

# Sulphuric Acid Manufacture

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**Abstract** – The raw material for sulphuric acid manufacture is clean SO<sub>2</sub> gas. It comes from (i) burning molten by-product sulphur; (ii) roasting or smelting metal sulphide concentrates, and (iii) decomposing contaminated organic chemical process sulphuric acid catalyst. Efficient gas cleaning is required for metallurgical and contaminated acid decomposition gases, especially the former.

Sulphuric acid is made from SO<sub>2</sub> gas by (i) oxidizing the SO<sub>2</sub>(g) to SO<sub>3</sub>(g) in contact with supported liquid-phase catalyst then (ii) reacting the resulting SO<sub>3</sub>(g) with the water component of 98.5 mass% H<sub>2</sub>SO<sub>4</sub>, 1.5 mass% H<sub>2</sub>O acid.

This paper discusses the reasons for these process steps and indicates how acidmaking can be controlled and optimized. Special emphasis is placed on SO<sub>2</sub>(g) oxidation efficiency and how it is influenced by feed gas composition, feed gas temperature, catalyst composition, catalyst bed pressure, number of catalyst beds, and double versus single contact acidmaking.

In addition, a review of various other treatment methods for SO<sub>2</sub>-bearing gases is provided. A brief description of each process is included along with commentary on their technical and economic applicability for use at metallurgical facilities.

## **PART I: SULPHURIC ACID PRODUCTION FROM STRONG SO<sub>2</sub> GAS**

Around 200 million metric tons of sulphuric acid is manufactured per year – most of it from strong SO<sub>2</sub> (~10%) gas.<sup>1</sup> South Africa produces and consumes around 3 million tons per year of sulphuric acid.<sup>2</sup> A majority of the acid is used for making phosphate fertilizers, but it has a myriad of other uses.

### **Raw Materials, Products**

The starting material for sulphuric acid manufacture is clean, dry SO<sub>2</sub>, 8 to 12% in O<sub>2</sub>, N<sub>2</sub>, SO<sub>2</sub>, CO<sub>2</sub>, SO<sub>3</sub> gas. It is obtained:

- (a) by burning molten waste elemental sulphur (~70% of world production)
- (b) from high SO<sub>2</sub> strength metallurgical off-gases (~20%)
- (c) by decomposing spent (used) sulphuric acid catalyst (~10%).

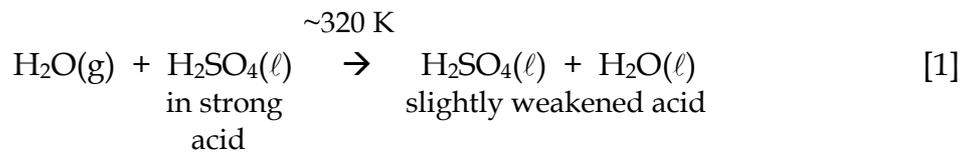
(a) and (c) beneficially make a useful product from waste. (b) beneficially removes SO<sub>2</sub> from smelting and roasting off-gases.

The product of sulphuric acid manufacture is liquid acid, 93 to 98% H<sub>2</sub>SO<sub>4</sub>, 2 to 7% H<sub>2</sub>O.

### Manufacturing Process

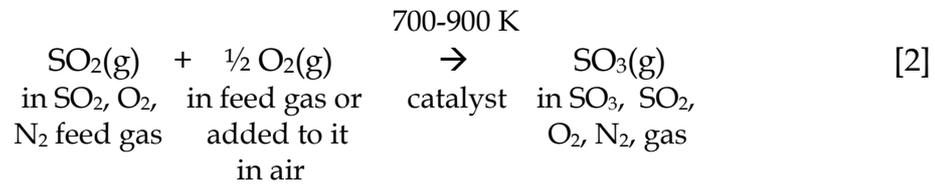
Sulphuric acid manufacturing consists of:

- (a) gas cleaning and removal of H<sub>2</sub>O(g) by condensation
- (b) gas dehydration with sulphuric acid desiccant, i.e.:



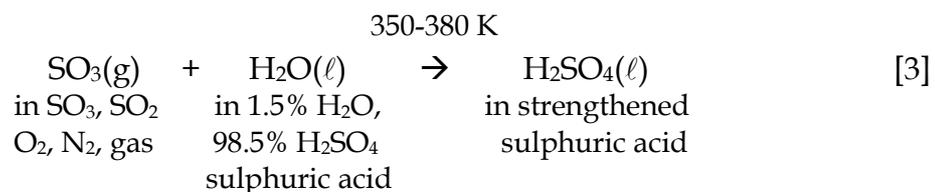
$$\Delta H = -80 \text{ MJ per kg-mole H}_2\text{O}(\text{g})$$

- (c) oxidation of SO<sub>2</sub> to SO<sub>3</sub> in contact with supported liquid phase catalyst, i.e.:



$$\Delta H = -100 \text{ MJ per kg-mole SO}_2(\text{g})$$

- (d) reaction of (c)'s SO<sub>3</sub> product with strong sulphuric acid to make strengthened sulphuric acid, i.e.:



$$\Delta H = -130 \text{ MJ per kg-mole H}_2\text{SO}_4(\ell)$$

- (e) mixing of (b)'s and (d)'s liquid products (+ water) to make the acid plant's range of products.

### Gas Cleaning

The gas entering dehydration must be dust free (0.001 to 0.01 g/Nm<sup>3</sup> of gas) to avoid plugging downstream SO<sub>2</sub>-oxidation catalyst. Dust is removed from the gas by a series of electrostatic precipitation and scrubbing steps. Metallurgical off-gas requires the most attention. Sulphur burning requires the least. Sulphuric acid catalyst decomposition gas is intermediate.

### Condensation and Dehydration

Acid plants must be built and operated so that liquid sulphuric acid is not produced in unexpected locations in equipment and flues. The easiest way to ensure this is to remove all H<sub>2</sub>O(g) from catalytic SO<sub>2</sub> oxidation input gas. It is removed by water-cooling condensation then dehydration with sulphuric acid desiccant. Typical H<sub>2</sub>O(g)-in-gas levels entering catalytic SO<sub>2</sub> oxidation are ~50 mg H<sub>2</sub>O(g) per Nm<sup>3</sup> of input gas.

In sulphur burning acid plants, it is the sulphur combustion air that is dehydrated (with no prior condensation).

### Catalytic SO<sub>2</sub> + ½ O<sub>2</sub> → SO<sub>3</sub> Oxidation

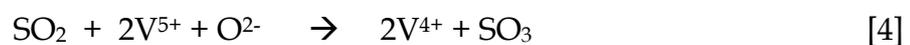
SO<sub>2</sub> is oxidized to SO<sub>3</sub> in preparation for H<sub>2</sub>SO<sub>4</sub> making. The oxidation is done by blowing clean dry SO<sub>2</sub> gas down through horizontal beds of Figure 1 catalyst. Industrially, the beds are typically 0.8 m thick and 10 m diameter.



