Production of Elemental Sulphur from SO$_2$
**RSR** (Rameshni SO$_2$ Reduction)

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Abstract

WorleyParsons’ innovative SO$_2$ reduction process efficiently recovers sulphur from SO$_2$ streams. Effluent gases from ore roasters and smelters and coal-fired power plants can be treated to reduce sulphur emissions. This exciting new process is an innovative combination of well-established processes of reaction of CH$_4$ and sulphur vapor to produce CS$_2$, followed by catalytic hydrolysis of CS$_2$ to H$_2$S, and Claus reaction of H$_2$S and SO$_2$ to sulphur. Key advantages are lower fuel consumption, reduced emissions, better product sulphur quality and better operational stability. The process is being named RSR (Rameshni SO$_2$ Reduction).

1. Introduction

Environmental regulatory agencies of many countries continue to promulgate more stringent standards for sulphur emissions from Industrial sources. Many plants around the world, ore smelters, in particular, are still allowed to emit large quantities of SO$_2$ because of their remote locations and the high cost of mitigation, but those exemptions are running out as governments become more environmentally responsible. With the renewed interest in high sulphur coal for power production and increased activity in the mining and metals sectors, it is necessary to develop and implement reliable and cost-effective technologies to cope with the changing requirements.

Sulphur dioxide is found in a many industrial gases emanating from plants involved in roasting, smelting and sintering sulfide ores, or gases from power plants burning high sulphur coal or fuel oils or other sulfurous ores or other industrial operations involved in the combustion of sulfur-bearing fuels, such as fuel oil. One of the more difficult environmental problems facing industry is how to economically control SO$_2$ emissions from these sources.

In general, smelter gases contain about 2% to 16% SO$_2$ by volume while gases from other sources may vary from 1% to 100% SO$_2$ with the other components usually comprising oxygen, nitrogen, carbon dioxide and water vapor.

Few commercially feasible processes for the reduction of SO$_2$ to elemental sulfur have been developed. The reduction of SO$_2$ to elemental sulfur has been investigated extensively over a period of nearly 100 years, and the basic SO$_2$ reduction process using a hydrocarbon reducing agent is discussed in many
articles and patents. Thermal and catalytic reduction processes have both been investigated over the years.

The general problems using hydrocarbon as a reducing agent are listed below.

- Low sulphur recovery efficiency
- High fuel consumption
- High cost
- Difficult operation
- Soot formation produces off-color sulphur and fouls catalyst beds
- By products, such as hydrogen and CO, increase the gas volume requiring larger plants

With catalytic processes, temperature control is very important because high temperatures can lead to uncontrolled reactions that produce increasing amounts of hydrogen and CO. Therefore, catalytic processes add the following additional problems.

- Limited ability to control temperature
- Limited ability to control side reactions
- Use of staged or switching reactors to control the temperature

Later work has suggested that the addition of elemental sulphur with the hydrocarbon reducing agent helps to initiate the reduction reactions and reduce soot and byproduct formation. While elemental sulphur in addition to hydrocarbon improves the process, it does not resolve all of the issues.

Considering all of the problems associated with the current technology, the ore roasting, smelting and clean coal technology leaders are looking for improved technology to convert SO₂ to sulphur where potential sulphuric acid supply exceeds demand. A new sulphur recovery technology that offers higher quality sulphur, improved recovery and lower energy consumption is needed. Over the past 50 years, WorleyParsons has actively pursued innovative schemes for the conversion of SO₂ to sulphur.

2. Industrial Practice

The usual approach has been to directly reduce SO₂ to sulphur by thermal or catalytic reaction with a hydrocarbon or carbonaceous fuel as the reducing agent. The hydrocarbon reducing agent can be a gas, liquid or solid. Natural gas, often considered as methane (CH₄) for simplicity, is the most commonly employed.

Development of the technology is seen in the following schemes. These schemes have been confined to laboratory or pilot scale research, conceptual patents or small-scale commercial units. There are several fundamental problems common to these efforts. In particular, byproduct formation of H₂S, CS₂, COS, H₂ and CO reduces sulfur recovery and fuel efficiency and requires larger equipment because of the
increased gas flow. Soot formation reduces the quality of the sulphur product and fouls the equipment and catalyst beds reducing the reliability of the unit.

### 2.1 Thermal Reduction of SO$_2$ to Sulphur

During 1909-11, S. W. Young investigated reduction of SO$_2$ with methane and other hydrocarbons on a laboratory scale. (1) Results were disappointing, and no further work was done along these lines for several years. It is assumed that inability to accommodate byproduct H$_2$S, CS$_2$ and COS was considered a key drawback.

