CONTROL OF SULFUR OXIDES

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Contents

1. Introduction
   1.1. Sulfur Oxides
   1.2. Environmental and Health Effects of SOₓ Emissions
2. SO₂ Control Strategies
3. Fuel Cleaning
   3.1. Sulfur in Fuels
   3.2. Fuel Desulfurization
   3.3. Desulfurizing Gaseous Fuels
   3.4. Desulfurizing Liquid Fuels
   3.5. Desulfurizing Solid Fuels
   3.6. Bergius Coal Hydrogenation Process
   3.7. Fischer-Tropsch Synthesis
   3.8. Synthetic Gasoline
4. Flue Gas Desulfurization Technologies
   4.1. Introduction
   4.2. Neutralizing Agents Used in Dry and Semi-dry Processes
   4.3. Basic Chemistry of FGD
   4.4. Wet FGD Processes
   4.5. Dry FGD Processes
   4.6. Fluidized Bed Desulfurization (FBC)
   4.7. Regenerative FGD Technologies
      4.7.1. Wet Regenerative Processes
      4.7.2. Dry Regenerative Processes
   4.8. FGD Technology Applications
5. Conclusions

Glossary
Bibliography
Biographical Sketches

Summary

Sulfur oxides are produced from the burning of fossil fuels, mainly coal and oil, and the smelting of metal ores that contain sulfur. Emissions of sulfur oxides cause serious
impacts on human health and the environment, both directly and as a result of the way they react with other substances in the air. Sulfur oxides are main precursors of atmospheric acidification, aerosol generation, and acidic dry and wet deposition.

This chapter summarizes various technologies available for controlling emissions of sulfur oxides. Approaches for reducing SO\textsubscript{x} emissions include using clean fuels, cleaning sulfur-containing fuels, and flue gas desulfurization techniques. Switching to low-sulfur fuels, or cleaning high-sulfur fuels, is an effective means of preventing SO\textsubscript{x} emissions as the amount of SO\textsubscript{2} produced directly depends on the sulfur content of fuel. Fuel cleaning is cost-effective in most cases, but it generates large quantities of solid waste and wastewater that should be properly treated and disposed of. Alkali sorbent injection and flue gas desulfurization (FGD) methods allow a relatively deep SO\textsubscript{x} removal. Flue gas desulfurization is carried out in either regenerable or once-through systems. Both systems are based on either wet or dry FGD processes.

1. Introduction

1.1. Sulfur Oxides

Sulfur oxides (SO\textsubscript{x}) comprise two distinct compounds, namely dioxide (SO\textsubscript{2}) and trioxide (SO\textsubscript{3}). Sulfur dioxide is a colorless, toxic gas with pungent odor formed when sulfur is oxidized:

\[ S + O_2 \rightarrow SO_2 \]  

Sulfur dioxide is highly soluble in water, forming sulfurous acid (H\textsubscript{2}SO\textsubscript{3}). Under combustion conditions (> 1000° C), SO\textsubscript{2} is stable. Conversely, SO\textsubscript{3} is stable in air at ambient temperatures and extremely reactive and corrosive.

Large quantities of SO\textsubscript{2} are produced from human activities, mainly burning elemental sulfur in fuels or roasting pyrite (FeS\textsubscript{2}) or sulfide ores of metals such as zinc, copper, lead, etc. The major sources of SO\textsubscript{x} emissions are fossil fuel fired power plants and boilers, metal ore smelters, oil refineries and transportation. Smaller stationary combustion sources such as coal burning for domestic heating also contribute to the problem, especially in urban areas during the winter. Fuel combustion contributes up to about 70 % of the total SO\textsubscript{2} emissions, with the balance attributed to oil refining, chemical and metallurgical industries (see Pollution Control in Industrial Processes). Almost all SO\textsubscript{2} emissions are anthropogenic, although there are also some natural sources, such as erupting of volcanoes and bush burning.

During combustion most of the sulfur in fuel is converted to SO\textsubscript{2}, with SO\textsubscript{3} being formed in small amounts. Sulfur dioxide emissions can easily be estimated from fuel consumption, simply by multiplying fuel consumption with twice its sulfur (S) content (mass units), since

- in mass units the amount of SO\textsubscript{2} is almost the double of that of fuel sulfur, and
- sulfur contained in fuel is converted almost quantitatively into SO\textsubscript{2} and SO\textsubscript{3}. 