**Figure 1:** Photograph of catalyst pieces, courtesy Haldor Topsøe A/S  
<http://www.haldortopsøe.com>  
The outside diameter of the largest piece (far left) is 20 mm.

Figure 2 is a stoichiometry-equilibrium curve for SO<sub>2</sub> oxidation. It shows that the reaction goes almost to completion at 600 K but not at 1000 K. This indicates that raising reaction temperature to increase reaction rate is counter-acted by a large decrease in maximum attainable (equilibrium) SO<sub>3</sub> production.

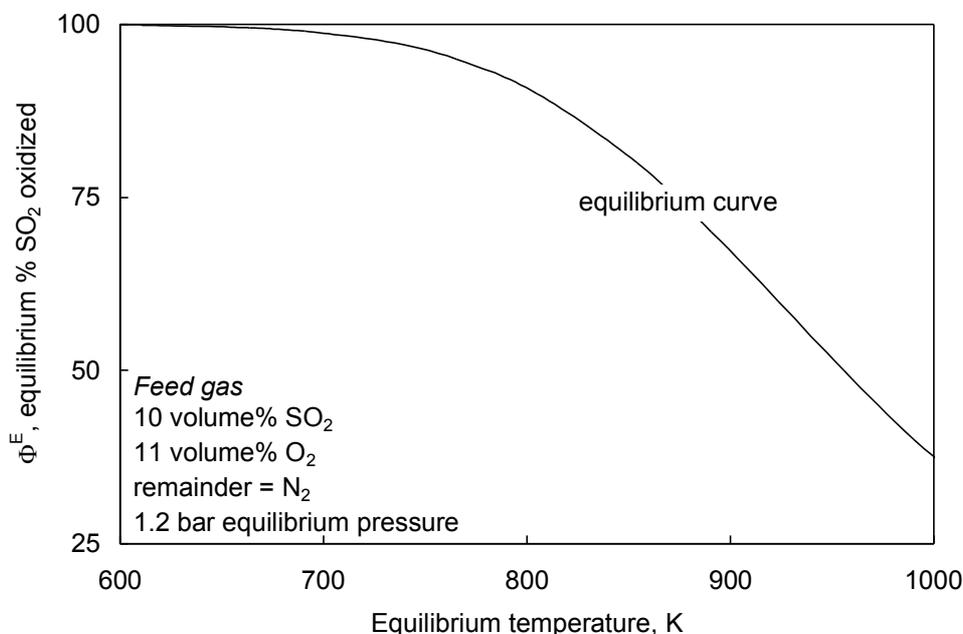
This problem is overcome by using catalyst, which promotes rapid SO<sub>2</sub> oxidation at cool temperatures (~700 K) where equilibrium SO<sub>3</sub> production is efficient. The catalyst is molten V, K, Na, Cs, S, O solution on porous silica substrate. A simplified reaction scheme with this catalyst is:



which combine to give:



Reactions [4] and [5] have lower activation energies than Reaction [2], giving rapid reaction at 700-900 K.



**Figure 2:** Maximum percentage of SO<sub>2</sub>-in-feed-gas that can be oxidized when equilibrium is attained in a bed of Figure 1 catalyst. It decreases markedly with increasing temperature. The curve applies only to the specified conditions.

#### *Catalyst Temperature Limitations*

The V, K, Na, Cs, S, O catalyst must be molten for Reactions [4] and [5] to occur. It typically melts around 680 K, slightly cooler when it contains cesium ions. Unfortunately, it begins to lose its catalytic power above about 900 K due to the formation of unreactive vanadate ions and by non-reversible reaction with the silica substrate.

Thus, SO<sub>2</sub> oxidation must be done between ~700 and 900 K. The industrial implications of this are discussed below.

#### **H<sub>2</sub>SO<sub>4</sub> Making**

In principle, H<sub>2</sub>SO<sub>4</sub>(*ℓ*) can be made by reacting the SO<sub>3</sub>(*g*) from catalytic oxidation with water. However, Reaction [3] is so exothermic that the product of reacting strong SO<sub>3</sub> with water would be hot H<sub>2</sub>SO<sub>4</sub> vapour. Condensation of H<sub>2</sub>SO<sub>4</sub>(*ℓ*) from this vapour is slow and expensive, so the SO<sub>2</sub>-water process is not used for strong gas. Instead, the SO<sub>3</sub>(*g*) is reacted with the H<sub>2</sub>O(*ℓ*) in strong sulphuric acid.

The small amount of H<sub>2</sub>O and the massive amount of H<sub>2</sub>SO<sub>4</sub> in Reaction [3]'s input acid avoids this problem. The small amount of H<sub>2</sub>O limits the extent of the reaction. The large amount of H<sub>2</sub>SO<sub>4</sub> warms only 25 K while it absorbs Equation [3]'s heat of reaction.

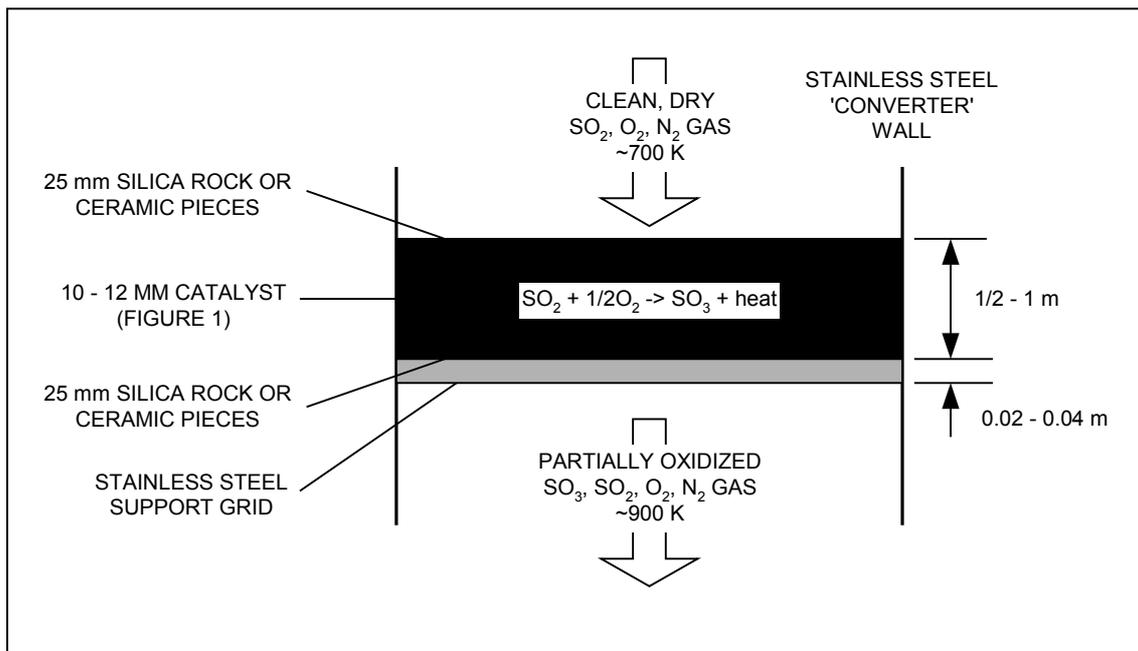
The above sections describe the basic steps of sulphuric acid manufacture. The rest of Part I discusses:

- (a) single- and multi-catalyst bed  $\text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{SO}_3$  oxidation
- (b) single and double contact acidmaking
- (c) optimization.