In a 1934 article, Yushkevich, and others, discuss in detail the various possible reaction products from the combination of SO$_2$ and a hydrocarbon reducing agent, including H$_2$S, COS, CS$_2$ and sulphur. Experiments suggested 900-1000°C as the optimum temperature. (2, 3)

In 1938, American Smelting and Refining Company (ASARCO) initiated investigations, which soon indicated that relatively low-grade SO$_2$ might be directly converted to reasonably pure sulphur by reduction with natural gas. (1) Laboratory and small-scale pilot operations were gradually expanded until a semi-commercial 5-tpd unit was operated during 1940-45. Gas from copper roasters or converters containing 5-8% SO$_2$ and 9-12% oxygen was combusted with sufficient natural gas to consume all the oxygen to CO$_2$, plus additional fuel to react with an appropriate portion of the SO$_2$ according to the following overall reaction with CH$_4$ as shown in Equation 1.

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

Considerable quantities of byproduct H$_2$S, COS and CS$_2$ were formed as well. Furnace temperatures of at least 1250°C were considered necessary to minimize soot, which will discolor the sulphur. The gases were then cooled and passed through a series of Claus stages for hydrolysis of COS and CS$_2$ to H$_2$S and reaction of residual H$_2$S and SO$_2$ to sulphur according to the Claus reaction.

This process is still employed today where potential sulphuric acid supply exceeds demand. While the technology has improved, soot formation still tends to reduce sulphur quality and catalyst life. In addition, fuel consumption and emissions are high.

In a 1978, Davy Powergas GmbH proposed a staged combustion process where hydrocarbon gas is burned at near stoichiometric conditions, followed by injection of supplemental CH$_4$ and SO$_2$ which react to form elemental sulphur. (4) It is also claimed that the presence of water vapor in the SO$_2$ feed stream suppresses soot formation. The process was never commercialized.

### 2.2 Catalytic Reduction of SO$_2$ to Sulphur

In a 1934, United Verde Copper Company proposed a process where a portion of the SO$_2$ stream is combined with CH$_4$ at 800-850°C in the presence of a metal sulphide catalyst to produce H$_2$S, which is subsequently reacted with the remaining SO$_2$ to yield sulphur according to the Claus reaction. (5) The
Claus stage preferably comprised a bed of granular absorbent, such as bauxite or charcoal, continually wetted by a thin film of liquid water which served to absorb the reaction heat and also carry away the product sulphur for subsequent recovery by filtration or sedimentation. The process was never commercialized, but would probably have suffered from the same temperature control and soot formation problems seen in later processes.

In 1965, Texas Gulf Sulphur patented the reduction of SO\(_2\) with hydrocarbons (e.g.: CH\(_4\)) at 750-1000°C using a catalyst such as alumina, initially achieving 40-60% sulphur recovery. (6) Two similar catalytic stages typically followed, whereby the second stage achieved the following at 390°C.

- Hydrolysis of byproduct COS and CS\(_2\) to H\(_2\)S
- Claus reaction of H\(_2\)S and SO\(_2\) to form sulphur
- Reduction of SO\(_2\) by CO and H\(_2\) to sulphur

Claus reaction of residual H\(_2\)S and SO\(_2\) further proceeded in the third stage for 95% overall sulphur recovery. No method of controlling the heat release from the reduction reactions is described and the process was never commercialized.

In 1975, Allied Chemical Corp. claimed to have discovered that, at SO\(_2\) concentrations on the order of 50% and higher, a small amount of elemental sulphur (0.1-3 mol-% of the feed gas as S\(_8\)) lowered the initiation temperature for SO\(_2\) reduction and favorably moderated the temperature rise and rate. The sulphur also expedited the reaction and minimized byproduct H\(_2\), CO, COS and CS\(_2\) formation. (3) Generation of H\(_2\) and CO is particularly counterproductive because it decreases sulfur recovery and fuel efficiency and requires larger equipment because of the increased tail gas volume. While the addition of the sulphur does lower the initiation temperature and moderate the temperature rise, the inlet temperature to the reactor is still about 600°C and the outlet temperature is very high at about 1000°C. Such high temperatures require the use of expensive reactors and heat exchangers.