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Not all SO₂ produced during combustion is emitted with the flue gases; some basic compounds in ash bind part of it. Spontaneous neutralization reduces the calculated emissions from coal (see Control of Pollution in the Chemical Industry). Ash behavior, however, must be evaluated in each specific case, on a basis of both composition and reactivity.

Sulfur trioxide is either emitted directly into the atmosphere or produced by oxidation of SO₂. Catalytic conversion of SO₂ to SO₃ is possible in the presence of particulates in the atmosphere, or of boiler deposits, dust, and other gaseous impurities in the flue gas, but generally it remains marginal. Particulates tend to catalyze the atmospheric conversion of SO₂ to SO₃ which combines with water vapor to form sulfuric acid mist (aerosols). Homogeneous NOₓ catalysts also oxidize SO₂ to SO₃. Emissions of hydrogen sulfide are detectable by its smell (see Odor Control).

At temperatures below its dewpoint (< 160° C, depending on moisture and SO₃ concentration), sulfuric acid condenses to an acid aerosol. Scavenging of SO₂ by soot flakes leads to low-temperature, carbon catalyzed sulfuric acid formation. This concept is used industrially as a means of flue gas cleaning, converting SO₂ into storable, but expensive sulfuric acid.

1.2. Environmental and Health Effects of SOₓ Emissions

Human exposure to sulfur dioxide can result in irritation of the respiratory system which can cause both temporary and permanent damage. The degree of harm is significantly higher in the presence of airborne particulates and aerosols.

Sulfur dioxide can cause both acute and chronic injury to plants and limit both their growth and crop yield. Other adverse effects of SO₂ are corrosion and damage of building materials and textile fibers.

2. SO₂ Control Strategies

Strategies for SO₂ control are based on either prevention of SO₂ pollution (firing clean fuel), or end-of-pipe treatment of flue gases. Since small-scale flue gas cleaning is often impractical, substitution of sulfur-containing fuels by clean fuel is desirable.

Prevention of SO₂ pollution involves switching to low-sulfur fuels, or else a reduction of fuel-sulfur before its firing. Since SO₂ emissions are directly proportional to the sulfur content of fuel, and also to the amount fired, a reduction in emissions can be achieved by switching to low-sulfur fuels and to higher quality ones. But low-sulfur fuels are not always available—low-sulfur fuel reserves are decreasing and are becoming unavailable in many areas—and cost more than less desirable high-sulfur qualities. For example, Bulgaria suffers from a combination of high-sulfur, low heating value lignite fuel (see Control of Pollution in the Chemical Industry).

Hence, various cleaning methods have been developed for desulfurizing sulfur-bearing fuels prior to their firing. This is rather easy for natural gas and light distillates, but less practical for heavy oil or solid fuels (see Control of Pollution in the Petroleum...
Industry). Treatment may involve a purely mechanical coal washing, chemical conversion, liquefaction (Bergius route) or gasification, with subsequent cleaning of the gas produced.

The end-of-pipe treatment is based on flue gas desulfurization (FGD). Numerous FGD processes have been developed and several have achieved commercial application, especially for large stationary sources, such as thermal power plants, oil refineries, industrial boilers and some types of industrial plants, e.g. sulfide ore roasters and smelters or Claus plants.

Another approach for SO$_2$ control is in-situ treatment, by fluidized bed combustion in the presence of limestone or dolomite.

3. Fuel Cleaning

Almost all fuels can be converted into a gaseous or liquid form, while eliminating sulfur. Technically feasible technologies are available, but their application generally stumbles over cost factors. Moreover, each process typically brings losses in energy content of the order of 15 to 40%. These factors hamper the introduction of new technologies, as long as cheap natural gas and oil remain in ample supply.

3.1. Sulfur in Fuels

Sulfur is an essential element, present, for instance, in gypsum deposits, many metal ores, fossil fuels, and proteins. All conventional fuels contain various sulfur-bound organic and inorganic compounds, and their sulfur content varies significantly:

- wood and cellulose-rich biomass (< 0.1 percent),
- natural gas (0 – 15 percent),
- crude oil (0.3 to several percent), and
- coal (0.5 to > 3.0 percent).

Low-S crude oil is called *sweet*, while high-S oil is *sour*.

Some waste is strongly enriched in sulfur, e.g. waste sulfuric acid or oleum, rubber, protein-rich or derived waste (hair, feathers, and leather). Historically, acid sludge, resulting from obsolete oil refining, was dumped in pools and such contaminated legacies are sooner or later to be removed and treated.