### Single- and Multi-Catalyst $\text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{SO}_3$ Oxidation

Figures 3 and 4 describe single catalyst bed  $\text{SO}_2$  oxidation. Figure 3 shows that warm  $\text{SO}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$  gas descends the hot catalyst bed causing:

- (a) its  $\text{SO}_2$  to be oxidized
- (b) the gas to be heated by the exothermic oxidation reaction.

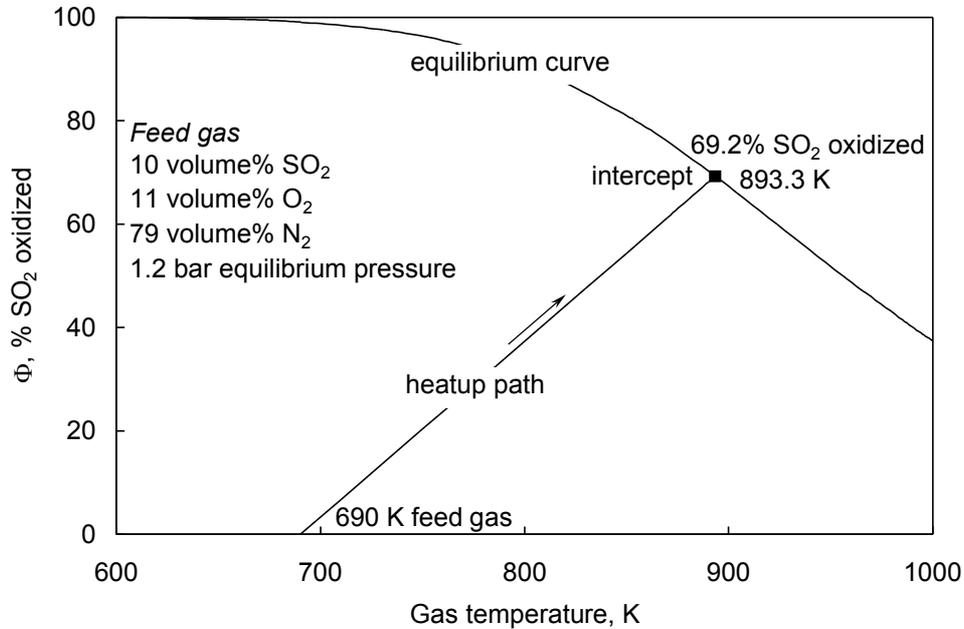


**Figure 3:** 'Bed' of catalyst pieces for oxidizing  $\text{SO}_2$  to  $\text{SO}_3$ . Industrial beds are 7-17 m diameter.

Figure 4 describes this behaviour on Figure 2's stoichiometry-equilibrium curve graph. It shows that:

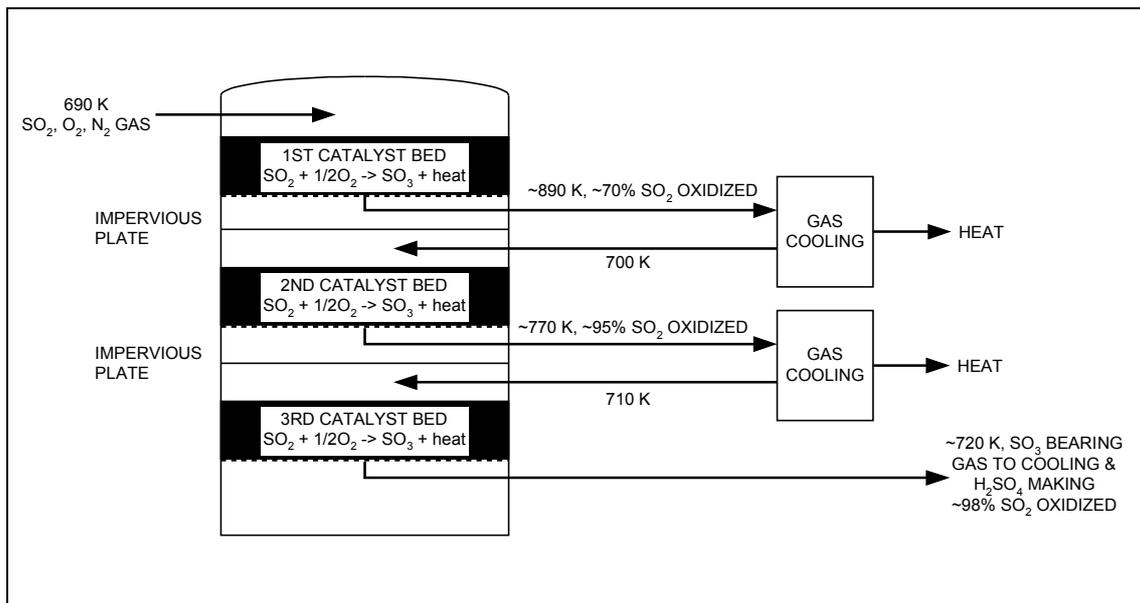
- (a) the gas warms as percent  $\text{SO}_2$  oxidation increases
- (b) maximum (equilibrium)  $\text{SO}_2$  oxidation is achieved at  $\sim 890$  K with about 70% of the input  $\text{SO}_2$  having been oxidized to  $\text{SO}_3$ .

This demonstrates that only  $\sim 70\%$  of input  $\text{SO}_2$  can be oxidized to  $\text{SO}_3$  in a single catalyst bed no matter how thick the bed.