In 1977, Allied Chemical presented an innovative 3-bed arrangement that was claimed to optimize reactant concentrations and temperatures. (7) The total SO\(_2\) stream is mixed with a portion of the CH\(_4\) and passed through the first reactor to effect reduction of a portion of the SO\(_2\) to H\(_2\)S and sulphur. Exit gas from the first reactor is mixed with the remaining CH\(_4\), and the resultant mixture split into two gas streams which are passed, in parallel, through a second and third reactor to further effect reduction of SO\(_2\) to H\(_2\)S and sulphur. Periodically, the flow in the first and third reactors is reversed to subject them to alternating heat absorbing and desorbing cycles (while the second reactor is always maintained in the same direction). Inlet gas temperatures to the second and third reactors are maintained within desired ranges by bypassing a portion of the SO\(_2\) and CH\(_4\) around the first reactor. A 25-tpd pilot plant was constructed in 1978 at a 115-MW coal-fired power plant. The cost and unreliability of the switching valves that are used for temperature control are major disadvantages of this process.
2.3 Catalytic Reduction of Sulphur to Intermediate H₂S

Early research on the recovery of sulphur from gypsum (CaSO₄·2H₂O) involved reduction roasting of gypsum with coal or natural gas to form calcium sulfide, which was subsequently processed to generate H₂S. In the laboratory, elemental sulphur was then produced by reacting H₂S with SO₂ at ambient temperature in a liquid medium. That latter concept led the Federal Bureau of Mines, beginning in 1968, to consider absorption of SO₂ (from nonferrous smelters) in a liquid medium subsequently regenerated with H₂S to precipitate sulphur. After screening many reagents, an aqueous solution of citric acid neutralized with soda ash to a pH of 4.5 was selected. (8)

At least three pilot plants were operated during 1971-76. The most recent was located at the Bunker Hill Co.’s lead smelter in Kellogg, Idaho. In the absence of an external source, H₂S was generated by the reaction of natural gas with sulphur vapor at 650°C over a proprietary catalyst as shown in Equation 2.

\[
\text{CH}_4 + 4 \text{ S} \rightarrow \text{CS}_2 + 2 \text{ H}_2\text{S} \quad (2)
\]

The product CS₂ was subsequently hydrolyzed with steam in a second catalytic stage at 315°C as shown in Equation 3.

\[
2 \text{ H}_2\text{S} + \text{CS}_2 + 2 \text{ H}_2\text{O} \rightarrow 4 \text{ H}_2\text{S} + \text{CO}_2 \quad (3)
\]

The so-called Citrate Process for Claus reaction of H₂S and SO₂ within a liquid absorbent was ultimately abandoned due to absorber corrosion and plugging problems. (9)

3. WorleyParsons Involvement with SO₂ Reduction to Sulphur

The first U. S. refinery Claus sulphur recovery plant was commissioned in California in 1949, and early involvement quickly established WorleyParsons predecessor, the Ralph M. Parsons Company (RMPCo), as a leader in sulphur technology. Around 1978, RMPCo began to pursue the intermediate reduction of recycled elemental sulphur as a means of overcoming some of the problems encountered with direct thermal reduction of SO₂ to elemental sulphur. Specifically, the process instability, side reactions that produce hydrogen and CO, and the formation of soot were considered.

During 1978-1980, a series of three U. S. patents by RMPCo, as described below, proposed innovations to reduce equipment costs and improve operability and product quality. A common theme is the efficient reduction of recycled sulphur to H₂S for subsequent reaction with SO₂ to produce sulphur, while minimizing the soot formation characteristic of direct SO₂ reduction.
3.1 WorleyParsons Sulphur Reduction by Submerged Hydrocarbon Combustion

In a 1978 patent, H₂ and CO are initially formed in a reducing gas generator by the partial combustion of a hydrocarbon fuel, with steam injection to suppress soot formation. The fuel can be gaseous (such as methane), liquid (such as kerosene, diesel or other fuel oil) or solid (such as coal or coke). (10)

![Diagram of WorleyParsons Sulphur Reduction by Submerged Hydrocarbon Combustion]

The reducing gas is sparged through molten sulphur, so that combustion temperatures are rapidly quenched by sulphur vaporization as shown in Figure 1. The firing rate is adjusted to produce a 250-450°C vapor stream with a nominal stoichiometric excess of hydrogen, which is then passed across a fixed cobalt-moly catalyst bed. Elemental sulphur is hydrogenated to H₂S. Byproduct COS and CS₂ are hydrolyzed to H₂S, and CO is hydrolyzed to CO₂ and H₂.

Sufficient reaction heat is generated that multiple beds with inter-stage cooling are typically required. Reactor effluent is cooled in the sulphur cooler to condense any residual sulphur vapor, particularly during non-routine operation, while remaining above the water dew point. The gas is then further cooled to condense most of the water vapor, yielding an H₂S-rich stream that can then be reacted with SO₂ in a conventional Claus reactor to produce elemental sulphur.