3.2. Fuel Desulfurization

Fuel desulfurization is State-of-the-Art in gas production, where it may be applied to gases (sour natural gas), and in oil refineries (naphtha, kerosene, and distillates). Heavy distillates can still be treated, but feature three phase, trickling bed, catalytic reactors. The high boiling point, coking tendency and ash content lead to frequent catalyst regeneration and often require replacement. Prior processing to lighter fractions by coking, fluid catalytic cracking or hydrocracking is often preferred over direct treatment of heavies (see *Control of Pollution in the Petroleum Industry*).
Desulfurization of fuel offers several advantages, based on:

- **Effect of concentration.** Fuel contains sulfur in a more concentrated solid or liquid form; in flue gas, it is considerably diluted by nitrogen and excess combustion air.
- **Effect of scale.** Using clean fuel, desulfurized at refineries, is simpler than installing pollution control at each small or medium-sized plant. Conversely, only large power plants can afford huge investment in large-scale FGD equipment, if fuel is supplied at lower cost.
- **Resource conservation.** Desulfurization separates sulfur from fuel, yielding elemental sulfur that is marketable, easily recovered, shipped, and handled.

The sulfur recovered is marketed and eventually converted into sulfuric acid in chemical industry.

### 3.3. Desulfurizing Gaseous Fuels

Gaseous fuels include natural gas, liquefied petroleum gases (LPG), refinery gas, cracking gas, producer gas, town gas, fermentation gas, etc. Sulfur mainly appears as hydrogen sulfide (H\textsubscript{2}S), carbonyl sulfide (COS), and mercaptans (R-SH, in which R or C\textsubscript{n}H\textsubscript{2n+1} is an alkyl group).

Inorganic sulfur (H\textsubscript{2}S, COS) is removed mainly by:

- scrubbing, washing out sulfur-bearing compounds using selective absorption liquors, or
- chemical conversion, after capturing the gases on reactive solid adsorbents like iron oxides.

Processes separating H\textsubscript{2}S and COS from the mainstream have been available for many decades (see wet scrubbing). A sulfur-rich gas is eventually recovered by stripping to

- regenerate and recycle the absorption liquor, and
- recover a concentrated stream, converted into elemental sulfur or sulfuric acid by the Claus process.

Organic sulfur can be extracted, mildly oxidized to less offensive compounds or treated by hydrodesulphurization.

**Claus Process**

The Claus process is often used in oil refineries, downstream of fuel desulfurization HDS-processes, for converting gaseous H\textsubscript{2}S into molten sulfur. It features two balanced steps:

- A thermal oxidation step, in which H\textsubscript{2}S is oxidized at high temperatures (1000 to 1400 °C) to SO\textsubscript{2}, with some H\textsubscript{2}S being converted to elemental S, or remaining
unconverted.
- A catalytic step, in which the remaining H₂S reacts with SO₂ on a catalyst at lower temperatures (200 to 350° C), producing molten elemental sulfur.

The main reactions are:

\[
\text{Step 1: } 2 \text{H}_2\text{S} + 3\text{O}_2 \rightleftharpoons 2\text{SO}_2 + 2\text{H}_2\text{O} \quad (2)
\]

\[
\text{Step 2: } 2\text{H}_2\text{S} + \text{SO}_2 \rightleftharpoons 3\text{S} + 2\text{H}_2\text{O} \quad (3)
\]

These reactions are highly exothermic, releasing heat, recovered by generating low-pressure steam in heat exchangers, following the conversion stages.

Sulfur recovery of 94 to 97 % is achieved, using two or three successive catalytic stages. Factors such as concentration, contact time, and reaction temperature influence upon efficiency. Only some H₂S remains in the tail gas, and with further treatment recovery of over 99 % can be obtained.

Absorption on Iron Oxides

Inorganic sulfur is easily removed from gas streams such as synthesis gas or town gas by reaction of acid gases (H₂S and HCN) with a porous mass of iron oxide (Fe₂O₃). In this traditional process, gas flows through a series of fixed bed vessels, containing crude iron oxide pellets. The H₂S reacts forming mainly iron sulfide (FeS) and water. Additional air is supplied to the inlet gas in an amount about half of the theoretical oxygen, required to convert the iron sulfide back to the oxide and precipitate elemental S in the bed. Usually, three to four vessels operate in series, with the freshest mass in the last vessel, so that the sulfur at the outlet gas is rarely over one mg per Nm³ but organic S remains untreated. The removal of H₂S may be less complete and the life of the iron oxide mass proportionally shorter if a high S-content gas is treated.