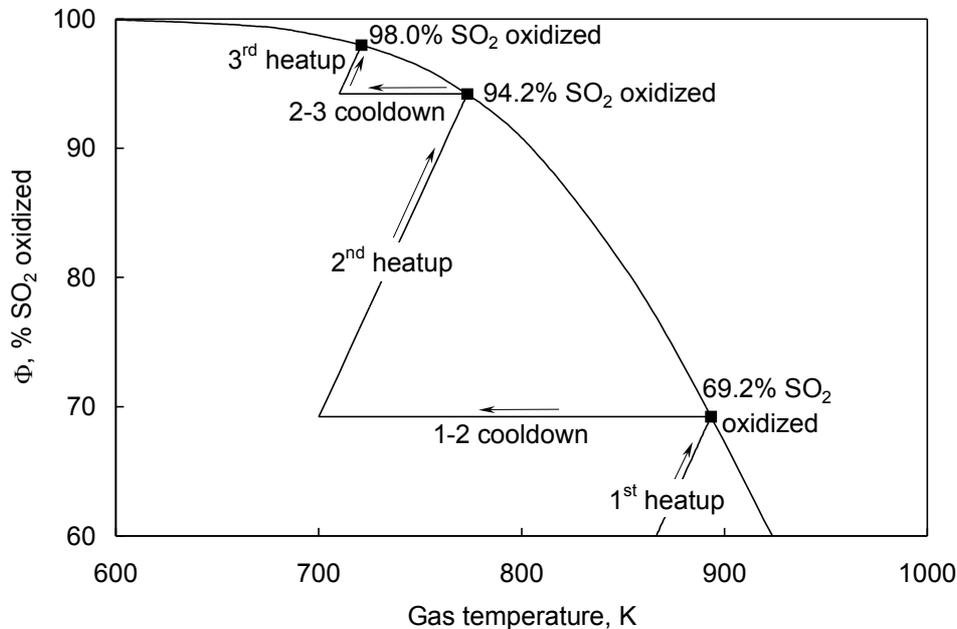


**Figure 4:** First catalyst bed heat-up path, equilibrium curve and equilibrium intercept point. Only ~70% of input SO<sub>2</sub> can be oxidized in a single catalyst bed. Multicatalyst bed oxidation with cooling between brings this up to 99+%, Figure 8. It can be deduced from this graph that a lower gas input temperature (say 670 K) will give a lower gas output temperature and a higher SO<sub>2</sub> oxidation efficiency.

The only practical way to circumvent this limitation is to use three or four sequential catalyst beds with gas cooling between, Figures 5 and 6.



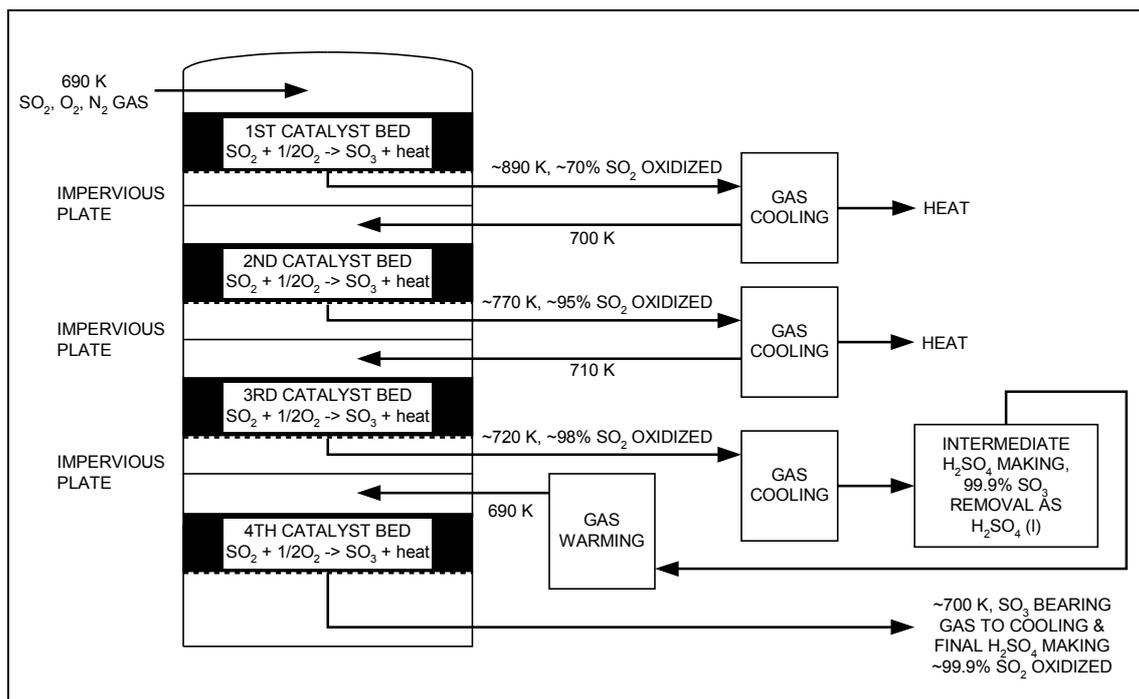
**Figure 5:** Schematic of single contact, 3 catalyst bed sulphuric acid plant. It is a single contact acid plant because it has only one H<sub>2</sub>SO<sub>4</sub> making step. Note gas cooling between catalyst beds. It is this that permits additional SO<sub>2</sub> oxidation in the next catalyst bed.



**Figure 6:** SO<sub>2</sub> oxidation efficiency in Figure 5's three catalyst bed acid plant. The efficiency increases with each succeeding bed, but with diminishing gain. A 4<sup>th</sup> bed will further increase efficiency, but it is better to remove the gas's SO<sub>3</sub> beforehand. This is the advantage of a double contact acid plant, Figure 7.

### Single Contact vs Double Contact Acidmaking

Figure 5 is a schematic flowsheet of a single contact acidmaking plant. SO<sub>3</sub> gas and 1.5% H<sub>2</sub>O, 98.5% H<sub>2</sub>SO<sub>4</sub> acid are contacted only once. Figure 7 is a schematic flowsheet of a double contact plant.



**Figure 7:** Schematic of 3-1 double contact acid plant. The increase in total SO<sub>2</sub> oxidation after each bed is notable. Note the intermediate H<sub>2</sub>SO<sub>4</sub> making step, bottom right.

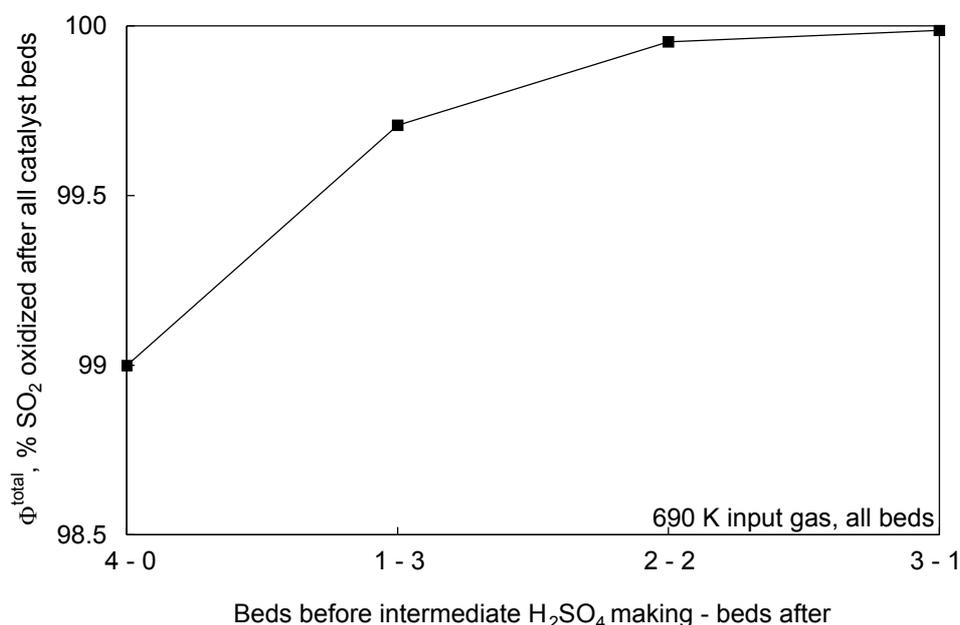
SO<sub>3</sub> gas and 1.5% H<sub>2</sub>O, 98.5% H<sub>2</sub>SO<sub>4</sub> acid are contacted twice with SO<sub>2</sub> + 1/2 O<sub>2</sub> → SO<sub>3</sub> oxidation between contacts.