The process has not been commercialized. The condensation of water from a sulphur-containing stream is likely to make the process difficult to operate because of frequent plugging of the water condenser by solid sulphur. If the water condensation step were omitted, the sulphur recovery efficiency of the process would be expected to decrease because the water vapor would unfavorably affect the equilibrium of the Claus reaction.
3.2 WorleyParsons Sulphur Reduction in a Reaction Furnace

In a 1979 patent, hydrogen and CO are similarly generated by partial oxidation of a hydrocarbon, gaseous or liquid, in the first zone of a 2-zone furnace, and a stoichiometric excess of liquid sulphur is injected into the second zone to quench temperatures to 800-1100°C as shown in Figure 2.

![Figure 2. WorleyParsons Sulphur Reduction in a Reaction Furnace](image)

A portion of the H₂ and CO react with the sulphur to form H₂S, COS and some CS₂, with about 50% of the total H₂S production being achieved in the furnace. The resultant vapor stream is rapidly cooled to 425°C or less in a waste heat boiler to suppress further formation of undesirable organic sulphur byproducts. The stream is then further cooled to condense and remove most of the residual sulphur.

The gas stream is then typically be reheated for conventional catalytic hydrogenation of sulphur and SO₂ to H₂S, hydrolysis of COS and CS₂ to H₂S and hydrolysis of CO to CO₂ and hydrogen. The reactor effluent is then cooled by conventional means to ultimately condense most of the water vapor, yielding an H₂S-rich gas stream that can be subsequently reacted with SO₂ in a conventional Claus reactor to yield elemental sulphur.

As with the previous process, this process has not been commercialized and the problems with water condensation described above would apply to this process.

3.3 WorleyParsons Thermal Reduction of SO₂

In a 1980 patent, a hydrocarbon fuel, gaseous or liquid, is partially oxidized in a reaction furnace to generate H₂ and CO and SO₂ added to the thermal reaction zone to react with the H₂ and indirectly, CO
(by virtue of water gas shift to \( CO_2 \) and \( H_2 \)) as shown in Figure 3. The firing rate is adjusted to yield a mixture of \( H_2S \) and \( SO_2 \) in the molar ratio of 2:1 as required by Claus stoichiometry. (12)

![Figure 3. WorleyParsons Combined SO2 Reduction and Claus Reaction](image)

Competing reactions are the formation of \( COS \) and \( CS_2 \) from the reaction of \( CO \) and free carbon with \( SO_2 \) and sulphur. Potential soot may be washed from the system by the introduction of liquid sulphur, which is recycled to enable consumption of extracted carbon.

The resultant vapor stream is rapidly cooled to 425°C or less to suppress further formation of undesirable organic sulphur byproducts. Elemental sulphur is recovered and recycled to the reactor for gasification of extracted carbon solids and tars.

Further sulphur recovery is achieved as the process gas proceeds through a series of conventional catalytic Claus stages. While the process has not been commercialized, it is an improvement over the thermal reduction processes in use today.

### 3.4 WorleyParsons Flue Gas Cleanup Process

Over the past 30 years, WorleyParsons' BSR (Beavon Sulphur Removal) technology has been successfully applied to the catalytic conversion of Claus tail gas \( SO_2 \), \( S_n \), \( COS \) and \( CS_2 \) to \( H_2S \) in over 80 tail gas treating units. In the early 1990's, RMPCo and a group of cosponsors extended that experience, through bench and pilot scale experiments, to develop the WorleyParsons Flue Gas Cleanup (FGC) process. (13) The key was development of a new catalyst system capable of virtually complete reduction of \( SO_n \), \( NO_x \) and \( O_2 \), without rapid catalyst deactivation from sulfation as typically experienced when conventional catalysts are exposed to free oxygen. (14) The principal disadvantage was the high fuel demand of \( O_2 \) scavenging.
3.5 WorleyParsons Catalytic SO$_2$ Hydrogenation

Recently, the BSR concept was similarly evaluated as a means of sulphur recovery from a concentrated smelter SO$_2$ stream as shown in Figure 4. In this case, however, it was assumed that the SO$_2$ had been concentrated by absorption in a conventional liquid solvent and then stripped from the solvent. The concentration step produces an O$_2$-free stream that can be hydrogenated with a conventional hydrogenation catalyst (cobalt-moly, for example).

