Furnace and Activation of unreacted Calcium) process, developed in Finland during the 1970s and 1980s by Tampella Power Oy (the current Kvaerner Pulping Power Division). The technology is nowadays owned by the Finnish Fortum Power and Heat (the Former Imatran Voima Oy). One unit in is operated Finland (at the Inkoo power plant), about 10 other units exist in North-America, Russia and China (LIFAC, 2000, Ryyppö and Ekman, 2000) - see Figure 3.22.

In the LIFAC process (Figure 3.21), limestone sorbent is injected into the upper furnace near the location of the superheater. It calcines (reaction R3-49) and partly reacts with SO₂ (reaction R3-46). Further downstream, in the activation reactor, the

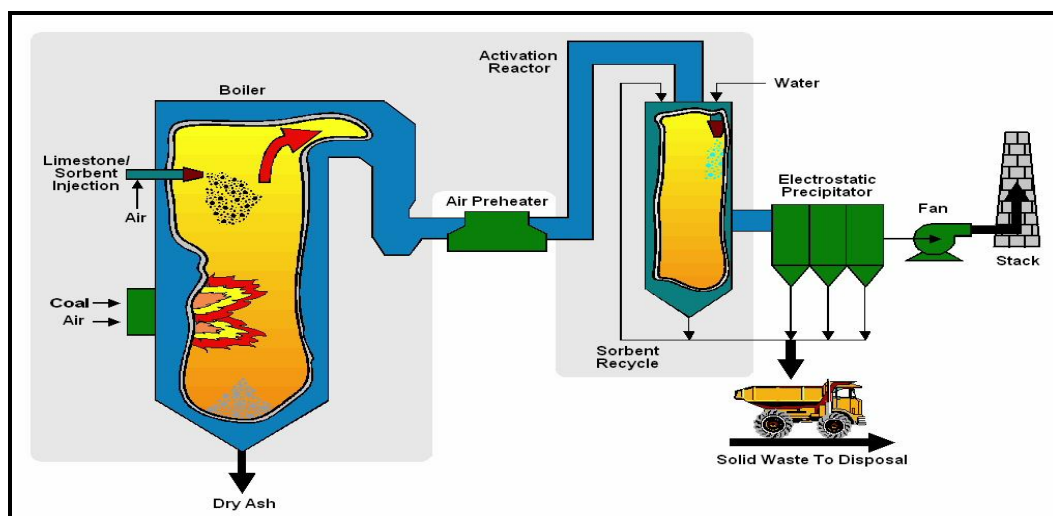


Figure 3.21 Schematic of the LIFAC process (from LIFAC, 2000)



Figure 3.22 LIFAC unit in Richmond (VI) USA (from LIFAC, 2000)

unreacted calcium oxide reacts with water at $\sim 400^{\circ}\text{C}$ to form calcium hydroxide (reaction R3-47) which is more reactive to SO_2 (reaction R3-48). The solid reaction products are collected together with fly ash in the electrostatic precipitator filter (Chapter 5) and are partly re-injected. Sulphur removal efficiencies of 65-85% were reported, depending on Ca/S ratio (typically 2-2.5), approach temperature, and sorbent fineness, for a boiler fired with coal with 1.4 - 2.8 %-wt sulphur (LIFAC, 2000).

The LIFAC system at Richmond Power & Light at Whitewater Valley Station, Unit No. 2, shown in Figure 3.22 (on the right side of the stack), is the first to be applied to a power plant using high-sulphur (2.0-2.9%) coal.

A system referred to as LIMB (Limestone Injection Multi-stage Burner) by Babcock & Wilcox Co is based on injection of limestone, lime or dolomitic limestone in the upper furnace, together with fuel in a Low- NO_x burner (Chapter 4). This method is reported to give 60~70 % sulphur removal plus ~ 50 % NO_x reduction (US DOE, 2000).