### *Advantage of Double Contact Acidmaking*

Figure 8 shows the advantage of double contact acidmaking. A four catalyst bed (4 - 0) single contact plant oxidizes only 99% of its feed  $\text{SO}_2$  causing 1% of the feed  $\text{SO}_2$  to leave in acid plant off-gas.

The Figure 7 (3 - 1) contact plant, on the other hand, oxidizes 99.9% of its feed  $\text{SO}_2$ , causing less than 0.1% of the feed  $\text{SO}_2$  to leave the acid plant. This is based on achieving equilibrium in each catalyst bed.

It does so because the feed gas to its after  $\text{H}_2\text{SO}_4$  making catalyst bed contains zero  $\text{SO}_3$  - allowing Reaction (2) to go almost to completion after intermediate  $\text{H}_2\text{SO}_4$  making.



**Figure 8:**  $\text{SO}_2$  oxidation efficiencies after all catalyst beds. 4 - 0 is a single contact plant with four catalyst beds. 3 - 1 is a double contact plant with three beds before intermediate  $\text{H}_2\text{SO}_4$  making and one bed after intermediate  $\text{H}_2\text{SO}_4$  making etc. The superior performance of double contact acid plants is notable. The optimum performance of the 3 - 1 arrangement is also notable.

### **Final Comments**

Sulphuric acid manufacture is most efficient when the acid plant is run continuously with ultra clean feed gas and ultra efficient dehydration.

Cool catalyst bed input gas temperatures (with low melting point Cs-enhanced catalyst) also help. They increase  $\text{SO}_2$  oxidation efficiency and avoid destructive overheating of the catalyst.

Acid plants are now being designed to capture every last MJ of energy. This endeavour should not, however, be allowed to interfere with continuous plant operation especially with metallurgical plants - where the valuable product is metal, not acid.

## PART II: OTHER TREATMENT METHODS FOR SO<sub>2</sub> BEARING GASES

Lower strength (0.5 - 5 vol.% SO<sub>2</sub>) gases are not continuously treated in traditional contact-type acid plants. Their low SO<sub>2</sub> strength requires a non-economical amount of supplemental fuel to be burned to maintain the catalyst beds at optimum SO<sub>2</sub> oxidation temperatures.

In addition, the complexity and capital cost of acid production may not be justified for low tonnage applications. Site-specific factors may not favour direct sulphuric acid production, *e.g.*, remote sites with poor or negative acid netbacks. Therefore, many alternative SO<sub>2</sub> treatment methods have been developed.

Most technologies have evolved as a result of the requirements of a number of industries and their specific process and regulatory mandates. SO<sub>2</sub> removal utilizing treatment methods other than contact acid plant technology is common in petroleum, power generation, incineration, as well as pulp and paper and is continuing to become more common in metallurgical installations.

Each industry has specific process characteristics and scrubbing needs. Many of the technical problems encountered in the past with scrubbing are the result of the misapplication of a scrubbing process. For example, a limestone slurry scrubber that works well on the steady, weak SO<sub>2</sub> strength gas generated in a coal-fired boiler will not be suitable for the stronger, fluctuating gas produced by metallurgical processes. The selection of an SO<sub>2</sub> scrubbing technology is usually a difficult task due to the large number of processes available (about 80 are presently commercially active). Some of them include:

- a) Scrubbing, producing by-products and/or wastes:
  - Direct Lime Slurry
  - Direct Limestone Slurry
  - 'Dry' sorbent, including spray drying and circulating dry scrubbers
  - Once-through Sodium
  - Magnesium Oxide
  - Various Dual Alkali processes
  - Seawater
  - Ammonia
- b) Regenerable processes producing high strength SO<sub>2</sub> gas streams for further treatment in a contact acid plant or similar
  - Absorption/regeneration of SO<sub>2</sub> in amine solutions
  - Wellman-Lord
  - Non-amine, organic scrubbing (*e.g.* Solinox®)
- c) Other acid producing processes such as:
  - Sulfacid®
  - Peroxide scrubbing
  - Petersen-Fattinger process
  - WSA (Wet gas Sulphuric Acid)

Several of the above processes have been used in the metallurgical industry in South Africa, including the following installations:

**Table I:** Summary of South African metallurgical SO<sub>2</sub> treatment processes

Location	Process	Gases Treated	Gas Volume Nm <sup>3</sup> /h	Inlet SO <sub>2</sub> Concentration vol.%, dry basis	Start-up Date
Lonmin Platinum	Sodium-lime, concentrated mode dual alkali	Electric furnace and converter	200 000	2	2003
Impala Platinum	Sulfacid®	Electric Furnace	50 000	1	2002
Anglo Platinum, Waterval Smelter	Petersen-Fattinger	Electric Furnace	65 000	0.5 - 1	2002

### Scrubbing

Table II presents an overview of some common commercial scrubbing processes grouped into their general class. It must be noted that there are several variations of each class. The key features of these processes are summarized below:

- **Lime slurry and limestone scrubbing** is suitable for relatively low SO<sub>2</sub> concentrations and moderate collection efficiencies. They have very high liquid circulation rates, can often be designed for zero effluent discharge, and can produce a marketable quality of gypsum.
- **Spray drying** and circulating dry scrubbers are applicable to hot gases with a significant amount of evaporative capacity. SO<sub>2</sub> absorption occurs as water evaporates leaving behind a dry mixture of sulphate and sulphite solids. Because final collection occurs in a baghouse (or ESP), there is no segregation of process and CaSO<sub>3</sub>/CaSO<sub>4</sub> solids.
- While there are several types of **dual alkali** processes in operation, they all use a soluble scrubbing agent (usually sodium or aluminum based), which is regenerated by reaction with another alkali (usually calcium based). These processes offer the advantages of solution scrubbing, a solid by-product and the ability to handle higher strength SO<sub>2</sub> gases. These advantages come at the cost of a more complex process.
- **Once through sodium processes** use soda ash or caustic and produce a solution of soluble sodium salts. They are simple and effective, but use a costly reagent, and have a liquid effluent. Seawater scrubbers are actually a form of this, making use of natural alkalinity in seawater (sodium bicarbonate).