The process is non-regenerative, as sulfur is normally not recovered. Once the iron oxide mass is saturated, it is removed and discharged. However, the mass can be burned for SO₂ recovery, e.g. roasted together with pyrite in a sulfuric acid plant. If available, it can also be fed into cement kilns, where the resulting SO₂ is converted into gypsum, the HCN into nitrogen and the iron oxide incorporated in cement clinker. Spent mass from the process should be disposed of and handled properly.

This method was widely used for cleaning town gas; its residues are still a source of soil contamination in many traditional industrial sites due to the improper past disposal of spent mass. Today, the process is obsolete and replaced by scrubbing in adequate liquors.

Removal of Organic Sulfur

As the previous processes remove only inorganic sulfur (mainly H₂S), the organic sulfur compounds remain in the fuel gas untreated. If such compounds are present in significant concentrations, it is necessary to remove them, to avoid smell, corrosion, and
pollution. Organic sulfur can be removed by catalytically converting the S-containing organic compounds to H₂S by hydrogenation, followed by catalytic conversion of H₂S by the Claus process.

**Synthetic Natural Gas**

Synthetic natural gas is easily converted into methane, using a nickel-based catalyst.

### 3.4. Desulfurizing Liquid Fuels

Sulfur in liquid fuels is present as thiols (mercaptans) R-SH, sulfides R-S-R’, disulfides R-SS-R’, thiophenes, and derivates. Such sulfur forms can be removed by catalytic hydrosulfurization (HDS).

**Hydrodesulfurization (HDS)**

HDS is based on catalytic hydrogenation of S-containing compounds to H₂S. The latter is recovered by scrubbing in suitable liquors, subsequent stripping from the effluent liquors, and converted to elemental S in the Claus process. At the same time N-containing compounds are converted to NH₃.

Catalytic activity is mainly related to sulfides of group VI, such as molybdenum (Mo) and tungsten (W), and group IX to X, such as cobalt (Co) and nickel (Ni), the latter acting as promoters. In general, a catalyst, molybdenum sulfide (CoMo/Al₂O₃) containing cobalt, is used. It is poisoned by H₂S and regenerated by running hydrogen through the reactor. Poisoned catalysts can also be recycled for metal recovery; before shipping they need to be deactivated, to avoid spontaneous oxidation of hydrogen, still present in the catalyst.

The most important HDS reactions are:

\[
\text{mercaptans } \quad RSH + H_2 \rightarrow RH + H_2S \\
\text{disulfides } \quad RSSR + 2H_2 \rightarrow R-R + 2H_2S \\
\text{sulfides } \quad RSR + H_2 \rightarrow R-R + H_2S
\]

The reactions take place in adiabatic fixed bed reactors, typically at 300 to 400° C and a hydrogen pressure of 1.0 MPa. The S-content of 1 to 5 % is typically reduced to 0.1 %. Higher operating temperatures are required for fuels with higher boiling point or higher S-content of the feedstock.

Originally, HDS was required for pre-treating feedstock to catalytic reformers using hydrogen produced by conversion of cycloparaffins (technical name naphthenes) into arenes (aromatics) in the same units. Large amounts of hydrogen are consumed in HDS and requirements are often a multiple of what is generated by catalytic reforming in a refinery, depending on the oil type treated. In this case, a dedicated hydrogen plant is
needed. Since hydrogen production is expensive, almost all hydrogen is recycled to the HDS-inlet.

Direct hydrodesulfurization is impractical for heavy oils, with high viscosity and sizeable ash content, causing fast fouling and coking of catalysts.

3.5. Desulfurizing Solid Fuels (see Control of Pollution in the Chemical Industry)

Solid fuels are subdivided in:

- coal qualities of different rank,
- lignite,
- peat,
- wood, and other forms of biomass (straw, animal dung).

In coal, the most abundant and widely used solid fuel, sulfur occurs both as inorganic minerals, mainly pyrite or marcasite (both with chemical formula FeS₂, but different crystalline structure), and as organic compounds incorporated in the combustible part of coal. Sometimes sulfur is present as sulfates. Depending on its origin, coal highly varies in S-content. Up to 70 % of sulfur in high-S coal is in pyritic or sulfate form, not chemically bound to the coal molecules. Inorganic Sulfur can be removed by mechanical means (coal washing), while organic Sulfur can only be eliminated using chemical hydrogenation or gasification processes.

Coal Washing

Coal is a low-cost fuel, supporting only limited extraction, beneficiation, or refining costs.