![Diagram of WorleyParsons Catalytic SO$_2$ Hydrogenation](image)

Figure 4. WorleyParsons Catalytic SO$_2$ Hydrogenation
In this process, hydrogen and CO generated by the partial oxidation of natural gas catalytically hydrogenates 2/3 of the SO$_2$ to H$_2$S, which subsequently reacts with the remaining SO$_2$ in a conventional Claus train to produce elemental sulphur.

In Claus tail gas treating applications, BSR sections typically combust natural gas at 70-80% of stoichiometric air, with steam injection at 1 kg/kg steam/fuel, to suppress soot formation. In the smelter case, the magnitude of the fuel demand warranted maximizing the air deficiency for increased yield of CO and H$_2$. With a high-intensity burner, good control of the air/fuel ratio and 3 kg/kg steam/fuel, clean operation at 60% of stoichiometric air is known to be feasible.

The flue gas is cooled in a waste heat boiler generating high-pressure steam, then subsequently cooled to its dew point by direct contact with recycle water in a desuperheater, which also serves to capture minor amounts of soot which may be present. Makeup water, which can be supplied by the downstream quench column blow down, is added as necessary to maintain liquid level.

The desuperheater off gas and 2/3 of the SO$_2$ are reheated and subsequently combined in the hydrogenation reactor, where the SO$_2$ is hydrogenated to H$_2$S and CO is shifted to CO$_2$ and H$_2$.

The reactor effluent is cooled by the generation of low-pressure steam, then further by direct contact with recycle water to condense most of the water vapor.

A portion of the quench column off gas is recycled, via a low-head centrifugal blower, to dilute the SO$_2$ to the H$_2$ reactor for temperature moderation. The recycle blower also serves to facilitate startup, shutdown and turndown of the RGG and hydrogenation sections.

H$_2$S-rich process gas from the quench column and the remaining 1/3 of the SO$_2$ are heated, and the two streams subsequently combined in the first converter of a conventional Claus train.

A conventional air demand analyzer continuously measures the H$_2$S and SO$_2$ concentrations in the tail gas exiting the final condenser, and automatically adjusts the split of raw SO$_2$ between the RGG and Claus sections to maintain the molar ratio of H$_2$S:SO$_2 = 2/1$.

While this concept is not in commercial operation at this time, each section of the process is well proven on a commercial scale and reliable in operation.
4. **WorleyParsons Innovative SO2 Reduction Process**

WorleyParsons’ innovative (patent pending) SO2 reduction process for sulphur recovery from an SO2 stream is a novel combination of two well-established processes. The scheme includes a CS2 section and a Claus section.

**CS2 section** – reaction of natural gas and recycled sulphur vapor to produce CS2

**Claus section** – subsequent concurrent catalytic hydrolysis of CS2 to H2S and reaction of H2S and SO2 to produce elemental sulphur in a conventional Claus unit

Compared to the existing technology, this process offers lower costs, lower fuel consumption, lower emissions, better reliability, and better sulphur product quality.

4.1 **SO2 Concentration**

While any SO2 concentration can be processed (following particulate removal), pre-concentrating the raw stream is generally desirable to reduce the Claus tail gas volume, thus (1) reducing the size of the Claus train, (2) increasing recovery, and (3) reducing incinerator fuel. For the SO2 concentration step, there are four well-known processes in the market.

Outokumpu offers a cold-water based process. The Labsorb (ELSORB) process uses a buffered aqueous solution of sodium salts of phosphoric acid as the solvent. Cansolv uses a chemical solvent based on a proprietary diamine.

ClausMaster (formerly Solinox) from Monsanto uses a physical solvent (tetra-ethylene-glycol dimethyl-ether).

A further advantage of such pre-concentration is that the incinerated Claus tail gas can be treated with the solvent to increase sulphur recovery efficiency to nearly 100%.

4.2 **CS2 Background**

Those of us focused on sulphur recovery tend to view CS2 as an undesirable contaminant rather than a useful feedstock. However, CS2 has been an industrially important chemical for over one hundred years.

Most of carbon disulfide produced worldwide goes into manufacturing viscose rayon and cellophane film. Carbon disulfide is also used in manufacturing numerous organic sulfur compounds for a variety of applications including rubber vulcanization accelerators, flotation chemicals, pharmaceutical intermediates, fungicides, and insecticides.

Carbon disulfide, CS2, is a highly volatile, flammable, clear, colorless, dense liquid that has many useful chemical and physical properties. Low concentrations of carbon disulfide naturally discharge into the at-
mosphere from certain soils, and carbon disulfide has been detected in mustard oil, volcanic gases, and crude petroleum. Carbon disulfide is an unintentional by-product of many combustion and high temperature industrial processes where sulfur compounds are present.