A number of decisions are required to select and define the most appropriate scrubbing technology for any given application. Key considerations in the selection process are as follows:

- Process operating conditions; of particular importance are SO<sub>2</sub> concentrations and the nature of fluctuations. Lime/limestone systems are typically limited to fairly weak gas of less than 6 000 to 8 000 ppm SO<sub>2</sub> and can be adversely affected by rapid changes in concentration. Temperature and water content impact the evaporative capacity of the gas and, therefore, the ability to achieve a water balance with zero water discharge.
- Performance requirements; outlet SO<sub>2</sub> targets in terms of concentration and efficiency needed to achieve this target.
- Disposal issues; both solid waste characteristics/disposal costs and wastewater issues need to be comprehended as part of the process selection.
- Process reliability/availability; many SO<sub>2</sub> scrubbing systems have incurred significant downtime, usually due to scaling.
- Operating versus capital costs, particularly as they relate to reagent, disposal and power costs.
- Site specific factors; there are usually a number of specific issues at each facility that require consideration. Existing equipment and auxiliary facilities, availability of reagents, water treatment facilities and disposal/re-use of by-products.

Many scrubbers produce a material that can be marketed, partially off-setting the operating cost of the scrubber and more importantly, eliminating waste disposal problems. The most common saleable by-product is gypsum for use in cement or wallboard manufacture. Nearly 75% of the gypsum produced by flue gas desulphurization (FGD) in the United States is used in wallboard.

Another, less common, saleable by-product is ammonium sulphate (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> produced by scrubbing SO<sub>2</sub> bearing gases with ammonia. The process is typically used for treating tail gases from contact type acid plants associated with fertilizer production facilities.

**Table II: Overview of Scrubbing Processes**

Process	Reagents	By-Products	Principal Reactions (H <sub>2</sub> O Not Always Shown)	Applicable Inlet SO <sub>2</sub> (ppm)	Proven Efficiency (%)	Order of Magnitude Capital Cost US\$/Nm <sup>3</sup> /h	Order of Magnitude Operating Cost US\$/t SO <sub>2</sub>	Typical Scrubbing Vessel
Lime Slurry	CaO	CaSO <sub>x</sub>	CaO + SO <sub>2</sub> = CaSO <sub>3</sub> 2H <sub>2</sub> O + CaSO <sub>3</sub> + 1/2O <sub>2</sub> = CaSO <sub>4</sub> •2H <sub>2</sub> O	<100-10 000	90-97	100-150	175	Open Spray Tower
Limestone Slurry	CaCO <sub>3</sub>	CaSO <sub>x</sub> (gypsum)	CaCO <sub>3</sub> + SO <sub>2</sub> = CaSO <sub>3</sub> + CO <sub>2</sub> 2H <sub>2</sub> O + CaSO <sub>3</sub> + 1/2O <sub>2</sub> = CaSO <sub>4</sub> •2H <sub>2</sub> O	1000-6 000	~95	100-150	150	Open Spray Tower
Spray Drying - Lime	CaO	CaSO <sub>x</sub>	1/2H <sub>2</sub> O + CaO + SO <sub>2</sub> = CaSO <sub>3</sub> •1/2H <sub>2</sub> O 2H <sub>2</sub> O + CaSO <sub>3</sub> + 1/2O <sub>2</sub> = CaSO <sub>4</sub> •2H <sub>2</sub> O	<100-3 000	90-95	125-200	200	Spray Tower + Bag-house
Dual Alkali (Lime Sodium)	CaO NaOH Na <sub>2</sub> CO <sub>3</sub>	CaSO <sub>x</sub> (gypsum)	2NaOH + SO <sub>2</sub> = Na <sub>2</sub> SO <sub>3</sub> + H <sub>2</sub> O H <sub>2</sub> O + Na <sub>2</sub> SO <sub>3</sub> + SO <sub>2</sub> = 2NaHSO <sub>3</sub> 2NaHSO <sub>3</sub> + Ca(OH) <sub>2</sub> = Na <sub>2</sub> SO <sub>3</sub> + CaSO <sub>3</sub> •1/2H <sub>2</sub> O + 1 1/2 H <sub>2</sub> O Na <sub>2</sub> SO <sub>3</sub> + Ca(OH) <sub>2</sub> = 2NaOH + CaSO <sub>3</sub>	1 200- 150 000 +	99+	125-175	175	Tray or Packed Tower
Dual Alkali (Dowa)	CaCO <sub>3</sub> Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	CaSO <sub>4</sub> • 2H <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub> Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + 3SO <sub>2</sub> + 3/2 O <sub>2</sub> = 2Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> 2Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + 3CaCO <sub>3</sub> = Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> •Al <sub>2</sub> O <sub>3</sub> + 3CaSO <sub>4</sub> + 3CO <sub>2</sub>	1 000-25 000	85-98	150	190	Tray or Packed Tower
Once Through Seawater	NaHCO <sub>3</sub> (CaO)	Na <sub>2</sub> SO <sub>3</sub> Na <sub>2</sub> SO <sub>4</sub>	2NaHCO <sub>3</sub> + SO <sub>2</sub> = Na <sub>2</sub> SO <sub>3</sub> + 2CO <sub>2</sub> + H <sub>2</sub> O Na <sub>2</sub> SO <sub>3</sub> + 1/2O <sub>2</sub> = Na <sub>2</sub> SO <sub>4</sub>	up to ~2 000	~98	very site specific	60-120	Tray or Packed Tower
Once Through Sodium	NaOH Na <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> SO <sub>3</sub> Na <sub>2</sub> SO <sub>4</sub>	2NaOH+SO <sub>2</sub> = Na <sub>2</sub> SO <sub>3</sub> +H <sub>2</sub> O Na <sub>2</sub> SO <sub>3</sub> + 1/2O <sub>2</sub> = Na <sub>2</sub> SO <sub>4</sub>	<100- 10 000+	99+	40-80	350-480	Tray or Packed Tower

## Regenerable Processes

**Amine absorb/desorb** (Cansolv<sup>®</sup> 3 and TurboSOx<sup>®</sup> 4) use amines to absorb SO<sub>2</sub> gas in a packed or tray tower absorber. The SO<sub>2</sub> rich amine is transferred to a desorb column and steam heated to strip high purity SO<sub>2</sub> gas and water vapour from the amine. The lean amine is returned to the absorber. The high strength SO<sub>2</sub> is cooled to condense water vapour and ducted to another facility, e.g. acid plant for additional processing to make sulphuric acid.

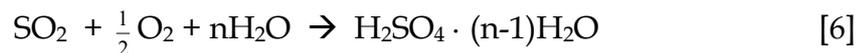
Amine absorb/desorb is well suited for treating gases with a wide range of fluctuating SO<sub>2</sub> concentrations, but is logistically difficult for applications without an on-site acid plant or similar. The process utilizes solution-based absorption and should be reliable, although there are comparatively few installations at present.

Other regenerable processes have a similar configuration, and similar implementation issues.

