SULPHUR DIOXIDE REMOVAL FROM STACK GASES
A REVIEW OF AVAILABLE METHODS

Report No. ARB-TDA-02-75

March, 1975

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Everett Biggs, Deputy Minister
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AIR RESOURCES BRANCH

Technology Development & Appraisal Section

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A REVIEW OF AVAILABLE METHODS

Ministry of the Environment,
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TORONTO, Ontario.

March, 1975
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SULPHUR DIOXIDE REMOVAL FROM STACK GASES
A LITERATURE REVIEW OF AVAILABLE METHODS

1. SUMMARY

An outline of the known methods available for sulphur dioxide removal from stack gases is given. The processes range from those which are being tested out on a large scale, to those which have not yet developed beyond the laboratory stage.

Evaluations from either technological or economic viewpoints have not yet been undertaken; all data, viewpoints and judgement contained in this review have been obtained from the available literature, and/or from various individuals during visits to desulphurization facilities.

Based on available reports from the U.S., commitments to control the $\text{SO}_2$ from power plant flue-gases have been made by about 40 utilities at over 50 plants. This represents over 35,000 MW of generating capacity and 93 systems of flue-gas desulphurization. Of these (including about 20 operational units) systems, the lime/limestone process has been the leader, as there was more experience behind the process and as there was no by-product marketing needed. Along with the vast improvements in the lime/limestone process, there has also been substantial progress made in the many processes which produce useful end-products, such as magnesium oxide scrubbing, Wellman-Lord (Powergas), Shell, Monsanto Cat-Ox and others.

While there have been many problems to date on the ongoing development of these processes, a stage appears to have been reached where a number of processes can be termed to be reliable and feasible. However, this has not deterred a number of utility companies from objecting to these
systems as being wasteful, unnecessary, uneconomic and unreliable. In some instances, the costs of a desulphurization system have indeed shown incredible increases between design and operating stages. In the case of lime/limestone systems, the disposal of the sludge has been a formidable problem, however, latest reports indicate that fixation of the sludge can be achieved within a reasonable time and budget.

Recommendations are being made to study some of the processes which may be useful and promising in our local conditions and context.
2. **RECOMMENDATIONS**

Detailed assessments be undertaken of those processes indicated in this review to be promising. These processes are:

- Wet Lime/Limestone Scrubbing
- Magnesium Oxide Scrubbing
- Double Alkali System
- Catalytic Oxidation System
- Citrate and Stauffer Processes
- Ammonia Scrubbing
- Methods producing sulphuric acid from smelter off-gases

Assessments of this nature should be completed by **December, 1975**.
3. OBJECTIVE

To prepare and review a list of the existing sulphur dioxide removal systems now available. This review is to be an initial step, prior to a detailed assessment of selected processes, which in turn will be followed by an assessment of the potential of these methods, as compared to the alternatives of process variations and fuel desulphurization, for the control of \( \text{SO}_2 \) emissions to the atmosphere.
4. A REVIEW OF SO₂ REMOVAL METHODS

4.1 Introduction

Sulphur dioxide emissions have received a lot of attention because of the effects on people, animals and vegetation. It has been estimated that the 1970 SO₂ emission for the U.S.A. was 35 million tons (including about 20 million tons from power plant operations). Unchecked, these emissions could triple over the next 30 years. In Canada, the comparable figure is about 6 million tons which includes about 5 million tons from sulphide ore smelting.

The following presents an extract of information from the sources noted in the references, regarding the sources of SO₂ and the present control methods, whether in use or being tested. It should be noted that no attempt is being made in this review to evaluate the processes either from technological or economical viewpoint, other than what is available from the sources mentioned.

4.2 Sources

The main sources of SO₂ emission are ore-smelting, coal and oil combustion, petroleum refining and the manufacture of sulphuric acid.

Ore-smelting processes - The SO₂ concentrations vary widely in different streams. In many cases, the SO₂ concentration is very dilute. However, in a majority of cases, concentrations of about 3% SO₂ or above can be reached, and a sulphuric acid reclaim system justified.
6. **Coal-burning plants**  - The SO\textsubscript{2} concentration generally varies between 500-3,500 ppm (estimated at %S in coal x 0.067 = %SO\textsubscript{2}) depending on the type of coal used. Various methods, both wet and dry, are being experimented with at present to desulphurize the stack gases. The large volumes of stack gases from each installation and proper disposal of any by-products are thought to be formidable problems.

**Oil-burning plants**  - The residual oil used varies in sulphur content from 1-3%. The crude oil from North American and African sources is low in sulphur content. This sulphur concentrates in the high boiling fractions during the refining and processing of crude.

**Petroleum Refineries**  - A number of operations are of a reducing nature and produce H\textsubscript{2}S. If the H\textsubscript{2}S formed is of sufficiently high concentration, it may be recovered. However, in many cases, the H\textsubscript{2}S containing streams may be flared or otherwise burnt to produce SO\textsubscript{2}, which can produce local problems.

**Sulphuric acid plants**  - Sulphur is usually burnt to produce SO\textsubscript{2} and then oxidized and absorbed to produce H\textsubscript{2}SO\textsubscript{4}. It has been estimated that about 3% of the sulphur burnt is usually emitted as SO\textsubscript{2}. The SO\textsubscript{2} concentration in stack gases is usually of the order of 3,000 ppm. There is also, sometimes, a H\textsubscript{2}SO\textsubscript{4} mist problem in the local area.

4.3 **Alternatives for SO\textsubscript{2} Control**

In some cases, it may be possible to control the ambient and ground level concentrations of SO\textsubscript{2} by the use of high stacks providing good dispersion. In cases where large amounts of SO\textsubscript{2} are emitted, this approach may be unacceptable because of acidic fallout.
The SO₂ emission may be avoided or at least controlled by the use of low-sulphur coals. This can only be a partial solution however, as these coals are much more expensive and the reserves are limited. It has been found that when low sulphur fuels are used, the collection of fly-ash in the electro-static precipitators presents problems. Modifications and additional equipment (eg., gas conditioning equipment) are required to reinstate the efficiency of the precipitators when an existing source is changed to burn low-sulphur coal.

Liquefaction and gasification processes in which a large part of the sulphur is removed during treatment are also being examined. Some of these processes have been used in Europe for a long time. The supply and economic situations in North America have, however, limited their uses in this continent. The high costs of these plants and the rapid changes currently occurring in the economy of North America are inhibiting development of this approach.

There may be room for operational control, meaning higher sulphur-containing fuels be used when and only when meteorological conditions permit. However, as is apparent, this is practicable only in some processes and industries.

The main thrust in sulphur dioxide removal is from the stack gas itself and many methods have been proposed. Some of the active organizations are presented in Section 8.1 (Appendix).

In the following review, the methods for desulphurization are subdivided based on the type of absorbents used for removal of SO₂ (ex., calcium compounds, alkaline materials, metal oxides and others).

Classification can also be made on the fact of whether the SO₂ is recovered in a useful form or in the form of a product intended for
It should also be noted that some methods are termed "dry" where some suitable material is injected in the boiler or in the gases and the product after absorbing the SO₂ is removed downstream in the solid form. In the "wet" processes, the SO₂ is either removed by scrubbing with a suitable solution or it is first absorbed on injected pulverized material and then the solids are removed by scrubbing with water or a suitable solution in a scrubber.
5. **REMOVAL PROCESSES**

5.1 Calcium Compounds (Lime/Limestone)

5.1.1 Dry Process

Pulverized limestone (CaCO₃) or dolomite (CaCO₃·MgCO₃) is introduced into the boiler furnace and is recovered downstream in the dry state by cyclones and electrostatic precipitators after reacting with the sulphur oxides.

![Diagram of a flue gas desulfurization system](image)

**Fig. 1**

The overall reactions are given by the following equation, although many side reactions can occur.

\[
\begin{align*}
\text{CaCO}_3 & \rightarrow \text{CaO} + \text{CO}_2 \\
\text{CaO} + \text{SO}_2 & \rightarrow \text{CaSO}_3 \\
\text{CaO} + \text{SO}_2 + \frac{1}{2} \text{O}_2 & \rightarrow \text{CaSO}_4
\end{align*}
\]
5.1.1.2 **Advantages**

(a) The off gases are not cooled in the $\text{SO}_2$ removal operations and the
plume thermal buoyancy is unimpaired.

5.1.1.3 **Disadvantages**

(a) In the limited contact time available, the reaction rate (diffusion
controlled) is usually too slow to permit reaction to be completed.
(b) Scaling of boiler tube is increased.
(c) The increased particulate loading of the effluent gases and the
change in particle characteristics results in excessive emissions
of particulate and a higher efficiency collector (ESP) is required.
(d) Differences in $\text{SO}_2$ concentrations across the boiler and gas ducts
present a problem in achieving either satisfactory (suitable) dis-
tribution of limestone or requires the use of excess absorbent.
(e) Disposal of the collected solids presents a further problem and in-
creases costs.

5.1.1.4 **Plants**

Test installations include E.P.A./T.V.A. at Shawnee's
100 MW coal-burning boiler, Steag (Germany) on 20 MW coal-burning boiler;
Criepi (Japan) on oil-fired boiler and Foster-Wheeler at Dairyland Power
Co-Op's 80 MW boiler.

5.1.1.5 **Status**

The present status of this process is at a standstill and
development has virtually been abandoned. However, because of the compar-
avatively uncomplicated equipment required, this method may be useful for
some small boilers with intermittent operation in spite of low (22-45%) removal efficiency.

5.1.2 Wet Process (Calcium Compounds)

In the wet processes, the $\text{SO}_2$ is either directly scrubbed out with absorbing solution or absorbed on solid particles and then the product is removed in a scrubber by either water or a suitable solution.

The chemistry of lime/limestone scrubbing for $\text{SO}_2$ is quite complex and it is not yet fully understood. It appears that the overall reaction is that of $\text{SO}_2$ with $\text{CaO}$ or $\text{CaCO}_3$ to form calcium sulphite, with some oxidation to sulphate. Many other side reactions can also take place:

\[
\text{CaCO}_3 + \text{SO}_2 + \frac{1}{2} \text{H}_2\text{O} \rightarrow \text{CaSO}_3 \cdot \frac{1}{2} \text{H}_2\text{O} + \text{CO}_2
\]

\[
\text{CaO} + \text{SO}_2 + \frac{1}{2} \text{H}_2\text{O} \rightarrow \text{CaSO}_3 \cdot \frac{1}{2} \text{H}_2\text{O}
\]

\[
\text{CaSO}_3 + \frac{1}{2} \text{O}_2 \rightarrow \text{CaSO}_4
\]

\[
\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2; \quad \text{CaO} + \text{SO}_2 \rightarrow \text{CaSO}_3
\]

The three major wet scrubbing methods are shown in Fig. 2:
Method 1, uses a slurry of ground limestone in the scrubber. Method 2, uses lime solution either from manufactured lime or prepared by calcining and slaking of the ground limestone, and in Method 3, ground limestone is injected into the boiler which is followed by a scrubber.

5.1.2.1 Advantages

i) Method 1 - It is a true add-on system and does not interfere with the boiler operation. It does not require expensive calcining as in Method 2. Good removal efficiency is obtainable.

ii) Method 2 - It is believed that lime produced quicker and more complete reaction with the SO₂.

iii) Method 3 - Fairly coarse limestone can be used, as long as the temperature at the point of injection is high enough to calcine it. This method is believed to alkalize the gases and have low corrosion rates.

5.1.2.2 Disadvantages

All of the 3 methods produce waste sludge. Other specific disadvantages are:

i) Method 1 - Requires fine grinding of the limestone and quite high hold-up rates. Scaling and corrosion rates can be high, and sometimes it is found that the SO₂ removal efficiency drops as the SO₂ inlet concentration rises.

ii) Method 2 - It is fairly expensive to calcine and produce CaO from CaCO₃.

iii) Method 3 - Generally, it is found to have lower efficiency
than Method 1. Fouling of boiler tubes and loss of efficiency in precipitators are known problems. In both Methods 1 and 3, very close control over sulphite-bisulphite proportions, PH, L/G, etc., have to be maintained to avoid scaling problems.