Carbon disulfide was first prepared nearly two hundred years ago by heating sulfur with charcoal. That general approach was the only commercial route to carbon disulfide until processes for reaction of sulfur and methane or other hydrocarbons appeared in the 1950s. Significant commercial production of carbon disulfide began around 1880, primarily for agricultural and solvent applications. Both the physical and chemical properties of carbon disulfide are utilized in industry. Commercial uses grew rapidly from about 1929 to 1970, when the principal applications included manufacturing viscose rayon fibers, cellophane, carbon tetrachloride, flotation aids, rubber vulcanization accelerators, fungicides, and pesticides.

In CS₂ production plants, H₂S is considered an undesirable byproduct. Therefore, it must be separated and recycled to the process as sulphur via a side stream Claus unit. However, for the SO₂ reduction to sulphur application, H₂S is preferred and CS₂ is a necessary intermediate.

Commodity CS₂ production also involves purification to 99.99% by multiple fractional distillation steps not applicable here and thus not discussed.

Vaporization of sulphur and subsequent reaction with natural gas is typically accomplished in an externally fired tubular heater, very similar to designs commonly used in ethylene cracking. Heat transfer to the tube coils occurs primarily by radiation with no direct contact of the flames. Design is critical to achieve uniform heating to avoid rapid corrosion at hot spots. The tubes are typically constructed of a high nickel-chrome alloy.

4.3 CS₂ Health and Safety Parameters

When it comes to the technical risks involved in application of this technology, we can refer to more than 20 industrial scale installations built during 1950-2005. Production of CS₂ in controlled conditions is highly reliable and a safe industrially proven method.

While CS₂ is hazardous, the process scheme does not produce CS₂, but rather employs the first step in the CS₂ production process to make a reducing gas that may be used to convert SO₂ to elemental sulfur. The gas produced by this first step is composed of about 1/3 CS₂ and 2/3 H₂S by volume. Of these gases, H₂S is the more poisonous gas and is present in larger concentrations. Overall, this reducing gas is no more poisonous than a typical feed gas to a sulfur recovery unit that contains over 90% H₂S. The reducing gas is then combined with concentrated SO₂ (>90% by volume), which is also a very poisonous substance, so the CS₂ is only one of several potentially dangerous chemicals.

While all of these gases are very poisonous, it is important to keep in mind that they will be contained within pipelines and equipment that will be designed, inspected, and maintained in the appropriate manner considering the potential danger. Furthermore, there is no storage of any of these chemicals, so the inventory is only what is contained within the pipelines and equipment. This unit, as any sulfur recovery
unit, will be equipped with H₂S area monitors that will alarm if a gas release is detected. Typically, H₂S area monitors in sulfur recovery units will measure less than 1 ppmv, well below any toxic or explosive levels. Since the CS₂ concentration is never more than 1/2 of the H₂S concentration at any point in the process, CS₂ concentration can be expected to be less than H₂S concentrations.

CS₂ may pose a greater fire and explosion hazard due to its relatively low ignition temperature; however, the gas will be contained within piping and equipment. The explosive limits are well above the fatally toxic levels so the greater danger is from exposure to the chemical rather than fire. The H₂S area monitors will detect any loss of gas containment and sound an alarm to alert the operators at levels well below the explosive limits. In addition, instrumentation and electrical equipment will be designed to the appropriate explosion-proof standard considering the potential danger.

Below are old US standards for exposure to CS₂, H₂S, and SO₂ that were enacted in the 1980s. A later court decision weakened the standards, but these are still widely quoted and should be considered good practice.

<table>
<thead>
<tr>
<th></th>
<th>CS₂ ppmv</th>
<th>H₂S ppmv</th>
<th>SO₂ ppmv</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEL*</td>
<td>4</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>STEL**</td>
<td>12</td>
<td>15</td>
<td>5</td>
</tr>
<tr>
<td>IDLH***</td>
<td>500</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

Explosive Limits (in air), %

<table>
<thead>
<tr>
<th>Explosive Limits (in air), %</th>
<th>CS₂</th>
<th>H₂S</th>
<th>SO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Explosive Limits (in air), %</td>
<td>1.3 – 50</td>
<td>4.3 – 44</td>
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</tbody>
</table>

Ignition Temperature, °C

<table>
<thead>
<tr>
<th>Ignition Temperature, °C</th>
<th>CS₂</th>
<th>H₂S</th>
<th>SO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ignition Temperature, °C</td>
<td>99</td>
<td>260</td>
<td>N/A</td>
</tr>
</tbody>
</table>