## Other Sulphuric Acid Processes

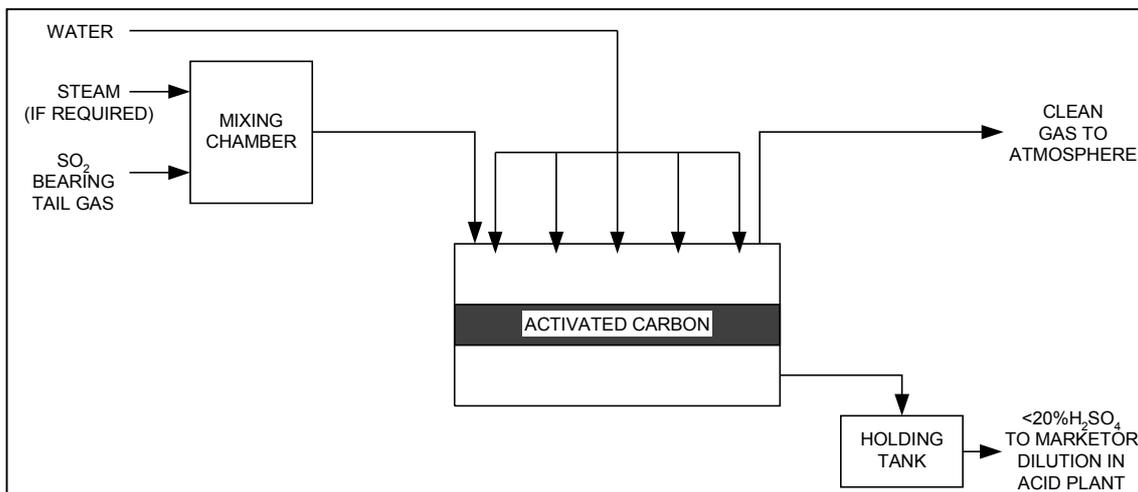
### Sulfacid<sup>®</sup> Process

SO<sub>2</sub>, H<sub>2</sub>O and O<sub>2</sub> react in an activated carbon catalyst to form H<sub>2</sub>SO<sub>4</sub> in the Donau Carbon<sup>5</sup> Sulfacid<sup>®</sup> process (Figure 9). The product of the process is weak (<20% H<sub>2</sub>SO<sub>4</sub>) sulphuric acid. Multiple activated carbon beds arranged in parallel are often used. The acid making reaction for the Sulfacid<sup>®</sup> process is as follows:



The process can treat feed gases with:

- less than 1 volume% SO<sub>2</sub>
- a minimum 7 volume% O<sub>2</sub>, and
- a maximum of 30 mg/Nm<sup>3</sup> of dust minimizing activated carbon fouling.



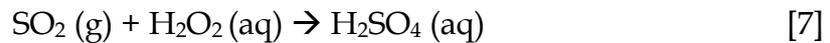
**Figure 9:** Sulfacid<sup>®</sup> process for removal of SO<sub>2</sub>. Feed gases are mixed with steam (if required) in the mixing chamber before entering the reactor holding the activated carbon catalyst.

Sulphuric acid is formed from the oxidation of SO<sub>2</sub> in the presence of H<sub>2</sub>O and activated carbon. The acid formed on the activated carbon is washed into a holding tank where it is pumped to the acid plant's acid circulation system for dilution or sold to customers.

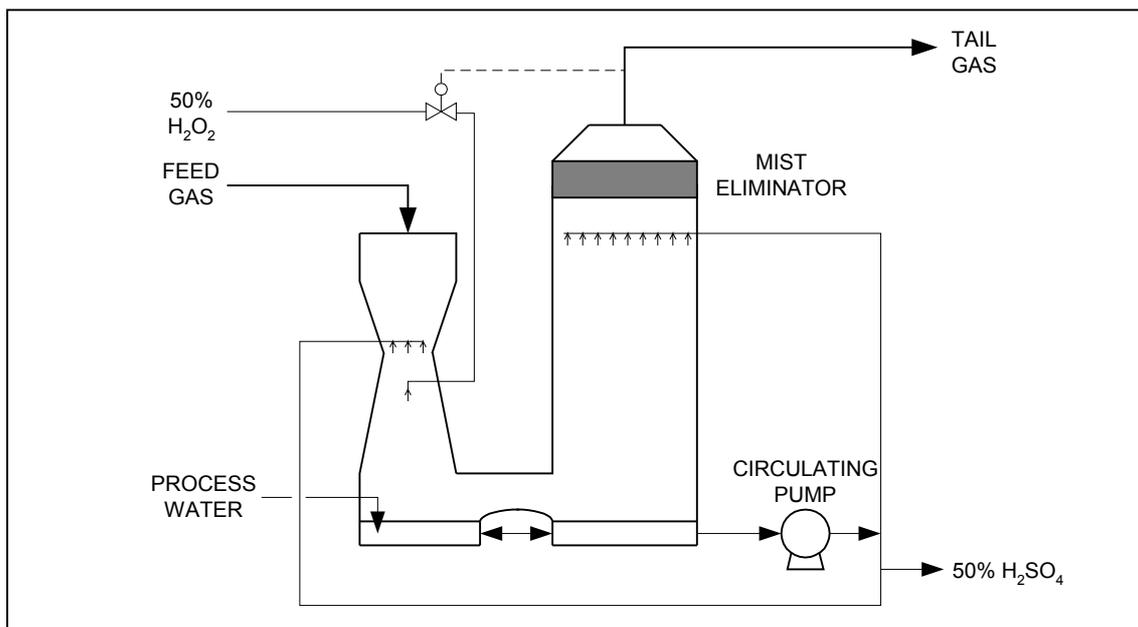
Sulfacid®'s advantages are its relatively low capital and operating cost and production of H<sub>2</sub>SO<sub>4</sub>. Its main disadvantage is that its acid product strength is weak <20% H<sub>2</sub>SO<sub>4</sub> making it difficult to sell to off-site customers. About 50 Sulfacid® plants are presently in operation.

### Peroxide Scrubbing

Lurgi Metallurgie and Süd-Chemie developed the Peracidox®<sup>6</sup> process specifically to remove residual SO<sub>2</sub> from tail gases from double absorption sulphuric acid plants. The process uses hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) to oxidise SO<sub>2</sub> to sulphuric acid:



Scrubbing is achieved by direct contact in a counter-current spray tower. The peroxide reacts with SO<sub>2</sub> in the first chamber and overflows to the second chamber. The bleed acid concentration is ~50% H<sub>2</sub>SO<sub>4</sub>, which can be recycled to the acid plant as dilution water or sold as a by-product should a market exist. A basic flow schematic is provided in Figure 10.



**Figure 10:** Peracidox® process flow schematic. 50% H<sub>2</sub>O<sub>2</sub> reacts with SO<sub>2</sub> forming a 50% H<sub>2</sub>SO<sub>4</sub> solution that is sent to the contact plant or market. Tail gases can be as low as 20 ppm SO<sub>2</sub>. H<sub>2</sub>SO<sub>4</sub> vapour and SO<sub>3</sub> are also removed from the feed gas stream.