5.1.2.3 Plants

A very large number of boilers in the U.S. are either operating, constructing, or planning lime/limestone scrubbing systems. Some of the more prominent ones are:

<table>
<thead>
<tr>
<th>Company</th>
<th>Place</th>
<th>Scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commonwealth Edison (Limestone)</td>
<td>Will County, Ill.</td>
<td>167 MW</td>
</tr>
<tr>
<td>Southern Calif. Edison (Lime/Limestone)</td>
<td>Mojave, Nevada</td>
<td>2 x 160 MW</td>
</tr>
<tr>
<td>T.V.A. (Limestone)</td>
<td>Widows Creek, Ala.</td>
<td>550 MW</td>
</tr>
<tr>
<td>Northern States Power (Limestone)</td>
<td>Sherburne City, Minn.</td>
<td>680 MW</td>
</tr>
<tr>
<td>Louisville Gas &amp; Electric (Limestone)</td>
<td>Paddy's Run, Kentucky</td>
<td>65 MW</td>
</tr>
<tr>
<td>Duquesne Light Co. (Lime)</td>
<td>Elrama, Pa.</td>
<td>425 MW</td>
</tr>
<tr>
<td></td>
<td>Phillips, Pa.</td>
<td>400 MW</td>
</tr>
<tr>
<td>Pennsylvania Power (Lime)</td>
<td>Mansfield, Pa.</td>
<td>2 x 800 MW</td>
</tr>
<tr>
<td>Montana Power (Lime)</td>
<td>Colstrip, Ma.</td>
<td>2 x 360 MW</td>
</tr>
</tbody>
</table>

5.1.2.4 Status

Despite the very large amount of work done in this field, there still is a rather inadequate knowledge of the factors affecting the scrubber operations and, therefore, continuous developmental work is taking place in the field. Another problem associated with the processes has been the tremendous amounts of sludge produced. It has been estimated that a 1,000 MW plan equipped with such a scrubbing system can produce about 1,500 tons/day of sludge (not including the fly-ash).

It is expected that in the near future, both the reliability
and the waste problems would be brought under control, if not fully, then to a certain degree.

5.2 Alkaline Materials

The alkalis that have received most attention are ammonium, sodium, potassium and lithium. Most of the methods involve the use of an aqueous solution in the scrubber; however, one of the major efforts has been in the use of a granular solid in the alkalized alumina (NaAlO₂ process). The alkali sorbents have the unique advantage that the sorbent can be regenerated by heating at a temperature not too far above the absorption temperature. Another favourable factor is due to the fact that the sulphite-bisulphite equilibrium can be used to decrease the temperature differential between absorption and regeneration.

5.2.1 Ammonium Compounds

Various methods have been devised for use of ammonia and ammonium compounds in the absorption of SO₂. While the majority of the work done to date has involved experiments with special designs of scrubbers for the contacting of stack gases and ammoniacal liquor, some work has also been devoted to injection of ammonia directly into the stack gas. In ammonia scrubbing, the principal reactions are:

\[
\begin{align*}
\text{NH}_3 + \text{H}_2\text{O} + \text{SO}_2 & \rightarrow \text{NH}_4\text{HSO}_3 \\
2\text{NH}_3 + \text{H}_2\text{O} + \text{SO}_2 & \rightarrow (\text{NH}_4)_2\text{SO}_3
\end{align*}
\]

Based on the end-product desired, the effluent from the scrubber may be regenerated in several ways as described in the following sections.
Recovery of SO₂ and Fertilizer Chemicals

5.2.1.1 Cominco

Cominco, in Trail, B.C. developed a process in the 1930's for treating the waste gases from sulphide ore smelting operations to produce sulphuric acid and Ammonium Sulphate, claiming a SO₂ removal efficiency of 96%. The reactions are:

\[
\begin{align*}
2NH_4HSO_3 + H_2SO_4 & \rightarrow (NH_4)_2SO_4 + 2SO_2 + 2H_2O \\
(NH_4)_2SO_3 + H_2SO_4 & \rightarrow (NH_4)_2SO_4 + SO_2 + H_2O
\end{align*}
\]

In a slight variation of this process (Fig. 3) the hot smelter gases are cooled with diluted H₂SO₄ and passed to two scrubbing towers where the gas is contacted with a solution containing Amm. Sulphite and Amm. Bisulphite. Part of the scrubbing solution is directed to a stripper where it is acidified with H₂SO₄ and stripped with air to give a gas stream containing SO₂.
which is used as a feed for an $H_2SO_4$ plant. The amm. sulphate is crystallized from the solution leaching the stripper.

Advantages and Disadvantages

The $H_2SO_4$ required for acidulation can be produced from the $SO_2$ evolved and, hence, when the plant is run for high bisulphite (to maximize the production of $H_2SO_4$), net $H_2SO_4$ is also available for sale along with the amm. sulphate. However, the sulphate which is considered to be an acceptable fertilizer in some parts of the world is not prized in North American and, hence, this process is not considered to be very attractive.

Status and Plants

While this process is various modifications can be considered to be fully developed, as it is in commercial use in smelter and sulphuric acid plants in the U.S.A., Czechoslovakia, Austria and India, it has never been tried on a large scale on a power plant in North America. However, T.V.A. is experimenting with various aspects of regeneration and other associated problems at a 4,000 cfm plant in Alabama.

5.2.1.1.2 NIIOGAZ

In the Niiogaz process (Fig. 4) the stack gas is cooled to
35°C by water in the first section of the scrubber where about 10% of the SO₂ is absorbed requiring the use of lime for neutralizing. Three stages of the scrubber are used for scrubbing with ammonia, the final stage (electrostatic precipitator) serving as a mist eliminator. The stripping to produce SO₂ is by steam heating. The ammonium sulphate formed in the stripper is also recovered.

**Advantages and Disadvantages**

While Niiogaz estimates indicate that this method may be preferable to lime or magnesia scrubbing, it is generally felt that the heat requirements for stripping would be tremendous.

**Status and Plants**

Apart from Russian plans, which include equipping of a 240 MW plant with this process, no other developmental work is known to be taking place in the West.

5.2.1.1.3 R.I.I.C. (Czechoslovakia)

R.I.I.C. (Czechoslovakia) have commercially applied the process shown in Fig. 5 in a sulphuric acid plant.

---

**Fig. 5**
The tail gases pass through 2 scrubbers in series, with about 90% absorption and the effluent is acidified with Nitric Acid. The NH₄NO₃ solution is pumped to a complex fertilizer plant and SO₂ is returned to the H₂SO₄ plant.

Advantages and Disadvantages

This method has the advantage of producing amm. nitrate which is considered to be a better fertilizer than the sulphate which is formed by some other ammonia scrubbing methods. However, it has been found that the SO₂ which is produced is contaminated with NO₂ and there is a significant presence of sulphates contaminating the nitrate stream.

Status and Plants

The only known commercial plant is a sulphuric acid plant in Czechoslovakia. Tests have been done in the West but, so far, no plans are known for a large size plant, either on sulphuric acid tail gases or on power plant flue gases.

5.2.1.1.4 I.P.R.A.N. (Romania)

I.P.R.A.N. (Romania) have developed the process illustrated in Fig. 6. The tail gases from the sulphuric acid plants are mixed with
NH₃ and scrubbed in a Venturi scrubber; the effluent is mixed with H₃PO₄ and then stripped of the SO₂. The ammonium phosphate solution is pumped to a complex fertilizer plant. The reaction is:

\[(NH_4)_2SO_3 + 2H_3PO_4 \rightarrow 2NH_4(H_2PO_4) + SO_2 + H_2O\]

Advantages and Disadvantages

While it would be an advantage to have this method applied to a sulphuric acid plant associated with a complex fertilizer plant; unfortunately this product is not regarded as an acceptable fertilizer on this continent. Large amounts of phosphoric acid are also required because of its low reactivity.

Plants and Status

At least 3 sulphuric acid plants are reported to be operating satisfactorily in Romania using this method; and it is considered to be commercially developed. No plans are known at this time to adopt it to power plant use anywhere.

5.2.1.2 Recovery of Sulphur and/or Amm. Sulphate

5.2.1.2.1 Fulham Station/Simon Carves in England developed the process shown in Fig. 7.
Flue-gases, after pre-cleaning in an electrostatic precipitator, are scrubbed with a re-circulating solution of Ammonia, sometimes the Ammonia is supplemented by amounts of $\text{H}_2\text{S}$ or Manganous ions to promote better oxidation of Ammonium sulphite to sulphate. The reactions are believed to be:

\[
\begin{align*}
\text{NH}_3 + \text{H}_2\text{O} + \text{SO}_2 & \rightarrow \text{NH}_4\text{HSO}_3 \\
2\text{NH}_3 + \text{H}_2\text{O} + \text{SO}_2 & \rightarrow (\text{NH}_4)_2\text{SO}_3 \\
(\text{NH}_4)_2\text{SO}_3 + \frac{1}{2} \text{O}_2 & \rightarrow (\text{NH}_4)_2\text{SO}_4
\end{align*}
\]

A portion of the solution is continuously withdrawn and filtered to remove fly-ash, then treated in an autoclave with amounts of sulphuric acid to give sulphur and Ammonium sulphate as follows:

\[
\begin{align*}
3(\text{NH}_4)_2\text{SO}_3 + \text{H}_2\text{SO}_4 + \text{H}_2\text{O} & \rightarrow 3(\text{NH}_4)_2\text{SO}_4 + \text{H}_2\text{O} + \text{S} \\
6(\text{NH}_4)\text{HSO}_3 & \rightarrow 3(\text{NH}_4)_2\text{SO}_4 + 2\text{H}_2\text{O} + 2\text{S} + \text{H}_2\text{SO}_4
\end{align*}
\]

**Advantages and Disadvantages**

Very high $\text{SO}_2$ removal efficiencies are indicated and the method produces both sulphur and sulphates which are easily stored and transported. The autoclaveing has further advantage of continuous or watchwise operation.

**Status and Plants**

In spite of the apparent success of the process on a 56,000 cfm plant operating on a coal-fixed boiler, no commercial development has been attempted for reasons which are unknown at the moment.

The generalized flow-sheet shown in Fig.8 has been studied by
T.V.A. (U.S.), Simon-Carves (U.K.), Cominco (Canada) and Niiogaz (U.S.S.R.). If the effluent from ammonia scrubbing with SO₂ is heated under pressure, ammonium sulphate and elemental sulphur are produced.

Advantages and Disadvantages

This process also produces elemental sulphur which along with the sulphate is easy to handle and can be used as an intermediate in other processes. However the chemistry of the method has proved to be quite complicated, and drawbacks include explosion hazard and corrosion in the reactor. The closed loop system can also accumulate various unwanted side-products.

Status and Plants

The process was developed to a fairly advanced level by Simon-Carves and Cominco. Pilot plant work in Russia may develop into large-scale installation. No plans of commercial installation in the U.S. are known at the present time.
5.2.1.2.3 **Showa-Denko** in Japan (Fig. 9) have developed a process for the thermal power station flue gases. In this process, ammonia and steam are injected ahead of the scrubber. Additional ammonia is used to convert ammonium bisulphite in the scrubber as follows:

\[
\text{NH}_4\text{HSO}_3 + \text{NH}_3 \rightarrow (\text{NH}_4)_2\text{SO}_3
\]

A portion of the circulating scrubbing solution is continuously withdrawn and filtered to remove fly-ash. The ammonium sulphite is then oxidized with air to form ammonium sulphate which is recovered in evaporator-crystallizer. SO\(_2\) removal efficiencies of 98% are claimed.

**Advantages and Disadvantages**

It is reported that the method of injection utilised reduces corrosion in the system. However because of the limited information available on the process, all the details are not available.
Status and Plants

This process is not believed to have yet been tried on any commercial size unit. The extent of the development is not known.

5.2.1.2.4 The I.F.P. process is presented in Fig. 10.

In essence the flue gases are scrubbed with aqueous ammonia to form an amm. brine that contains sulphites and bisulphites. The reactions are:

\[
\begin{align*}
\text{SO}_2 + \text{NH}_4\text{OH} & \rightarrow \text{NH}_4\text{HSO}_3 \\
\text{SO}_2 + 2\text{NH}_4\text{OH} & \rightarrow (\text{NH}_4)_2\text{SO}_3 + \text{H}_2\text{O} \\
(\text{NH}_4)_2\text{SO}_3 + 1/2 \text{O}_2 & \rightarrow (\text{NH}_4)_2\text{SO}_4
\end{align*}
\]

In the second stage of operations the brine is decomposed by the use of a small amount of sulphur with fuel gas or LPG combustion supplying the heat.
\[(\text{NH}_4)_2\text{SO}_4 \rightarrow (\text{NH}_4)_2\text{HSO}_4 + \text{NH}_3\]
\[2(\text{NH}_4)_2\text{HSO}_4 + \text{S} \rightarrow 3\text{SO}_2 + 2\text{NH}_3 + 2\text{H}_2\text{O}\]

The CO and H\(_2\) produced from combustion of the hydrocarbon are also used to reduce any SO\(_3\) to SO\(_2\):

\[\text{SO}_3 + \text{CO} \rightarrow \text{SO}_2 + \text{CO}_2\]
\[\text{SO}_3 + \text{H}_2 \rightarrow \text{SO}_2 + \text{H}_2\text{O}\]

H\(_2\)S is either generated on-site - or purchased and the standard Claus reaction takes place:

\[2\text{H}_2\text{S} + \text{SO}_2 \rightarrow 3\text{S} + 2\text{H}_2\text{O}\]

**Advantages and Disadvantages**

The process is a complex chemical operation, and hence it has been estimated that the capital and operating costs will be high. The availability of H\(_2\)S and the costs of the by-product sulphur will be important factors in the final assessment of this process.