*OSHA Permissible Exposure Limit - 8 hour time weighted average
**OSHA Short Term Exposure Limit
***OSHA Immediately Dangerous to Life or Health level - 30 minutes
OSHA = US Occupational Safety and Health Administration

4.4 Process Chemistry

Pure elemental sulfur vapor is catalytically reacted with natural gas to produce hydrogen sulfide (H₂S) and carbon disulfide (CS₂), according to the following endothermic reactions shown in Equations 4, 5, and 6.

\[
\begin{align*}
\text{CH}_4 + 2 \text{S}_2 & \rightarrow \text{CS}_2 + 2 \text{H}_2\text{S} \quad (4) \\
2 \text{C}_2\text{H}_6 + 7 \text{S}_2 & \rightarrow 4 \text{CS}_2 + 6 \text{H}_2\text{S} \quad (5) \\
\text{C}_3\text{H}_8 + 5 \text{S}_2 & \rightarrow 3 \text{CS}_2 + 4 \text{H}_2\text{S} \quad (6)
\end{align*}
\]

However, the C₃⁺ content of the feed gas should be < 1% to minimize side reactions resulting from cracking.

At 400-700°C, reaction 1 equilibrium exceeds 99.9%. Approximately 5-10% excess sulfur is typically maintained to minimize byproduct H₂, as shown in Equation 7, for example, in the case of methane.
\[
\text{CH}_4 + S_2 \rightarrow CS_2 + 2 H_2S \quad (7)
\]

After cooling the stream to condense residual sulfur, the concentrated H\(_2\)S/CS\(_2\) is reheated and combined with the essentially pure sulfur dioxide (SO\(_2\)) in a fixed catalyst bed, where the H\(_2\)S and SO\(_2\) react to form elemental sulfur according the Claus reaction shown in Equation 8.

\[
2 H_2S + SO_2 \rightarrow 3 S + 2 H_2O \quad (8)
\]

CS\(_2\) is concurrently hydrolyzed to H\(_2\)S consuming water from Reaction 8 to supply additional H\(_2\)S according to Equation 9.

\[
CS_2 + 2 H_2O \rightarrow CO_2 + 2 H_2S \quad (9)
\]

The reactor effluent is cooled to condense most of the sulfur vapor. Since reactions 8 and 9 are exothermic, the bulk of the gas stream is recycled, following reheating, to the reactor to dilute the reactants as necessary to limit the temperature rise.

The Claus reaction is equilibrium-limited, and the tail gas is ultimately passed through second and third conversion stages to achieve 98% overall sulfur recovery.

### 4.5 CS\(_2\) Section Process Description

The natural gas feedstock and liquid sulfur are separately preheated to 650°C, at 500 kPag, in an externally fired tubular heater. The heater design is similar to designs commonly used in ethylene cracking. Heat transfer to the tube coil occurs primarily by radiation with no direct contact of the flames. Design is critical to achieve uniform heating to avoid rapid corrosion at hot spots. The tubes are typically constructed of a high nickel-chrome alloy.

The liquid sulfur vaporizes at around 450°C, at which temperature it exists mainly as S\(_8\). Subsequent superheating to 575-650°C results in endothermic decomposition to smaller, more reactive, species (S\(_6\) and S\(_2\)). This dissociation is also favored by the reduction in partial pressure of the sulfur vapor as H\(_2\)S and CS\(_2\) are formed in the reactor. Consequently, it is desirable to preheat the vapor to the maximum reaction temperature before combination with the natural gas, to minimize the reactor temperature drop resulting from the endothermic dissociation of the sulfur.

The gas and sulfur vapor are then mixed, typically in a special venturi nozzle. The combined steam flows through a radiantly heated pipe coil, where some reaction takes place, before entering an adiabatic catalytic reactor containing activated alumina catalyst. The gas hourly space velocity is typically 100-400 volumes of gas per hour/unit volume of catalyst.

As mentioned, 5-10% excess sulfur is typically fed to maximize natural gas conversion and minimize side reactions. Assuming a fairly constant SO\(_2\) rate, it is expected that the sulfur rate would be maintained.
fairly constant, and the methane automatically adjusted to achieve the optimum ratio of \( \text{H}_2\text{S}:\text{SO}_2 = 2:1 \) at the SRU.

Effluent gas from the final CS\(_2\) reactor is cooled to 340°C in a waste heat boiler generating high-pressure (4200 kPag) steam, then subsequently to 150°C by the generation of low-pressure (350 kPag) steam to condense most of the residual sulphur vapor, which drains to the collection pit. (The typical CS\(_2\) scrubber is not required in the present scheme.)