Coal washing (i.e. beneficiation) requires first finely milling, to liberate the denser ash and pyrite particles, then removing these particles by wet (jigging) or dry methods (air classification), as used in ore dressing.

About 50 % of pyritic (inorganic) sulfur, or about 20 to 30 % of total S, can be removed by coal washing. This is a cost-effective approach in controlling SO₂ emissions and removing ash, thus reducing fly ash emissions, but it also generates large quantities of solid waste and acid wastewater, which must be properly treated and disposed of.

3.6. Bergius Coal Hydrogenation Process

The Bergius process was developed for hydrogenating coal to oil, typically at 400° C and 2-4 MPa pressure, using inexpensive, non-regenerated catalysts. Today, the process is far too expensive for commercial application.
Bibliography


Biographical Sketches

Sarantuyaa Zandaryaa is Postdoctoral Research fellow at the United Nations University (UNU) and the Tokyo University in Japan. She is an Environmental Engineer by training.

She was born in Bayanbulag, Mongolia. Her educational background includes B.Sc. (1993) and M.Sc. (1995) from Mongolian University of Science and Technology and Ph.D. in Environmental Engineering (2001) from University of Rome “La Sapienza”, Italy. She obtained Diploma on Environmental Management at the International Postgraduate Programme on Environmental Management (CIPSEM) at Dresden University of Technology, Germany, in 1997. She was a Visiting PhD student at Pennsylvania State University, USA, in 1999.

Dr. Sarantuyaa Zandaryaa was Professor of Environmental Engineering and Head of Environmental Engineering Department at the Mongolian University of Science and Technology. She has lectured at European universities for academic, policy-making, and international audiences and worked on several national and international research projects. She received a research grant “Young Researchers’ Project 2001-2002” from University of Rome “Tor Vergata”, Italy. She advised and coordinated UN-ESCAP environmental projects in Mongolia.

Her current research focuses on environment and sustainability, with emphasis on zero emissions approach and material flow analysis for assessing sustainability at national and local levels and integrating environmental considerations into economic and social policy-making. She has also been involved in research activities on urban ecosystems management.

Dr. Zandaryaa is author/co-author of numerous refereed research journal and conference papers, and

She was awarded full scholarships from the Government of Mongolia and Ministry of Foreign Affairs of Italy. In 2002, she was awarded Japan Society for the Promotion of Science (JSPS) Postdoctoral Fellowship. She is a member of the Mongolian National Committee for UNESCO-International Hydrology Programme (IHP).

Alfons Buekens was born in Aalst, Belgium; he obtained his M.Sc. (1964) and his Ph.D (1967) at Ghent University (RUG) and received the K.V.I.V.-Award (1965), the Robert De Keyser Award (Belgian Shell Co., 1968), the Körber Foundation Award (1988) and the Coca Cola Foundation Award (1989). Dr. Buekens was full professor at the Vrije Universiteit Brussel (VUB), since 2002 emeritus. He lectured in Ankara, Cochabamba, Delft, Essen, Sofia, Surabaya, and was in 2002 and 2003 Invited Professor at the Tohoku University of Sendai.

Since 1976 he acted as an Environmental Consultant for the European Union, for UNIDO and WHO and as an Advisor to Forschungszentrum Karlsruhe, T.N.O. and VITO. For 25 years, he advised the major industrial Belgian Bank and conducted more than 600 audits of enterprise.

Main activities are in thermal and catalytic processes, waste management, and flue gas cleaning, with emphasis on heavy metals, dioxins, and other semi-volatiles. He coordinated diverse national and international research projects (Acronyms Cycleplast, Upcycle, and Minidip). Dr. Buekens is author of one book, edited several books and a Technical Encyclopedia and authored more than 90 scientific publications in refereed journals and more than 150 presentations at international congresses. He is a member of Editorial Boards for different journals and book series.

He played a role in the foundation of the Flemish Waste Management Authority O.V.A.M., of a hazardous waste enterprise INDAVER, and the Environmental Protection Agency B.I.M./I.B.G.E. He was principal ministerial advisor in Brussels for matters regarding Environment, Housing, and Classified Enterprise (1989). Since 1970 he has been a Member of the Board of the Belgian Consumer Association and of Conseur, grouping more than a million members in Belgium, Italy, Portugal, and Spain.

He is licensed expert for conducting Environmental Impact Assessments (Air, Water, Soil) and Safety Studies regarding large accidents (Seveso Directive).