**Status and Plants**

Parts of this process (Claus Reaction) have been proven in commercial size units, however the sulphate decomposition and the SO\(_2\) reduction are to be tried out on a demonstration plant in the near future.

5.2.1.3 **Recovery of Ammonia**

Ugine-Kuhlman/Weiritmann developed the process shown in Fig.11 in France.
Ammonia is injected into the flue-gas ahead of an aqueous scrubber. A portion of the recirculating scrubbing solution containing ammonium sulphite, bisulphite and sulphate is withdrawn and treated with lime slurry to liberate ammonia. The calcium salts are removed, along with the flyash.

Advantages and Disadvantages

While good (93-97%) efficiencies of SO$_2$ removal have been reported, and while further advantage of being able to regenerate ammonia for re-use is present; it is felt that the operation of the reactor and the disposal and treatment of the sludge will cause problems.

Status and Plants

Very little information is available regarding the development
of the process. As far as it is known, no commercial size plant is either operating or in the planning stage.

5.2.2 Sodium Compounds

5.2.2.1 Recovery of H₂S

Sodium Aluminate Process is shown in Fig. 12 in one of its versions.

Various organizations, e.g. U.S. Bureau of Mines, W.R. Grace & Co., M.W. Kellog Co., A.V.C.O. (all U.S.) were involved in the development of this process. In the version of the process depicted above, the stack gas, after cleaning, is contacted with the solid absorbent in a fluidized reactor operated between 300-350°C. The reaction is:

\[ 2\text{NaAlO}_2 + \text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{Na}_2\text{SO}_4 + \text{Al}_2\text{O}_3 \]
Tests show that about 90% removal of SO₂ is attained. The loaded absorbent is heated to 650-700°C and then regenerated in a fluidized bed by the action of a reducing gas (reformed gas, etc.) as follows:

\[
\text{Na}_2\text{SO}_4 + \text{Al}_2\text{O}_3 + 3\text{H}_2 \rightarrow 2\text{NaAlO}_2 + \text{H}_2\text{S} + 2\text{H}_2\text{O}
\]

**Advantages and Disadvantages**

The method is attractive because of the simplicity and has been found to be less energy-consuming than some comparable methods. However, because of the problems associated with the absorbent attrition and the high capital costs. It should also be noted that proper handling of H₂S requires a lot of care.

**Status and Plants**

As far as it is known, C.E.G.B. (U.K.) did some developmental work in the past on a powerplant flue-gas side-stream; along with some other companies named above who also ran tests. Because of the associated problems the experimental work was suspended and no plans for the use of the process in a large scale plant have been reported.

5.2.2.2 Recovery of SO₂

5.2.2.2.1 Wellman-Lord process is illustrated in Fig. 13.
This is the most developed alkaline sulphite-absorption process for SO$_2$ removal, and is based on the temperature dependent absorption-desorption of SO$_2$ by certain sulphites. This process is most suitable for gas streams with SO$_2$ concentration of 0.15 - 2%. In a power plant the stack gases have to be cleaned of the particulate matter; in a sulphuric acid plant the tail gases are humidified before this process is used. The gas-stream is contacted in the scrubber with a counter-current flow of sod. sulphite and bisulphite with the following reaction, resulting in an SO$_2$ absorption of about 90%:

\[
\text{SO}_2 + \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} \rightarrow 2\text{NaHSO}_3
\]

\[
\text{Na}_2\text{SO}_3 + \frac{1}{2}\text{O}_2 \rightarrow \text{Na}_2\text{SO}_4
\]

The scrubber effluent is stripped of the SO$_2$:

\[
2\text{NaHSO}_3 \rightarrow \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} + \text{SO}_2
\]

and the sod. sulphite crystals are precipitated, redissolved, and sent to the scrubber. The SO$_2$ is concentrated before being sent to a sulphuric acid plant.

**Advantages and Disadvantages**

Because of the formation of some sulphates which cannot be regenerated as above, the absorption solution has to be periodically purged of the sulphates; this aspect is one of the major problems of this process.

**Status and Plants**

This process has been operational for over 9000 hours on a commercial basis since June 1971 at the Japan Synthetic Rubber's Chiba
plant on the flue-gases from a 75MW equivalent oil fired boiler.

Other installations present and proposed include sulphuric acid tail gas treatment at Olin Corporation's Paulsboro, New Jersey Plant; Northern Indiana Public Service's demonstration project at D.A. Mitchell 115 MW boiler plant in Gary; and the treatment of tail gases from sulphur production at Standard Oil in El Segundo, California.

5.2.2.2 Stone and Webster/Ionics process is shown in Fig. 14.

![Diagram of the Stone and Webster/Ionics process](image)

The flue-gases, after particulate removal and cooling, are scrubbed with a solution of caustic soda with the following reactions:

\[
2\text{NaOH} + \text{SO}_2 \rightarrow \text{Na}_2\text{SO}_3 + \text{H}_2\text{O}
\]

\[
\text{Na}_2\text{SO}_3 + \text{SO}_2 + \text{H}_2\text{O} \rightarrow 2\text{NaHSO}_3
\]

\[
\text{NaOH} + \text{NaHSO}_3 \rightarrow \text{Na}_2\text{SO}_3 + \text{H}_2\text{O}
\]

The effluent from the scrubber is treated with dilute sulphuric acid,
forming $\text{SO}_2$ and $\text{Na}_2\text{SO}_4$. The $\text{Na}_2\text{SO}_4$ is electrolyzed in a cell to give $\text{NaOH}$ for recycling and dilute $\text{H}_2\text{SO}_4$ for stripping of the $\text{SO}_2$. This process is used for flue-gases from power plants and is about 80% efficient in $\text{SO}_2$ removal.

**Advantages and Disadvantages**

The major problem with this process seems to be the vast amounts of electrical power required for the electrolytic cell. However, regeneration could be carried out during the hours of low power demand from the grid; this, of course entails an extra cost factor for storage of the solution till regeneration. Minimizing of sulphate production (which is usual in processes like this) and bleeding of the same is another, not insurmountable, problem.

**Status and Plants**

Pilot plant tests at Tampa Electric's Gannon Station in Florida indicated problems with the cell components, which were resolved to a degree during 1970-71. Presently E.P.A. and Wisconsin Electric have embarked on a development program at the Valley Plant which is expected to last until 1976.

5.2.2.2.3 Johnstone and co-workers at University of Illinois developed the process shown in Fig. 15.
The flue-gases are scrubbed with Na$_2$SO$_3$ solution:

\[
\text{Na}_2\text{SO}_3 + \text{SO}_2 + \text{H}_2\text{O} \rightarrow 2\text{NaHSO}_3
\]

A major portion of the scrubber effluent liquor is reacted with Zno to produce zinc sulphite, which is calcined to generate SO$_2$ and to recycle the ZnO:

\[
\begin{align*}
2\text{NaHSO}_3 + \text{Zno} + 1.5\text{H}_2\text{O} & \rightarrow \text{ZnSO}_3 \cdot 2.5\text{H}_2\text{O} + \text{Na}_2\text{SO}_3 \\
\text{ZnSO}_3 \cdot 2.5\text{H}_2\text{O} & \rightarrow \text{ZnO} + \text{SO}_2 + 2.5\text{H}_2\text{O}
\end{align*}
\]

A side stream from the scrubber effluent is treated with lime to ppt CaSO$_3$. The resulting slurry is treated with part of the SO$_2$ generated to produce soluble Calcium Bi-sulphite and hence Calcium Sulphate which can be filtered off:

\[
\begin{align*}
\text{CaO} + \text{NaHSO}_3 & \rightarrow \text{Na}_2\text{SO}_3 + \text{CaSO}_3 + \text{H}_2\text{O} \\
\text{CaSO}_3 + \text{SO}_2 + \text{H}_2\text{O} & \rightarrow \text{Ca(HSO}_3)\text{)}_2 \\
\text{Ca(HSO}_3\text{)}_2 + \text{NaSO}_4 & \rightarrow 2\text{NaHSO}_3 + \text{CaSO}_4
\end{align*}
\]

**Advantages and Disadvantages**

The zinc sulphite is regenerated thermally with the advantage that little disproportionation occurs; however the formation of the sulphates requires a complicated side-stream treatment system. The formation of Na-Zn double salts could also cause some problems.

**Status and Plants**

Even though the pilot plant test results were quite good, the process was never developed fully. Recently Aerojet General did an
evaluation of this method for E.P.A. and reported it to be a method comparable to some others in use today.

5.2.2.3 Others

5.2.2.3.1 A process depicted in Fig. 16 has been developed by The Koyo Iron Works, Japan, and involving the use of NaOH or Na$_2$CO$_3$ as the absorbing medium for desulphurisation of flue gases from an oil-fired plant.

![Fig. 16](image)

As shown, the flue gases are introduced into the top of a spray drying tower at the top of which the NaOH or Na$_2$CO$_3$ is atomized and sprayed into the gases. The reactions are:

\[
2\text{NaOH} + \text{SO}_2 \rightarrow \text{Na}_2\text{SO}_3 + \text{H}_2\text{O}
\]

or

\[
\text{Na}_2\text{CO}_3 + \text{SO}_2 \rightarrow \text{Na}_2\text{SO}_3 + \text{CO}_2
\]

Depending on the excess of O$_2$, some Na$_2$SO$_4$ is also formed. The water of the solution is dried by the heat of the flue gases and powdered solid mixture of the by-product Na$_2$CO$_3$, Na$_2$SO$_3$ etc. is removed by multi-cyclones, electrostatic precipitators and the flue gases released to the stack. Removal efficiencies of 80-90% are claimed.
Advantages and Disadvantages

The advantages seem to include by-products which are easy to store, transport, etc; with possible uses in the Kraft pulping industry. The gases released to the atmosphere have no requirements for re-heating. However, any carry-over of NaOH may present a problem.

Status and Plants

The process has not been tried on coal-burning plants. Reportedly, a commercial plant - an oil-fired boiler at a pulp mill is undertaking a large-scale test of this process.

5.2.2.3.2 The Double-alkali process (Fig. 17) has been developed by a number of organizations, notably, General Motors, Chemico, A.D. Little, etc.

The flue-gas is contacted with a solution of Na₂SO₃/NaHSO₃ in the absorber. A Ca(OH)₂ slurry is mixed with the absorber effluent in the caustizer.

The reactions in the two vessels are:
\[
\begin{align*}
\text{Na}_2\text{SO}_3 & \quad + \quad \text{SO}_2 & \quad + \quad \text{H}_2\text{O} & \quad \rightarrow & \quad 2\text{NaHSO}_3 \\
\text{NaHSO}_3 & \quad + \quad \text{Ca(OH)}_2 & \quad \rightarrow & \quad \text{NaOH} & \quad + \quad \text{CaSO}_3\cdot\frac{1}{2}\text{H}_2\text{O} & \quad + \quad \frac{1}{2}\text{H}_2\text{O} \\
\text{Na}_2\text{SO}_3 & \quad + \quad \text{Ca(OH)}_2 & \quad + \quad 2\text{H}_2\text{O} & \quad \rightarrow & \quad 2\text{NaOH} & \quad + \quad \text{CaSO}_4\cdot2\text{H}_2\text{O} \\
\text{NaOH} & \quad + \quad \text{NaHSO}_3 & \quad \rightarrow & \quad \text{Na}_2\text{SO}_3 & \quad + \quad \text{H}_2\text{O}
\end{align*}
\]

The pptd. Calcium compounds are removed and the overflow along with the make-up of Na\textsubscript{2}SO\textsubscript{3} returns to the absorber. An important variation in this process involves use of limestone (less expensive) for regeneration of the bisulphite, and lime for the regeneration of the sulphate.

**Advantages and Disadvantages**

The advantage of the process is to cause particulate and SO\textsubscript{2} removal in one scrubber. Tests so far have indicated very little scaling, corrosion, etc. However, the separation of fly-ash from the remainder of the stream is one of the big problems.

**Status and Plants**

Pilot-plant tests by General Motors and Chemico will be followed by E.P.A. (2MW boiler at Nevada Power Co.'s Reid Gardner plant) and A.D. Little/C.E.A. (20 MW unit, Services Co. plant). Evaluation should be available around the end of 1975.

**Sodium Carbonate**

Scrubbing is employed at some locations. This is depicted in Fig. 18.
Either commercial soda-ash or impure soda, carbonate which is mined (called Trona) is used to produce the scrubbing slurry. The boiler flue-gases go through the venturi followed by a sieve-tray separator. Mist eliminators are used at the exit to the separator. The sludge produced can be put in evaporation ponds or dewatered before treatment or disposal.