### 4.6 Claus Section

As shown in Figure 5, the gas H\(_2\)S+CS\(_2\) gas stream is indirectly reheated with high-pressure steam to 210°C. The essentially pure SO\(_2\) stream is similarly heated, and combined with the CS\(_2\)/H\(_2\)S in a conventional Claus reactor containing a fixed bed of activated alumina catalyst.

While lower temperatures directionally favor Claus conversion efficiency, reheating is necessary to maintain conditions above the dew point to avoid loss of catalyst activity due to condensed sulfur. (If condensation does occur, as possibly due to temporary loss of preheat, the effect is reversible by restoring normal temperatures.)

Effluent gas from the No. 1 SRU reactor is cooled to 340°C in the SRU waste heat boiler by the generation of high-pressure steam, then subsequently to 150°C by the generation of low-pressure steam in the No. 2 sulfur condenser to condense most of the residual sulfur vapor, which drains to the collection pit.

The bulk of the process gas is recycled to the No. 1 SRU reactor, via a low-head centrifugal blower and steam reheater, to dilute the reactants as necessary to limit the exothermic temperature rise. (Similar tail gas recycle blowers are commonly employed in the industry to moderate high Claus reaction furnace temperatures resulting from oxygen enrichment.)
Figure 5. WorleyParsons Innovative SO₂ Reduction Process
Ultimately the process gas is sent to the second Claus stage, comprising the No. 2 steam reheater, No. 2 sulfur reactor and No. 3 sulfur condenser, for further reaction of residual H₂S and SO₂. A Titania catalyst may be used in the lower half of the bed to ensure complete conversion of potential residual CS₂. The reactants are sufficiently dilute at this point that tail gas recycle is not required, and the second and third stage reactors are thus considerably smaller.

A similar No. 3 SRU stage follows (without titania catalyst) to achieve an overall sulfur recovery efficiency of 98%.

A conventional air demand analyzer continuously measures the H₂S and SO₂ concentrations in the tail gas exiting the final condenser, and automatically adjusts the natural gas rate to maintain the molar ratio of H₂S:SO₂ = 2/1. As mentioned, provisions would be included to maintain a reasonable excess of sulfur vapor, but precise control is not required.

Residual H₂S in the tail gas is oxidized at 650°C by the combustion of fuel gas with excess air in a natural draft stack discharging to atmosphere. Any residual combustibles in the tail gas (CH₄, H₂S and possibly H₂) generate oxidation heat, and thus directionally reduce burner fuel demand.

Nearly 100% SO₂ recovery efficiency can be achieved by treating the incinerator tail gas with the SO₂ concentrating solution before it is released to the atmosphere.

5. Conclusion

WorleyParsons innovative SO₂ reduction process is a significant improvement over the existing SO₂ reduction processes. A combination of two well-proven processes, WorleyParsons’ SO₂ reduction process offers several advantages compared to the existing technologies.

All component operations are well proven on large commercial scales.

Superior fuel efficiency. For example, 0.20 lb fuel/lb SO₂ vs. 0.34 for the previous BSR hydrogenation route (a 40% reduction).

High sulphur recovery efficiency of up to 98% without a tail gas unit and nearly 100% with a tail gas unit.

Soot formation is virtually eliminated improving product quality and unit reliability.

The methane-sulphur reaction is endothermic making it much easier to control the temperature and side reactions.
Since the process gas is not diluted by combustion products, tail gas rates are much lower, resulting in significantly lower emissions, less incinerator fuel and smaller second and third Claus stages.

Compared with conventional Claus reaction furnaces, for example, tube side processing affords better mixing, thus minimizing undesirable side reactions. The heater design, while sophisticated, is fairly standard with a reputation for reliable operation.

The highest process temperature is 650°C, versus 1,000-1,300°C in competing technologies, thus requiring less expensive materials of construction.

High quality sulphur is virtually assured.

Compared to the existing technology, this process offers lower costs, lower fuel consumption, lower emissions, better reliability, and better sulphur product quality.

Where sulfuric acid production is not an option, historically available processes for large scale SO\textsubscript{2} recovery as elemental sulphur are inherently problematic in terms of operability, emissions, product quality and fuel consumption. WorleyParsons’ innovative SO\textsubscript{2} reduction process is the clear choice in overcoming those drawbacks.

6. References


5. U. S. patent 1,967,263, Rosenstein, L., Recovery of Sulfur, United Verde Copper Company, July 24, 1934.