Advantages and Disadvantages

Good reliability and efficiency of SO₂ removal can be achieved. However, as in limestone slurry systems, disposal of the sludge can be a big drawback. The availability of the naturally occurring Trona and the costs of commercial sodium carbonate as alternatives also need to be taken into account.

Status and Plants

This process has been used since April/1974 in Nevada Power's Reid-Gardner plant with about 80% reliability and without any major problems. However, the sulphur content of the coal used is less than 1% and there is a shortage of Trona material.

5.2.3 POTASSIUM COMPOUNDS

5.2.3.1 Regeneration of SO₂

Wellman-Lord process (Fig. 19) involves the absorption of SO₂ in K₂SO₃; and heat stripping of the SO₂:

\[ K₂SO₃ + SO₂ \rightarrow K₂S₂O₅ \]

\[ K₂S₂O₅ \rightarrow K₂SO₃ + SO₂ \]
Status and Plants

Tests done at Baltimore Gas & Electric's Crane Station were halted due to plugging from fly-ash. At present, the status of the process is unknown, however, T.V.A. have been reported to be planning absorption of SO₂ on a K₄P₂O₇ and K₂P₂O₇ mixture.

5.2.3.2 PRODUCTION OF H₂S

5.2.3.2.1 Consolidated Coal Co. developed the method (Fig. 20) in which Potassium Formate (KCHO₂) is used as absorbent. The thiosulphate produced

![Flow Diagram](image-url)
at 200°E is further treated with KCHO₂ giving K₂CO₃ and KHS at 540°F. The sulphide is reacted with CO₂ and water to produce H₂S and K₂CO₃. Regeneration of the formate is achieved by reacting K₂CO₃ with CO at 1000 psi and 540°F. The reactions are:

\[
\begin{align*}
2\text{KCHO}_2 + 2\text{SO}_2 &\rightarrow \text{K}_2\text{S}_2\text{O}_3 + 2\text{CO}_2 + \text{H}_2\text{O} \\
4\text{KCHO}_2 + \text{K}_2\text{S}_2\text{O}_3 &\rightarrow \text{K}_2\text{CO}_3 + 2\text{KHS} + 2\text{CO}_2 + \text{H}_2\text{O} \\
2\text{KHS} + \text{CO}_2 + \text{H}_2\text{O} &\rightarrow \text{K}_2\text{CO}_3 + 2\text{H}_2\text{S} \\
\text{K}_2\text{CO}_3 + 2\text{CO} + \text{H}_2\text{O} &\rightarrow 2\text{KCHO}_2 + \text{CO}_2
\end{align*}
\]

Advantages and Disadvantages

Potassium has the advantage that its formate is nonvolatile stable and highly soluble. It is also reported that formation of sulphates is minimized due to the inherent chemistry in this method.

Status and Plants

During tests a simulated flue-gas (0.3% SO₂) was used and removal efficiencies of about 90% were obtained. Further pilot-plant work is reported to be scheduled at Philadelphia Electric's Phoenixville station.

5.2.3.2.2 Garrett Research & Development Co. were reported to be developing a process using a slurry of K₂CO₃ in molten Potassium Thiocyanate as absorbent. The resulting K₂SO₃ is separated and roasted with coal to K₂S, which is reacted with CO₂ and H₂O to H₂S and K₂S. The K₂S is converted to KHCO₃ which is separated and calcined to give K₂CO₃ for recycling. As far as is known, only laboratory tests have been done on this process.
5.2.4 Alkali Mixtures

Atomics International (North American Rockwell Co.) have developed the process known as the Molten Carbonate process (Fig. 21), in which

![Figure 21: Molten Carbonate Process Diagram](image)

the absorbent is a eutectic mixture of 35% K₂CO₃, 33% Na₂CO₃ and 32% Li₂CO₃. At the scrubbing temperature of 800°F this mixture is a clear liquid. Before entering the scrubber, the fly-ash is removed. The reactions in the scrubber are:

\[
M₂CO₃ + SO₂ \rightarrow M₂SO₃ + CO₂ \quad (M=\text{Metal ion})
\]

Some oxidation to M₂SO₄ also takes place. Following filtration, the liquid is heated to 1100°F:

\[
4M₂SO₃ \xrightarrow{\text{heat}} 3M₂SO₄ + M₂S
\]

The sulphates are reduced by reducing gas:

\[
M₂SO₄ + 4H₂ \rightarrow M₂S + 4H₂O
\]
\[
M₂SO₄ + 4CO \rightarrow M₂S + 4CO₂
\]

In the regenerator H₂S is produced as follows:

\[
M₂S + CO₂ + H₂O \rightarrow M₂CO₃ + H₂S
\]
The regenerated carbonate is re-used in the scrubber. The $H_2S$-rich stream ($30\% H_2S$) is fed to a Claus reactor.

Advantages and Disadvantages

It is a fairly promising process. Control of corrosion and very good mists elimination (to avoid loss of absorbent) are essential in this method. It should be noted that in an add-on system, the flue-gases will have to be heated to 800°F before scrubbing. A $SO_2$ removal efficiency of about 95% was reported on flue-gases.

Status and Plants

It is reported that Consolidated Edison Company plan to develop the process at the Arthur Kill plant.

5.3 Various Metal Oxides

5.3.1 Magnesium Oxide

The Magnesium system for removal of $SO_2$ from stack gases is analogous to the system used in the pulping industry. Wood chips are digested (Fig. 22) with $Mg\ (HSO_3)_2$ solution to dissolve out the lignin and separate
the pulp (cellulose). The waste liquor is concentrated and burnt in a recovery furnace in an oxidizing atmosphere. The carbon burns out, leaving MgO and SO\textsubscript{2}. The combustion gases pass over boiler tubes to produce steam and then through a dust collector to separate the MgO. The MgO is washed and hydrated by heating the slurry to 200°F. The Mg(OH)\textsubscript{2} produced is used in the scrubber to remove the SO\textsubscript{2}. The Mg(HSO\textsubscript{3})\textsubscript{2} produced is recycled to the pulping operation.

In the stack gases, the concentration of SO\textsubscript{2} is usually much less than in the process described above; also, the object is to produce MgSO\textsubscript{3} rather than Mg(HSO\textsubscript{3})\textsubscript{2}. This MgSO\textsubscript{3} can be calcined to produce MgO and SO\textsubscript{2}.

5.3.1.1 Recovery of SO\textsubscript{2}

5.3.1.1.1 Niiogaz method (Fig. 23): the absorption of SO\textsubscript{2} by MgO is carried out in a co-current scrubber and a side stream of effluent slurry is dried in a spray drier. The dried material is mixed with coal and calcined in a fluid bed furnace at about 900°C. The off-gases from the calciner containing SO\textsubscript{2} are cleaned and sent to a sulphuric acid plant. The MgO is re-used as shown.
Advantages and Disadvantages

While details are not available, it is reported that oxidation was not a problem and that scaling and side-reactions were minimal.

Status and Plants

An efficiency of about 92% was reported on the tests conducted at a sintering plant. Plant scale installations are in operation (others are under construction) in U.S.S.R. It is understood that the process can be used on power plants also, based on tests with a power plant side stream (0.3% SO₂). About 95% efficiency was achieved for SO₂ removal in these tests.

5.3.1.1.2 Grillo-Werke AG in Germany developed the process shown in Fig. 24.
This process is similar in principle and operation to the Niiogaz method described above. However, small amounts of MnO₂ are mixed with the absorbent. It is claimed that MnO₂ increases the SO₂ absorption rate and prevents loss of MgO activity.

A side stream of the recirculating absorbent is treated with H₂SO₄ to leach out and prevent the loss of manganese. A filtration step follows to remove the ash. In some cases an oxidation unit is provided to precipitate and remove the iron compounds.

Advantages and Disadvantages

So far the process has been used on oil-burning power plants and sulphuric acid tail gases only, with SO₂ removal efficiencies of about 90%. It is expected that fly-ash removal facilities would be required prior to the installation of the process on coal-burning power plants.

Status and Plants

While the process is apparently considered to be fully developed, no plans for a commercial unit installation are known in North America. It is understood that Mitsui (Japan) and Grillo are jointly undertaking more tests.

The Chemico Magnesium Oxide Scrubbing process is shown in Fig. 25.
Particulate matter is first removed; then the SO$_2$ is scrubbed with MgSO$_3$-MgO slurry. Crystals of MgSO$_3$.6H$_2$O are separated from a side stream. Carbon is added to reduce sulphate and the mixture calcined to evolve SO$_2$ and regenerate MgO. The calciner exit gas contains about 15% SO$_2$; this can be converted to H$_2$SO$_4$. The main and side reactions are believed to be:

\[
\begin{align*}
MgO & + SO_2 + 6H_2O \rightarrow MgSO_3.6H_2O \\
MgSO_3 & + 1/2 O_2 + 7H_2O \rightarrow MgSO_4.7H_2O \\
MgSO_3.6H_2O & \rightarrow MgSO_3 + 6H_2O \\
MgSO_4.7H_2O & \rightarrow MgSO_4 + 7H_2O \\
MgSO_3 & \rightarrow MgO + SO_2 \\
MgSO_4 & + 1/2 C \rightarrow MgO + SO_2 + CO_2
\end{align*}
\]

Advantages and Disadvantages

While the method obviously offers advantages of producing material that can be re-used at good efficiency, it should be noted that the cost estimates have been increasing at an exceedingly rapid rate. An additional problem of release of MgO to the atmosphere remains along with severe corrosion and erosion problems.

Status and Location

The 150 MW oil-fixed Boston Edison Mystic no. 6 plant operated between April 72 – June 74. While the process chemistry was proven, the long-term reliability still has to be demonstrated. The scrubber availability was also very low. The calcining facilities were operated by Essex Chemicals at Rumford, R.I.
The testing is to be continued at Potomac Electric and Power's Dickerson station (half of the flue-gases from 190 MW coal-fixed plant) and Philadelphia Electric's 120 MW coal-fixed Eddystone plant.

Apparently many variations of this process exist, among them are the Kawasaki Heavy Industries' method of using Mg(OH)$_2$ recovered from seawater for absorption and the Showa-Denko method (Fig. 26), where 80% SO$_2$ removal has been reported. In this process, the MgSO$_3$ formed in the absorption vessel is drawn off in a side stream to be decomposed at about 1400°F and MgO (solid) recycled. While the tests have been on a very small scale, advantages seem to include - no need for gas reheat, no extra energy for removing the free water or the water of formation associated with the MgSO$_3$. However, good dust removal may be difficult at such high temperatures. More details are not available at present.

5.3.2 Manganese Oxide

A substantial amount of research has been done on Manganese
Oxides because of their great affinity for SO₂. In the U.S., the Bureau of Mines and T.V.A. originated the work on this; however, the most prominent method developed so far is by Mitsubishi Heavy Industries in Japan (Fig. 27 and 28). The absorbent used is MnOₓ (where x = 1.5 - 1.8), which forms MnSO₄ (some MnSO₃) after reaction with SO₂. The gases go through
a cyclone and an electrostatic precipitator, where the particulate matter is removed and recycled. The loaded sorbent is treated with Ammonia and aerated giving the reactions:

\[
\begin{align*}
\text{MnSO}_4 + 2\text{NH}_4\text{OH} & \rightarrow \text{Mn(OH)}_2 + (\text{NH}_4)_2\text{SO}_4 \\
\text{Mn(OH)}_2 + \frac{1}{2}(x-1)\text{O}_2 + (y-1)\text{H}_2\text{O} & \rightarrow \text{MnO}_x\text{yH}_2\text{O}
\end{align*}
\]

where \( x = 1.5 - 1.8 \)
and \( y = 0.1 - 1.0 \)

The Amm. sulphate is separated and crystallized by the standard methods and the absorbent is returned to the initial reactor.

**Advantages and Disadvantages**

The process has the advantage of good SO\(_2\) absorption (about 90%), no cooling of gases and ease of retro fitting to existing plants. However the end-product Amm. sulphate is considered not to be particularly attractive in the North American market and any discharges of Manganese compounds into the atmosphere may not be satisfactory.

**Status and Location**

So far the process has only been tested on oil-fired power plants and it is not known what effect large amounts of fly-ash will have on it. Testing is reported to be continued and a 110 MW boiler in Japan may be tried for suitability.

5.3.3. **Copper Oxide**

5.3.3.1 In the dry state CuO absorbs SO\(_2\) at 300°- 550°C and this can be regenerated. The U.S. Bureau of Mines has produced a conceptual design to regenerate SO\(_2\) shown in Fig. 29.
Sorption is carried out in a fluidized bed and regeneration in a moving bed; the sorption temperature is about 300°C and the regeneration by reduction at about 400°C. The dust removal is by an electrostatic precipitator. Methane from natural gas is used in the regenerator to reduce sulphide formation and CuSO₄ reacts with it to give a gas containing about 38% SO₂. The absorbent CuO is produced by oxidation by carrier air at about 465°C. The reactions are:

\[
\begin{align*}
\text{CuO} + \text{SO}_2 + 0.5\text{O}_2 & \rightarrow \text{CuSO}_4 \\
\text{CuSO}_4 + 0.5\text{CH}_4 & \rightarrow \text{Cu} + \text{SO}_2 + 0.5\text{CO}_2 + \text{H}_2\text{O} \\
\text{Cu} + 0.5\text{O}_2 & \rightarrow \text{CuO}
\end{align*}
\]

Advantages and Disadvantages

The major problem has been the attrition and loss of absorbent; and loss of absorbent efficiency because of plugging of pores.
of the particle. While the details are not available, it was also noted that the absorption rates for \( \text{SO}_2 \) were "low", requiring very large reactors.

**Status**

Some other tests were done using cupric oxide absorbents absorbed on alumina or silica support; these were found to have good attrition resistance. The present status of the process is not known.

5.3.3.2 The other copper oxide process has been developed by the Shell Co. and it produces elemental sulphur. This is depicted in Fig. 30 and Fig. 30A.
The process involves flue-gases from oil-combustion and employs cupric oxide on alumina support as absorbent. The absorbent is held in a number of thin, flat layers in 2 specially designed reactors. One reactor is on absorbing duty while the other regenerates by reduction with H₂/CO; both of these operations are at 400°C. It is to be noted that the absorption step is also the copper oxidation step:

\[
\begin{align*}
&\text{Cu} + \frac{1}{2} \text{O}_2 \rightarrow \text{CuO} \\
&\text{Cu} + \text{SO}_2 + 0.5\text{O}_2 \rightarrow \text{CuSO}_4 \\
&\text{CuSO}_4 + 2\text{H}_2 \rightarrow \text{SO}_2 + \text{Cu} + 2\text{H}_2\text{O}
\end{align*}
\]

Part (2/3) of the SO₂ is reduced to form H₂S by use of hydrogen:

\[
3\text{H}_2 + \text{SO}_2 \rightarrow \text{H}_2\text{S} + 2\text{H}_2\text{O}
\]

This is mixed with the remainder (1/3) of the SO₂ stream to produce elemental sulphur in Claus reactors. The off-gases from the Claus reactors are recycled to the SO₂ absorption reactor.

The maximum SO₂ content in the flue-gas that can be treated with this process is thought to be 0.5%, with elemental sulphur recovery calculated at about 88%.

**Advantages and Disadvantages**

Problems are associated with the fact that heavy-dust loading from a coal-burning plant could foul the catalyst, and that flue-gases may not have enough residual oxygen to oxidize the copper. Where possible, the reactors are positioned between the boiler economizer and the air preheater where the flue-gas temperature is close to 750°F.

**Status and Location**

The first commercial plant has gone on stream at the
Showa Yokkaichi Sekiyu refinery in Japan, after demonstration of the process at the Shell refinery in Pernis, The Netherlands. Operational reports are awaited.

5.3.4 Zinc Oxide

Some information is available from patents and laboratory test results on the use of ZnO for absorption of SO$_2$ from flue-gases. In one method, a slurry of ZnO was used with efficiency of 70-80% which increased to 80-90% with addition of small amounts of NaOH, NH$_3$ or KOH. In another method, the SO$_2$ is absorbed in a fluidized bed of ZnO and the regeneration of SO$_2$ and ZnO is achieved by steam-heating at 275°C. Details are presently not available, however, it is known that neither process has progressed beyond small scale tests.

5.4 Other Methods

Various other methods exist for removal of SO$_2$ from flue-gases. These consist of adsorption, catalytic oxidation/reduction, and many physical separation methods.

5.4.1 Carbon Adsorption

Carbon is used in many forms for adsorption of SO$_2$; however, it has been found that the highly active adsorbent surface catalyzes the oxidation of SO$_2$ to SO$_3$ which, reacting with the moisture in the gas, forms H$_2$SO$_4$ in the pores of the adsorbent. This H$_2$SO$_4$ can either be removed as the acid itself or it can react with the carbon to produce SO$_2$;(2H$_2$SO$_4$ + C→2SO$_2$ + 2H$_2$O + CO$_2$) at a higher temperature.

Some of the more prominent processes are:
5.4.1.1 Regeneration of SO₂

5.4.1.1.1 The earlier Reinluft process which was used in many plants in Germany for some years during the 1950's and 1960's has now been refined by Chemiebau and is depicted in Fig. 31.

In this process, the adsorbent carbon flows down countercurrent to the stack gas. The undersize is screened out and used as fuel in the boiler. In the desorber, hot gas desorbs the SO₂ in an internal heat exchange arrangement by which the carbon is first heated and then cooled. A side stream of SO₂-rich gas is taken off.

Advantages and Disadvantages

Reports claim 70-85% SO₂ removal efficiency, with a simultaneous removal of fly ash, no requirement for re-heat of gases, a readily available adsorbent material and good regeneration. It suffers from attrition problems of the adsorbent.

Status and Location

While trial installations were operated at various power
plants in Germany, no plans for any facilities have been reported for North America.

In the Bergbau-Forschung method shown in Fig. 32, coke made from coal is extruded or pelletized and is used in a cross-flow mode to the flue-gases in a double-shelled vessel. The loaded sorbent flows to the desorber where hot sand regenerates the SO$_2$. The sand and carbon are then separated and re-used.

Advantages and Disadvantages

The separation of the sand and the carbon is reported to be difficult and unless very good operational control is maintained, dust plugging of lines is a possibility.

Status and Location

It is reported that larger scale tests are planned. It is
also reported that Foster-Wheeler are co-operating in developing the process to a point where the SO₂ would be reduced to elemental sulphur. A demonstration unit is being set up at Gulf Power's Florida plant.

A process jointly developed by Sumitomo Shipbuilding and Kansai Electric in Japan involves adsorption of SO₂ in a cross-flow chamber and regeneration of the SO₂ by use of an inert gas at a high temperature. While problems were encountered with adsorbent conveying and loss of adsorbent efficiency with time, the plans call for a test on 62.5 MW equivalent side stream from a 250 MW power boiler plant in Japan. Details are not available at present.

5.4.1.2 H₂SO₄ Production

5.4.1.2.1 For a power plant flue-gas containing 0.1 - 0.3% SO₂, the desulphurization is carried out by the Hitachi process as shown in Fig. 33. Many other similar designs are available now.

The gases, after de-dusting, are passed to a set of 5 adsorption towers packed with fixed beds of carbon; at any one time 3 towers are absorbing
SO₂, one is being washed to recover the H₂SO₄ and the last one is being dried prior to resumption of adsorption. Part of the hot gas is used to dry the carbon in the drying tower, after which it rejoins the rest of the gas and is demisted, before release to the stack.

Advantages and Disadvantages

Pilot-plant tests have indicated overall desulphurisation efficiencies of about 90%, good exit gas temperatures for plume buoyancy, and ease of retro-fitting.

Status and Location

The testing is being scaled up to a 150 MW power station boiler in Japan, according to some reports.

5.4.1.2.2 The German Lurgi Company have developed the so-called Sulfacid process (Fig. 34) in which adsorption and desorption are carried out in the same bed. The H₂SO₄, which is formed in the bed from the catalytic oxidation of SO₂ and further reaction with the moisture in the flue-gas, is continuously washed and removed. This weak acid is used to cool the incoming gases in a Venturi scrubber-concentrator, which can concentrate the weak acid to about 25-30%. It has been found during tests that if countercurrent scrubbing were to be used (instead of the co-current Venturi),

---

![Diagram](image-url)
concentration of about 70% could be achieved with power plant flue-gas.

Advantages and Disadvantages

The effects of large amounts of dust from smelters and coal-fired plants are considered to be significant drawbacks to this process. The efficiency of $\text{SO}_2$ removal on suitable gases is about 95%, and the process appears to be relatively simple with commercial grade acid production which could be used in fertilizer or other such industry not requiring high purity. The cleaned flue-gases will, however, need substantial reheating before being discharged to the atmosphere.

Status and Location

Several sulfacid units have been in use for some years on small industrial boilers and sulphuric acid plants, mainly in Germany. So far as is known no decisions have been made to equip any large industrial boiler on this continent with this process.

Production of Elemental Sulphur and/or $\text{SO}_2$

The Westvaco process is shown in Figure 35.
The stack gases enter a fluid bed adsorber operated at about $220^\circ$F where the $\text{SO}_2$ is adsorbed by the carbon. The loaded adsorbent reacts with the $\text{H}_2\text{S}$ (produced further downstream in the process) to form elemental sulphur and/or $\text{SO}_2$:

$$3\text{H}_2\text{S} + \text{H}_2\text{SO}_4 \rightarrow 4\text{S} + 4\text{H}_2\text{O} \quad (1)$$

$$\text{H}_2\text{SO}_4 + \text{H}_2\text{S} \rightarrow \text{SO}_2 + \text{S} + 2\text{H}_2\text{O} \quad (2)$$

The proportion of $\text{S}/\text{SO}_2$ formed depends on the temperature; at the lower temperatures, equation (2) is favoured. Of the total sulphur formed, a small part is stripped out by steam and is condensed. The remainder retained on the carbon is converted to $\text{H}_2\text{S}$ by a stream of $\text{H}_2$ or other reducing gas at about $1000^\circ$F, and the carbon is returned to the adsorber:

$$\text{S} + \text{H}_2 \rightarrow \text{H}_2\text{S}$$

**Advantages and Disadvantages**

The pilot-plant results seem to indicate that any residual dust in the gases pass through the fluid bed adsorber without a loss of efficiency and that the losses of carbon are very limited. Further advantages are the sulphur product and operation at normal flue-gas temperatures of $250^\circ$ - $450^\circ$F.

**Status and Location**

Pilot plant tests on up to 20,000 ft$^3$/hr. flue-gases from an oil-fired boiler have been carried out at Charleston, S.C. under a contract partially funded by EPA. It is projected that a demonstration plant of 15 MW may be set up in the near future.
Oxidation/Reduction Methods

A significant proportion of work done associated with the removal of SO₂ has been concerned with the concentration of the SO₂ usually by sorption/desorption as a first step. However, many researches have been aimed at conversion of the SO₂ within the main body of the gas either by oxidation or by reduction. While this step means large equipment size for the ability to handle the total volume of the gases, it avoids the expense and complexity of the separation of SO₂. The more prominent oxidation/reduction methods are described in the following sections.

Oxidation Methods

Production of H₂SO₄

The catalytic oxidation of SO₂ to SO₃ is the basis of the contact process for the commercial production of sulphuric acid. This conversion is largely dependent on the temperature and on the amount of excess oxygen present in the gas. The SO₃ produced is absorbed in H₂SO₄ solution to produce the acid.

Because of the conversion (as described above) efficiency of SO₂ being less than 100%, significant amounts of SO₂ are emitted to the atmosphere. To minimize this SO₂ emission the Double-Contact method was developed in Germany, by Farbenfabriken Bayer and is shown in Fig. 36A.
The SO₂ stream passes through the usual H₂SO₄ plant equipment - which are catalyst stages with intercooling followed by absorption of the resulting SO₃ in intermediate strength H₂SO₄. After this passage the stream is reheated by heat exchange with the absorber inlet gas and passed through a final catalyst stage and then another absorber. In practice the last catalyst bed is designed to produce about 10% SO₂ conversion. The method allows the total conversion to be up to 99.8% instead of the usual 95.5 - 98.5%.

Advantages and Disadvantages

It has been found that the optimum concentrations of SO₂ in the inlet gas stream should be 7 - 10%; and under normal operations the outlet concentrations can be brought down to 100 ppm. It should be noted that the effects of elements like chlorides, fluorides, mercury, lead, etc. can be very harmful on the catalyst. It can be regarded as a good add-on method.

Status and Location

Since the first double-contact plant was built in 1964, over 30 units have been installed, and variations of the process are being adopted for other SO₂ emission sources.

The double-contact process has been adapted by Monsanto and others for application on power plants etc. where the SO₂ concentration is below the minimum required for proper operation of that process. This new process is called the Monsanto Cat-Ox process. There are two variations of this process - integrated and re-heat. In the integrated system the flue-gases are at 850°F and can be put to the converter after removal of particulate; in the re-heat system the gases are at a lower temperature
and are cleaned and then re-heated to 850°F before entering the converter. Fig. 36B shows the process as installed at Illinois Power Company's Wood River plant. (Re-heat mode).

Fig. 36 B

After particulate removal by use of electrostatic precipitators, the flue-gas is heated from 300°F to 850°F before it enters the converter chamber containing V₂O₅ catalyst. The emerging gases preheat the incoming flue-gases and are further cooled in a packed-bed absorbing tower which operates in conjunction with an external heat exchanger. During cooling the H₂O and the SO₃ combine to produce H₂SO₄ which is condensed. The hot acid is cooled and is split into the recycle stream to the absorber and the storage. The Brinks mist collector system eliminates the H₂SO₄ mist from the gases released to the stack at 250°F.

Advantages and Disadvantages

While the advantages include no solid disposal problem, small need for operating labour, raw materials or regeneration of any kind, the equipment is large and expensive, and the product is commercial grade acid with some fly-ash and catalyst contamination.

Status and Location

The 100 MW installation funded by E.P.A. and Illinois Power was started up initially in Sept. 1972, however, mechanical and
operating problems have plagued the facilities. The modifications and repairs are expected to be completed soon, after which assessments could be made. The main concerns are corrosion, plugging, and contamination of catalyst. A removal efficiency of 80-90% is expected in this kind of design.

5.4.2.1.1.3 A process for treating tail-gases from Claus plants shown in Fig. 37, is known as the Topsoe-SNPA process.

The gases are heated to about 1000°F to convert all the S, H₂S, CO, etc. to the oxidized forms, cooled in a waste heat boiler and passed to a 2-stage converter with interstage cooling. The gases, after cooling, go to a 2-stage concentrator-absorber where the acid-contact is provided, before demisting and return to atmosphere.

Advantages and Disadvantages

The SO₂ concentration in the flue-gases is about 1.2%, thus modifications might be required for treatment of power plant flue-gases. Large amounts of fuel necessary for heating the gases can also be cut back by use of a catalytic incineration method (also developed by
Topsoe) which allows lower temperature operation.

**Status and Location**

All the details of the process are not available, except that one unit has been in operation on a Claus plant in Lacq, France for some time.

### 5.4.2.1.2 Other End-Products

#### 5.4.2.1.2.1 The Kiyoura T.I.T. process (Fig. 38) is used to produce Ammonium sulphate.

It involves catalytic oxidation of \( \text{SO}_2 \) at high temperatures, then adding ammonia to produce \( (\text{NH}_4)_2\text{SO}_4 \), which is collected and removed in a dust collection equipment.

\[
2\text{NH}_3 + \text{SO}_3 + \text{H}_2\text{O} \rightarrow (\text{NH}_4)_2\text{SO}_4
\]

**Advantages and Disadvantages**

This process was tested in a small pilot-plant at Omuta, Japan using flue-gas from an oil-burning boiler plant. Plugging of the
cooler was a problem, but was resolved. The disadvantages seem to be high capital investment and an end-product which is not too desirable. The overall efficiency was about 90% in the test.

**Status and Location**

Future plans are not known at this time.

5.4.2.1.2.2 Other methods include absorption of SO$_3$ (after oxidation) by various agents viz. oil shale, red mud, phosphate rock, zinc oxide, sodium sulphate, etc. None of these are thought to be anywhere near a commercial plant test because of various problems. Another method uses the NO$_2$ in the flue-gas to oxidize the SO$_2$; producing, in the end, both H$_2$SO$_4$ and HNO$_3$, thus both NO$_x$ and SO$_2$ are eliminated. This method could be useful for smelter and refining flue-gases, however, it has been abandoned due to high capital costs.

5.4.2.2 Reduction Methods

Most of the work done on reduction of SO$_2$ to elemental sulphur uses one of four reducing agents - H$_2$S, CO, C, or CH$_4$. Most of the methods were developed for use on smelter gases only and substantial modifications might be necessary to treat large volumes of power plant flue-gases. A number of these processes described below were discontinued because of the high costs. Present and future potential is largely unknown.

5.4.2.2.1 The catalytic reduction of SO$_2$ by H$_2$S is the basis of the Claus process. This has been modified for use at lower temperatures for the removal of SO$_2$ from waste gases. The Ontario Research Foundation tested this process on power plant flue-gases and waste gases from copper-nickel smelter and concluded that, while it was unsuitable for use with the power plant
flue gases, smelter gases with 1% $\text{SO}_2$ concentration could be usefully treated this way. The method (Fig. 39) involves the reaction at 100-150°C over a catalyst which is treated with hot reducing gases at 300-500°C to condense the sulphur. About 2/3 of the sulphur is recycled to form $\text{H}_2\text{S}$ and 1/3 is a saleable product. The reaction is:

$$2\text{H}_2\text{S} + \text{SO}_2 \rightarrow 3\text{S} + 2\text{H}_2\text{O}$$

Similar tests have been done by Peter Spence (U.K.), Princeton Research (U.S.) and others. While not many details are available on the actual tests, catalyst poisoning remains the main problem when treating gases with small concentrations of $\text{SO}_2$. 
5.4.2.2 The Chevron Co. reacts CO with SO₂ over copper supported on alumina at 1000°F, with 90% removal:

\[ \text{2CO} + \text{SO}_2 \rightarrow \text{2CO}_2 + \text{S} \]

The side reaction can produce COS, a highly toxic substance. The capital cost of the equipment is expected to be high. No further details are available, except that critical control of the combustion system would have to be maintained for the correct concentrations of CO₂ in the flue-gases.

5.4.2.3 Cominco at Trail, B.C. had developed a process in which SO₂ and oxygen were blown through a bed of incandescent coke which reduced the SO₂ to elemental sulphur. The process was discontinued in 1943, however a smelter in Spain is still apparently using it. Other processes that were under development or being used for some time and then discontinued due to economic considerations were the Boliden process (where the waste gases, after being blown through a bed of coke were further reduced by reducing gases) and the ICI process (where the bed of coke was maintained at 800-900°C and was followed by another catalyst tower). No reports of any revival of interest in any of these processes are available.

5.4.2.4 The Methane Reduction processes include the Asarco, Texas Gulf Sulphur and Allied Chemical methods.

5.4.2.4.1 In the Asarco process sufficient natural gas is added to the smelter gases (Fig. 39A) to convert to sulphur as follows: (while side reactions produce
These reactions take place in a steel chamber at 1250°C. In the next stage of the process the SO₂ reacts with COS over alumina catalyst at 425-450°C:

$$\text{SO}_2 + 2\text{COS} \rightarrow 2\text{CO}_2 + 3\text{S}$$

The sulphur is removed at this stage and the H₂S is removed in the next stage.

**Advantages and Disadvantages**

According to available information, the process is very sensitive to concentrations of SO₂ and O₂ in the waste gases. Substantial amounts of natural gas are required and some products formed in the side-reactions (such as COS, H₂S) can be difficult to handle.
Status and Location

This process was also discontinued in the 1940's, however, a new pilot-plant is trying to develop variations of this process further at El Paso, Texas, on copper smelting operations.

5.4.2.4.2

The Texas Gulf Sulphur Process was tested in pilot-plant stage at INCO'S iron-ore reduction plant at Copper Cliff, Ontario. The process involves the recovery of sulphur from waste gases by direct reduction of $\text{SO}_2$ with methane at 1500°F, in presence of Alumina Catalyst. This is followed by 2 reaction stages for conversion of $\text{H}_2\text{S}$ and COS to sulphur.

According to reports the process will produce good quality sulphur from waste gases containing 8% or more $\text{SO}_2$ and low concentrations of oxygen. While details of the pilot-plant tests are not available, it is believed that inspite of good results, commercial development of the process was not proceeded with, because of high costs.

5.4.2.4.3

The Allied Chemical process at Falconbridge, Ontario reduces the $\text{SO}_2$ in the gases from the conversion of pyrrhotite to sponge iron. The plant (Fig. 39B) is designed to remove 90% $\text{SO}_2$ from the roaster gases containing
12-13% $\text{SO}_2$. The gases are put through cyclone separators and then passed through heat-exchangers and a 2-stage cooling and condensing tower where contact is provided with dil. $\text{H}_2\text{SO}_4$ solution. After removal of acid mist the gas is heated above the acid dew point and mixed with natural gas, before being pushed through a heat exchanger. The main reactions in the reduction reactor (catalytic), which follows, are:

$$\text{CH}_4 + 2\text{SO}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 2\text{S}$$

$$4\text{CH}_4 + 6\text{SO}_2 \rightarrow 4\text{CO}_2 + 4\text{H}_2\text{O} + 4\text{H}_2\text{S} + 2\text{S}$$

The sulphur produced is condensed out before the gas enters the 2-stage Claus reactor where the following exothermic reaction takes place:

$$2\text{H}_2\text{S} + \text{SO}_2 \rightarrow 3\text{S} + 2\text{H}_2\text{O}$$

All the sulphur is collected by condensation and any residual $\text{H}_2\text{S}$ is incinerated before being exhausted to atmosphere.

**Advantages and Disadvantages**

As in other reductant systems, concentrations of $\text{SO}_2$ and $\text{O}_2$ play a critical role in the reactions, however the process is reported to have the capability of handling higher levels of oxygen with added capital expense.

**Status and Location**

The plant at Falconbridge, Ont. is reported to have operated since 1970 without any great problems. Some changes regarding the materials of construction and mechanical equipment were made. The $\text{SO}_2$ removal efficiency has been reported to be 90%. A similar $\text{SO}_2$ reduction plant may be installed at Northern Indiana Public Service's Gary, Inc., plant on the tail end of the Wellman-Lord $\text{SO}_2$ recovery process on a 115 MW coal-fixed
5.4.3 Organic Sorbents

Many organic solids and liquids can absorb large amounts of $\text{SO}_2$. The list could include various amines, amides, ketones, alcohols, ion exchange resins, nitrogenous polymers, etc. While a few like dimethylaniline and xylidene have been used on smelter gases (4-6% $\text{SO}_2$), none has been considered to be useful for large volumes of power plant flue-gases with very small concentrations of $\text{SO}_2$, in which cases even small losses of the sorbent with the purified gases pose a significant economic and pollution problem. Various side reactions and decomposition products are further drawbacks. A couple of more important processes are described as follows.

5.4.3.1 In the Asarco process (Fig. 40) the smelter gases (5% $\text{SO}_2$) are cleaned...
of particulate and contacted counter-currently with Dimethylaniline (DMA), and then contacted with dilute H₂SO₄ to remove last traces of the SO₂ and the DMA. Steam stripping is used to regenerate the SO₂ and the DMA. Efficiency of 99% SO₂ removal is reported. Two small smelters in the U.S. are said to be still using this process.

5.4.3.2 In the Lurgi Sulphidine process, a suspension of xylidene (C₆H₃(CH₃)₂NH₂) or toluidene (C₆H₄CH₃NH₂) in water is used as absorbent for SO₂:

\[
\begin{align*}
C₆H₃(CH₃)₂NH₂ + SO₂ + H₂O & \rightarrow C₆H₃(CH₃)₂NH₃HSO₃ \\
2C₆H₃(CH₃)₂NH₂ + SO₂ + H₂O & \rightarrow (C₆H₃(CH₃)₂NH₃)₂SO₂
\end{align*}
\]

Thermal stripping is used for regeneration. Acute need for removal of all sorbent from the purified gases has meant the discontinuation of development work for this process, which had been used industrially in Germany for some time.

5.4.4 Some Other Notable Processes

5.4.4.1 One method developed by the Union Carbide Corp. called "Purasiv S" is being tested on the tail gases (about 3500 ppm SO₂) at Coulton Chemical's Spent H₂SO₄ plant, at Oregon, Ohio. The process is shown in Fig. 41. The SO₂ is absorbed in a custom-made molecular sieve adsorbent.
On regeneration of the sieve by heat, the SO$_2$ is recycled for conversion to H$_2$SO$_4$. The effluent gases have average SO$_2$ concentration of 50 ppm. All the details are not at hand.

Another method has been developed by Chiyoda Chemical Co. in Japan (Fig. 42). The SO$_2$ is absorbed and the H$_2$SO$_3$ formed is oxidized over a catalyst as follows:

$$\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3$$
$$\text{H}_2\text{SO}_3 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{SO}_4$$

Part of the sulphuric acid is neutralized with calcium salts to continuously crystallize and separate as gypsum (which can be used as construction material in Japan because of lack of naturally occurring gypsum). The remainder of the sulphuric acid and the mother liquor from the centrifuge separating the gypsum are recycled to the absorber.

$$\text{H}_2\text{SO}_4 + \text{CaCO}_3 + \text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{CO}_2$$
Advantages and Disadvantages

While the design calls for removal of particulate matter in the pre-scrubber and absorber, it is not known whether large amounts of fly-ash would not contaminate and upset the reactions. The crude sulphuric acid may also be a problem in re-use. While it is reported that the gypsum produced can be used in Japan, it may not be so in North America.

Status and Location

It is reported that 15 installations of this process would be completed on boilers, Claus Plants etc. by the end of 75. Some of these have been operational for about 2 years. One of the first coal-fixed boiler to use this method is being readied for start-up in Spring of 1975. This is a 20 MW demonstration plant at Gulf Power's Scholz, Florida plant.

5.4.4.3 Two methods involving acidic solutions of sodium salts have been developed. These are the sodium citrate process (U.S. Bureau of Mines, Salt Lake City) and sodium phosphate or Powerclaus process (Stauffer Chemical Co. Conn.)

5.4.4.3.1 The Citrate process takes advantage of the fact that the absorption of the SO₂ in aqueous solution is pH-dependent, increasing at higher pH. Incorporating the buffering agency of Sodium Citrate and Citric acid to inhibit fall of pH in the solution, substantially higher SO₂ loadings can be obtained. The thiosulphate ion serves a major role in the complex formations by inhibiting oxidation to sulphate so that the regeneration of SO₂ by H₂S can produce reusable absorbent solution.

Fig. 43 depicts the test-unit of the process as installed at Terre Haute,
Indiana, designed by the consortium of Pfizer, Peabody and Arthur McKee. It used a 2000 cfm side-stream from a coal-fired boiler. The gases are cooled and then put through a venturi scrubber to remove the flyash. The absorption of $SO_2$ is carried out in a 10% solution of sodium citrate and citric acid.

The reactions are:

$$SO_2 + H_2O \leftrightharpoons HSO_3^- + H^+$$
$$H^+ + HCit^- \leftrightharpoons H_2Cit^-$$

Various side reactions produce thiosulphates and polythionates. The regeneration of the solution is done by the addition of $H_2S$ gas (generated later in the process) into a stirred reactor. A whole series of reactions are believed to take place, some of the major ones being:

$$4HSO_3^- + 2H_2S \leftrightharpoons 3S_2O_3^{2-} + 2H^+ + 3H_2O$$
$$S_2O_3^{2-} + 2H_2S + 2H^+ \rightarrow 4S + 3H_2O$$
$$8HSO_3^- + H_2S + 2H^+ \leftrightharpoons 3S_3O_6^{2-} + 6H_2O$$
The precipitated sulphur is separated by melting and the solution (after removal of quantities of the sodium sulphate decahydrate) can be reused. Part of the product sulphur is converted to H₂S.

**Advantages and Disadvantages**

The process seems quite simple to operate and for retrofitting to existing units. Advantages seem to be good removal efficiencies (over 90%), high-purity end-product and lack of any significant scaling or corrosion (in the test-unit). Control of H₂S may be problematic in a large-scale unit.

**Status and Location**

Since the tests were completed in Terre Haute, the consortium mentioned above has split up, and the process may be marketed by the individual companies separately. The process may be scaled up to a large demonstration unit. Control of both boiler and smelter gases is envisaged by this process. Magna Copper Company, Arizona and Bunker Hill Co., Idaho are other locations for development of this process.

5.4.4.3.2 The Stauffer Powerclaus process is depicted in Fig. 44. After removal of
the fly-ash, the gases are cooled and saturated and scrubbed with a (10% sat.) Sodium Phosphate solution. The $\text{SO}_2$-rich solution is led to the Sulphur recovery section where the reaction with $\text{H}_2\text{S}$ (generated later in the process) yields elemental sulphur and water. The product sulphur is either sold or used to produce the $\text{H}_2\text{S}$. A small amount of sodium sulphate produced is also sold.

Advantages and Disadvantages

This process is very similar to the Citrate process and has the same advantages and disadvantages. The pilot-plant seemed simple to operate without any major scaling or corrosion problems, it had good (over 90%) $\text{SO}_2$ removal efficiencies and produced a good quality end-product. Once again $\text{H}_2\text{S}$ may present some problems in a large-scale unit. Both Citrate and Stauffer processes are reported to have an advantage in economic terms over most other processes being developed at present.

Status and Location

The process has been tried out at NorthEast Utilities' Norwalk Harbour plant on a 115 cfm side stream. As the plant burns oil for power generation, a liquid slurry containing some fly-ash was added to the absorber to simulate coal burning conditions. Further testing was at Stauffer's plant at Dobb's Ferry, New York. The $\text{SO}_2$ removal efficiencies ranged from 90-95%. A test site for a 25-100 MW plant is being sought at present for further development.

Processes such as gaseous diffusion and membrane separation, centrifuging, condensation techniques, mass spectrometer methods have been tried but most of them are very expensive and show many constraints.
6. CONCLUSIONS

Of the processes discussed in this report, the following may be included in a list of the most developed methods for flue-gas desulphurization:

- Wet lime/limestone scrubbing
- Magnesium oxide scrubbing (e.g. - Chemico)
- Double alkali system (e.g. - General Motors)
- Catalytic oxidation (e.g. - Monsanto)
- Wet sodium-based scrubbing/regeneration (e.g. - Wellman-Lord)

A number of other processes are soon expected to reach the stage where a commercial plant size installation may be tried. Some of these processes are:

- Copper oxide & carbon adsorption (e.g. - Shell, Westvaco)
- Acidic solution absorption (e.g. - Citrate, Stauffer)
- Oxidation and acid absorption (e.g. - Chiyoda)
- Ammonia scrubbing (e.g. - I.F.P.)

Some of the processes have had many operational problems; e.g. - some have high corrosion/erosion rates and maintenance problems with the equipment tested so far; some produce unacceptably high amounts of sludges which are difficult to harden and dispose of in spite of continuous research; while some processes may work well at one location because of local advantages and peculiarities of the chemical material in the flue-gas; they may not be particularly suitable in another location. In some cases, tremendous increases have been noted from the projected estimates and while the process may be reliable, it can turn out to be uneconomic.

In addition to the above-noted processes, most of which have
so far mainly been used only for the treatment of power-plant flue gases; reduction processes (e.g. Allied Chemical) have been used for desulphurization of smelter gases for some time.

In order that a better insight be gained into aspects of some of these processes operated under local conditions, it is being recommended that further detailed studies be carried out. Of the developed processes listed, the Wellman-Lord (Davy Powergas) method is not being included in the initial detailed study because of the present requirement of substantial bleed stream (non-regenerable sulphates). The Shell, Westvaco and Chiyoda processes are also expected to be studied in detail once sufficient information is available. The Citrate, Stauffer, Ammonia, and smelter off-gas processes are being included in the list of an immediate study because of the apparent potential and local interest.

Rapidly changing economic situations have meant that cost estimates for the processes have varied considerably; however, most projections have capital costs ranging between $50 - $100/KW and the operating costs between 1.5 - 8 mills/KW-hr.
7. **MAIN REFERENCES**


### Appendix

#### Organizations Active in Research on Sulfur Oxide Removal from Stack Gases

<table>
<thead>
<tr>
<th>Country</th>
<th>Organizations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Austria</td>
<td>Österreichische Stickstoffwerke AG</td>
</tr>
<tr>
<td>Belgium</td>
<td>C. Neveu-Francesch et Groux, Chemiebau</td>
</tr>
<tr>
<td>Canada</td>
<td>Cominco Ltd., McGill University, Ontario Hydro</td>
</tr>
<tr>
<td>Czechoslovakia</td>
<td>Fuel Research Institute of Chemical Equipment, Research Institute of Inorganic Chemistry</td>
</tr>
<tr>
<td>France</td>
<td>Electricité de France, Etablissements Fullmann, Institut Français de Pertule</td>
</tr>
<tr>
<td>Hungary</td>
<td>State Office for Technical Development</td>
</tr>
<tr>
<td>Italy</td>
<td>Associazione Termotecnica Italiana</td>
</tr>
<tr>
<td>Japan</td>
<td>Central Research Institute of Electric Power Industry, Hitachi, Ltd., Japan Engineering Consulting Company, Kawasaki Heavy Industries, Ltd., Mitsubishi Heavy Industries, Ltd., Resources Research Institute, Sumitomo Chemical Company, Ltd., Tokyo Institute of Technology, Chiyoda Chemical Co., Ltd.</td>
</tr>
<tr>
<td>Netherlands</td>
<td>Shell Oil Company</td>
</tr>
<tr>
<td>Poland</td>
<td>Copernicus University, Federzshinskii Technological Institute, Institute of Chemical Technology, Institute of Scientific Research, Politechniki Wroclawskiej</td>
</tr>
<tr>
<td>Romania</td>
<td>Inorganic Chemistry and Fertilizer Engineering Institute (PRAN)</td>
</tr>
<tr>
<td>Sweden</td>
<td>A.B. Båsica</td>
</tr>
<tr>
<td>USSR</td>
<td>All-Union Association on Gas Cleaning and Dust Collection, Levon Chemical Research Institute of the Ministry of Chemical Industry of the USSR, Leninov Technologicheskii Institute, State Scientific Research Institute of Gas Purification for Industry and Sanitation (NIIOGAZ), Ya. V. Samoilow Science Institute of Fertilizer and Insectafungicides (NIUF)</td>
</tr>
<tr>
<td>United Kingdom</td>
<td>BOC Industrial Laboratories, Central Electricity Generating Board, Esso Research Centre, Imperial Chemical Industries Limited, National Coal Board, Peter Spence and Sons Limited</td>
</tr>
</tbody>
</table>
8.2 ALPHABETICAL LISTING OF THE

MAJOR DESULPHURIZATION PROCESSES
<table>
<thead>
<tr>
<th>PROCESS</th>
<th>PROCESS TYPE</th>
<th>BY-PRODUCTS</th>
<th>GENERAL COMMENTS</th>
<th>STATUS &amp; LOCATION</th>
<th>REFERENCE IN REPORT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allied Chemical</td>
<td>Reduction with Nat.gas</td>
<td>Sulphur</td>
<td>Inlet gases 12-13% SO₂, about 90% S recovery.</td>
<td>Prototype Falconbridge, Ont., plant in operation since 1970.</td>
<td>5.4.2.4.3</td>
</tr>
<tr>
<td>Ammonia</td>
<td>Dry/Wet Reaction, Regeneration.</td>
<td>S, SO₂, H₂SO₄, Fertilizer</td>
<td>Many variations of reaction/regeneration process.</td>
<td>T.V.A./E.P.A. testing parameters at Alabama.</td>
<td>5.2.1</td>
</tr>
<tr>
<td>Asarco</td>
<td>Absorption with DMA</td>
<td>SO₂</td>
<td>Good removal efficiency. DMA emission problem.</td>
<td>In use at 2 small U.S. smelters only.</td>
<td>5.4.3.1</td>
</tr>
<tr>
<td>Asarco</td>
<td>Reduction with Nat.gas</td>
<td>Sulphur</td>
<td>Reactions involve COS (highly toxic).</td>
<td>New Pilot Plant at El Paso, Texas being set up.</td>
<td>5.4.2.4.1</td>
</tr>
<tr>
<td>Atomics International</td>
<td>Na, K, Li Carbonates Absorption.</td>
<td>H₂S</td>
<td>Good efficiencies. High heat requirements.</td>
<td>Consolidated Edison, N.Y. to develop at Arthur Kill Plant.</td>
<td>5.2.4</td>
</tr>
<tr>
<td>Bergbau-Forschung</td>
<td>Carbon adsorption</td>
<td>SO₂</td>
<td>Separation of desorbing sand &amp; carbon difficult.</td>
<td>Foster-Wheeler collaboration at Gulf Power, Fla.</td>
<td>5.4.1.1.2</td>
</tr>
<tr>
<td>Chemico - Basic</td>
<td>MgO scrubbing &amp; regeneration.</td>
<td>SO₂</td>
<td>Corrosion, erosion, MgO emissions may be problematic</td>
<td>Full-scale tests at Boston Edison, Pepco, Philadelphia Electric.</td>
<td>5.3.1.1.3</td>
</tr>
<tr>
<td>Chevron</td>
<td>Reduction with CO</td>
<td>S</td>
<td>Side reaction produces high toxic COS. Expensive.</td>
<td>Not known.</td>
<td>5.4.2.2.2</td>
</tr>
<tr>
<td>Chiyoda</td>
<td>Oxidation/Absorption</td>
<td>Gypsum</td>
<td>May be problems with large amounts of flyash.</td>
<td>First installation on coal-fired plant at Gulf Power, Florida.</td>
<td>5.4.4.2</td>
</tr>
<tr>
<td>Citrate</td>
<td>Sodium Citrate/Citric Acid</td>
<td>S</td>
<td>Effective process, good by-product. Needs large-scale testing.</td>
<td>Pilot plant test at Terre Haute, Indiana.</td>
<td>5.4.4.3.1</td>
</tr>
<tr>
<td>Cominco</td>
<td>Amm. Sulphite/bisulphite</td>
<td>SO₂ &amp; (NH₄)₂ SO₄</td>
<td>By-product Amm. Sulphate - not too desirable.</td>
<td>Only tried on sulphuric acid plants so far.</td>
<td>5.2.1.1.1</td>
</tr>
<tr>
<td>PROCESS</td>
<td>PROCESS TYPE</td>
<td>BY-PRODUCTS</td>
<td>GENERAL COMMENTS</td>
<td>STATUS &amp; LOCATION</td>
<td>REFERENCE IN REPORT</td>
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<tr>
<td>Cominco</td>
<td>Reduction with coke.</td>
<td>S</td>
<td>Operational problems. Details not known.</td>
<td>Discontinued in 1940's. No new information.</td>
<td>5.4.2.2.3</td>
</tr>
<tr>
<td>Consolidated Cpal Company</td>
<td>KCHO2 absorption/CO regeneration.</td>
<td>H2S/CO2</td>
<td>Good efficiencies in the tests.</td>
<td>Further work planned at Philadelphia Electric, Phoenixville.</td>
<td>5.2.3.2.1</td>
</tr>
<tr>
<td>Double Alkali</td>
<td>Na2SO3/NaHSO3/Ca(OH)2</td>
<td>Calcium salts</td>
<td>Separation of fly-ash and disposal of waste problems.</td>
<td>Parma, Ohio pilot plant; further testing by E.P.A.</td>
<td>5.2.2.3.2</td>
</tr>
<tr>
<td>Garrett Research</td>
<td>Pat. Thiocyanate/Carbonate</td>
<td>H2S/K2S</td>
<td>Complex process. Control of sulphides problem.</td>
<td>Only lab tests known so far.</td>
<td>5.2.3.2.2</td>
</tr>
<tr>
<td>Grillo</td>
<td>MgO(+MnO2) scrubbing.</td>
<td>SO2</td>
<td>Flyash may affect the process efficiency.</td>
<td>Tried on oil-burning and H2SO4 plants only.</td>
<td>5.3.1.1.2</td>
</tr>
<tr>
<td>Hitachi</td>
<td>Carbon Adsorption towers.</td>
<td>H2SO4</td>
<td>Good efficiency, exit buoyancy, easy to retrofit.</td>
<td>150 MW power plant in Japan reported testing.</td>
<td>5.4.1.2.1</td>
</tr>
<tr>
<td>I.F.P.</td>
<td>Aqueous NH3 scrubbing.</td>
<td>Sulphur</td>
<td>Complex process, good by-product.</td>
<td>Pilot-plant may be tried soon.</td>
<td>5.2.1.2.4</td>
</tr>
<tr>
<td>I.P.R.A.N.</td>
<td>NH3 injection and H3PO4 regeneration.</td>
<td>SO2 + NH4(H2PO4)</td>
<td>End-product not considered attractive in North America.</td>
<td>Process tried on H2SO4 tail gases only in Romania.</td>
<td>5.2.1.1.4</td>
</tr>
<tr>
<td>Johnstone</td>
<td>Na2SO3/ZnO/Calcination</td>
<td>SO2</td>
<td>Complicated process. Losses due to disproportionation.</td>
<td>No new information since Aerojet-General's report to E.P.A.</td>
<td>5.2.2.2.3</td>
</tr>
<tr>
<td>Kiyoura - T.I.T.</td>
<td>Oxidation and NH3 absorption</td>
<td>Ammonia Sulphate</td>
<td>Good efficiency, High capital cost. Unattractive by-product.</td>
<td>Pilot plant work at a small Japanese oil-fired plant.</td>
<td>5.4.2.1.2.1</td>
</tr>
<tr>
<td>PROCESS</td>
<td>PROCESS TYPE</td>
<td>BY-PRODUCTS</td>
<td>GENERAL COMMENTS</td>
<td>STATUS &amp; LOCATION</td>
<td>REFERENCE IN REPORT</td>
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<tr>
<td>Koyo Iron Works</td>
<td>Spray of NaOH or Na₂CO₃</td>
<td>Na₂SO₃</td>
<td>Simple process. Carry-over of NaOH may cause problems.</td>
<td>Not yet tried on coal-burning plant. Being used in Japan.</td>
<td>5.2.2.3.1</td>
</tr>
<tr>
<td>Lime/Limestone (dry)</td>
<td>Dry injection &amp; collection.</td>
<td>Mixture of SO₃, SO₄, etc.</td>
<td>Scaling, low efficiency and product disposal major problems.</td>
<td>Testing at T.V.A., Dairyland Co-op., Wisconsin, etc.</td>
<td>5.1.1</td>
</tr>
<tr>
<td>Lime/Limestone (wet)</td>
<td>Dry/wet injection, wet collection.</td>
<td>Mixture of SO₃, SO₄, etc.</td>
<td>Scaling, corrosion, final sludge disposal problems.</td>
<td>Operational in Kentucky, Illinois, Nevada, Kansas, etc.</td>
<td>5.1.2</td>
</tr>
<tr>
<td>Lurgi Sulfacid</td>
<td>Carbon adsorption</td>
<td>H₂SO₄</td>
<td>1 bed adsorption/desorption. Acid contamination possible.</td>
<td>Small H₂SO₄ plants operational in Germany.</td>
<td>5.4.1.2.2</td>
</tr>
<tr>
<td>Lurgi Sulphidine</td>
<td>Xylidene/Toluidene</td>
<td>SO₂</td>
<td>Prevention of absorbant emissions is major concern.</td>
<td>Further development work not reported.</td>
<td>5.4.3.2</td>
</tr>
<tr>
<td>Mitsubishi</td>
<td>MnO₂ &amp; NH₄OH</td>
<td>Amm. Sulphate</td>
<td>Effective process. MnO₂ emission may not be satisfactory.</td>
<td>Testing reported in Japan only.</td>
<td>5.3.2</td>
</tr>
<tr>
<td>Monsanto Cat-Ore</td>
<td>Oxidation to SO₃ &amp; absorption.</td>
<td>H₂SO₄</td>
<td>Theoretically advantageous; low-grade end-product.</td>
<td>Wood River (IU.) plant has significant start-up problems.</td>
<td>5.4.2.1.1.2</td>
</tr>
<tr>
<td>Niiogaz</td>
<td>Scrubbing with NH₃ solution.</td>
<td>SO₂ and (NH₄)₂SO₄</td>
<td>High heat requirements for stripping of SO₂.</td>
<td>Developments have been restricted to Russia.</td>
<td>5.2.1.1.2</td>
</tr>
<tr>
<td>Niiogaz</td>
<td>MgO scrubbing</td>
<td>SO₂</td>
<td>Good efficiencies reported on sintering plants.</td>
<td>Not yet used on full-scale power plant gases.</td>
<td>5.3.1.1.1</td>
</tr>
<tr>
<td>O.R.F.</td>
<td>Low temperature reduction with H₂S.</td>
<td>S</td>
<td>May be useful for smelter gases with 1% SO₂.</td>
<td>No new info. since test results released.</td>
<td>5.4.2.2.1</td>
</tr>
<tr>
<td>PROCESS</td>
<td>PROCESS TYPE</td>
<td>BY-PRODUCTS</td>
<td>GENERAL COMMENTS</td>
<td>STATUS &amp; LOCATION</td>
<td>REFERENCE IN REPORT</td>
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<tr>
<td>R.I.C.</td>
<td>NH₃ scrubbing &amp; HNO₃ regeneration.</td>
<td>SO₂ and (NH₄)NO₃</td>
<td>Product contamination with NOₓ &amp; sulphates.</td>
<td>Tried only on sulphuric acid tail gases in Czech.</td>
<td>5.2.1.1.3</td>
</tr>
<tr>
<td>Reinlust-Chebiebau</td>
<td>Carbon adsorption</td>
<td>SO₂</td>
<td>Moderate efficiency, no re-heat, simultaneous removal of fly-ash.</td>
<td>Reports of trial installations in Germany.</td>
<td>5.4.1.1.1</td>
</tr>
<tr>
<td>Shell</td>
<td>CuO on Alumina absorption.</td>
<td>S</td>
<td>Effective; low O₂ or high flyash concentration could upset process</td>
<td>Japanese Refinery testing full-scale after Dutch demonstration.</td>
<td>5.3.3.2</td>
</tr>
<tr>
<td>Showa-Denko</td>
<td>NH₃ &amp; Steam Injection</td>
<td>(NH₄)₂ SO₄</td>
<td>Large amounts of flyash may cause problems.</td>
<td>Testing restricted to Japan. Extent unknown.</td>
<td>5.2.1.2.3</td>
</tr>
<tr>
<td>Simon-Carves/Fulham</td>
<td>NH₃ Scrubbing</td>
<td>S &amp; (NH₄)₂ SO₄</td>
<td>Good pilot plant results.</td>
<td>Presently unknown.</td>
<td>5.2.1.2.1</td>
</tr>
<tr>
<td>Sodium Aluminate</td>
<td>Solid absorbent and regeneration.</td>
<td>H₂S</td>
<td>Effective process, high capital costs.</td>
<td>No large scale tests reported.</td>
<td>5.2.2.1</td>
</tr>
<tr>
<td>Stauffer Powerclaus</td>
<td>Sodium Phosphate</td>
<td>S</td>
<td>Effective process, good by-product, needs large scale testing.</td>
<td>Testing at Norwalk and Dobbs Ferry, New York.</td>
<td>5.4.4.3.2</td>
</tr>
<tr>
<td>Stone &amp; Webster/Ionics</td>
<td>NaOH scrubbing, electrolysis.</td>
<td>SO₂</td>
<td>Power costs may be high. Sulphate elimination problem.</td>
<td>E.P.A./Wisconsin Elec. developing process.</td>
<td>5.2.2.2.2</td>
</tr>
<tr>
<td>Texas Gulf Sulphur</td>
<td>Reduction with Methane</td>
<td>S</td>
<td>Good pilot plant results. High costs.</td>
<td>Pilot plant tests at Copper Cliff, Ontario.</td>
<td>5.4.2.2.4.2</td>
</tr>
<tr>
<td>Topsoe - S.N.P.A.</td>
<td>SO₂ oxidation/absorption</td>
<td>H₂SO₄</td>
<td>Reheat may be required. Reheat concentration has to be quite low.</td>
<td>Tried on Claus Plant in France.</td>
<td>5.4.2.1.1.3</td>
</tr>
<tr>
<td>U.S. Bureau of Mines</td>
<td>Fluidized bed CuO Absor</td>
<td>SO₂ Regeneration</td>
<td>Attrition, loss of absorbent &amp; low efficiencies.</td>
<td>Being developed with various catalyst supports.</td>
<td>5.3.3.1</td>
</tr>
<tr>
<td>PROCESS</td>
<td>PROCESS TYPE</td>
<td>BY-PRODUCTS</td>
<td>GENERAL COMMENTS</td>
<td>STATUS &amp; LOCATION</td>
<td>REFERENCE IN REPORT</td>
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</tr>
<tr>
<td>U.S. Bureau of Mines</td>
<td>Sodium Citrate/Citric acid</td>
<td>S</td>
<td>Effective process, good by-product. Needs large scale testing.</td>
<td>Tests at Bunker Hill, Idaho; Terre Haute, Indiana.</td>
<td>5.4.4..3.1</td>
</tr>
<tr>
<td>Ugine-Kuhlman</td>
<td>NH₃ injection &amp; reaction with Lime</td>
<td>Ammonia Regeneration.</td>
<td>Disposal of sludge problem. Good SO₂ removal.</td>
<td>Not known at present.</td>
<td>5.2.1.3</td>
</tr>
<tr>
<td>Union Carbide Purasiv</td>
<td>Molecular Sieve adsorption</td>
<td>SO₂</td>
<td>Seems suitable for only low SO₂ concentration.</td>
<td>Being tested at Oregon, Ohio.</td>
<td>5.4.4.1</td>
</tr>
<tr>
<td>Wellman-Lord</td>
<td>Sodium Sulphite/bisulphite</td>
<td>SO₂</td>
<td>Main problem purging of sulphates, effective process.</td>
<td>Chiba (Japan), Olin (Paulsboro), N.I.P.S. (Gary) etc.</td>
<td>5.2.2.2.1</td>
</tr>
<tr>
<td>Wellman-Lord</td>
<td>K₂SO₃ absorption</td>
<td>SO₂</td>
<td>High energy requirements and flyash-plugging.</td>
<td>Probable further testing.</td>
<td>5.2.3.1</td>
</tr>
<tr>
<td>Westvaco</td>
<td>Carbon Adsorption</td>
<td>S/SO₂</td>
<td>Fluid bed adsorber, good pilot plant results.</td>
<td>Tests supported by EPA at Charleston, S.C.</td>
<td>5.4.1.3</td>
</tr>
</tbody>
</table>