The advantages of the Peracidox® process include its simplicity, small footprint, high SO<sub>2</sub> removal efficiency and low capital cost. Its biggest disadvantages are its high operating cost due to peroxide and its relatively low acid strength product (~50% H<sub>2</sub>SO<sub>4</sub>). For these reasons the Peracidox® process is most suited for acid plant tail-gas treatment where SO<sub>2</sub> concentrations are consistently low or only temporarily high (e.g. during acid plant start-up). In

this case Peracidox<sup>®</sup> is economical because peroxide consumption is small and its initial capital costs are low.

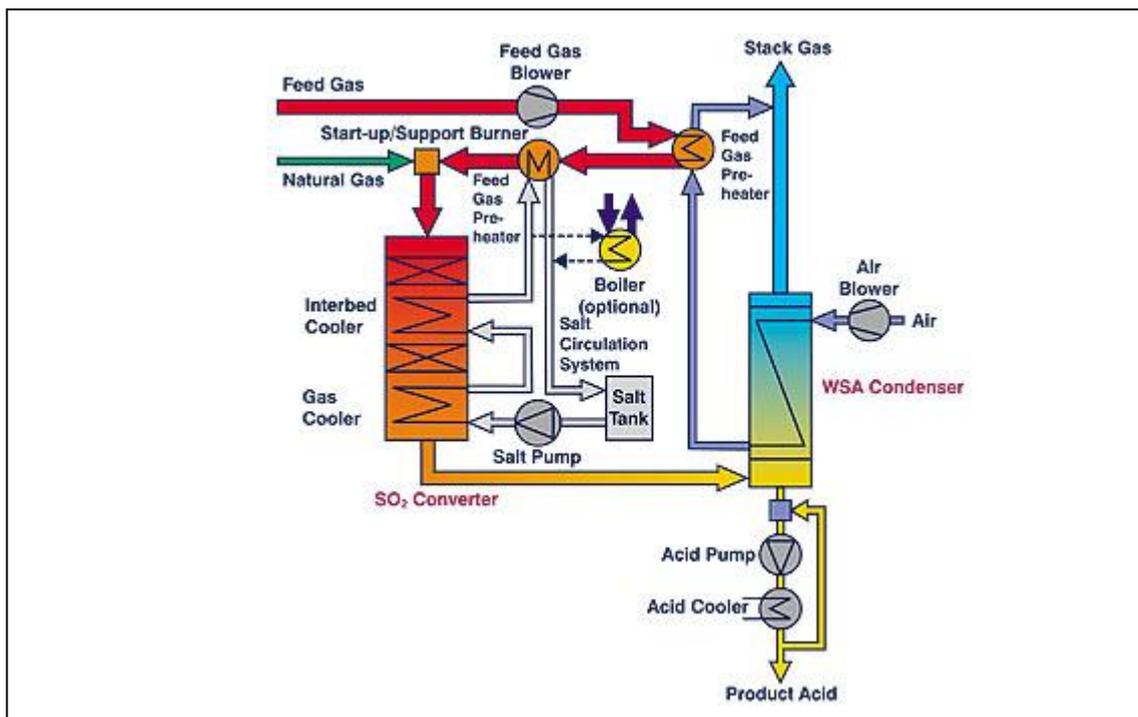
### Petersen-Fattinger Process

The chemistry of this process is based on the lead chamber process commonly used in the early 1900's. SO<sub>2</sub> and H<sub>2</sub>O bearing feed gases are contacted in a series of packed towers with 65% H<sub>2</sub>SO<sub>4</sub> containing nitrosyl sulphuric acid (NOHSO<sub>4</sub>) to promote the formation of H<sub>2</sub>SO<sub>4</sub> from SO<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>O<sup>7</sup>. The acidmaking reaction generates NO(g) and NO<sub>2</sub>(g), which are subsequently reabsorbed into higher strength acid to form more acid catalyst. Nitric acid must be added to ensure correct levels of NOHSO<sub>4</sub> are present for catalysis. Product acid is in the form of 70-76% H<sub>2</sub>SO<sub>4</sub> with some nitrosyl present.

The process advantages are its relatively high strength acid product (76% H<sub>2</sub>SO<sub>4</sub>) and low operating cost. Its disadvantages are its materials of construction sensitivity, presence of NO<sub>x</sub> in tail gas, presence of nitrosyl compounds in its product acid and, currently, only one large-scale commercial installation.

### WSA (Wet gas Sulphuric Acid)

Haldor Topsøe's WSA (Wet gas Sulphuric Acid)<sup>8</sup> process treats wet, low SO<sub>2</sub> concentration (0.2% - 6% SO<sub>2</sub>) gases. SO<sub>2</sub> bearing gases are first cooled and cleaned in a gas cleaning plant before being heated, sent through a converter for catalytic oxidation of SO<sub>2</sub> to SO<sub>3</sub> and passing through a glass tube condenser where H<sub>2</sub>O in the gas combines with SO<sub>3</sub> to produce strong (98% H<sub>2</sub>SO<sub>4</sub>) sulphuric acid. A basic flow diagram is provided in Figure 10.



**Figure 10:** WSA process flow schematic. A natural gas burner is used to provide supplemental heat for catalytic SO<sub>2</sub> oxidation. Heat generated in the catalyst beds during catalytic SO<sub>2</sub> oxidation is recovered in a molten salt circulation system, which is used to heat incoming feed gas.

WSA's advantages are its strong acid product (98% H<sub>2</sub>SO<sub>4</sub>) and its ability to treat wet, SO<sub>2</sub> bearing gases ranging from 1.4% SO<sub>2</sub> to 6.5% SO<sub>2</sub> while oxidizing 98-99%<sup>9</sup> of its incoming feed gas SO<sub>2</sub>. Its only disadvantage for metallurgical application is a limited number of installations.

### Final Comments

Sulphur dioxide streams tend to fall into two categories - low strength and high strength. High strength gases (>5% SO<sub>2</sub>) are treated in contact type acid plants, where the total SO<sub>2</sub> tonnage justifies the expense and complexity. Low strength gases (0 - 2% SO<sub>2</sub>) are typically treated in scrubbers with neutralizing agents producing various by-products, e.g. gypsum, or waste streams for disposal.

Peracidox<sup>®</sup> and Sulfacid<sup>®</sup> processes are efficient at removing SO<sub>2</sub> from gases, but produce weak H<sub>2</sub>SO<sub>4</sub> making their use less widespread.

The WSA process has the ability to produce strong 98% H<sub>2</sub>SO<sub>4</sub> while treating a wide range of low SO<sub>2</sub> strength (1.4% - 6.5%) gases making it an attractive process. Its use will likely continue to increase.

### REFERENCES

1. W.G. Davenport, M.J. King, *Sulfuric Acid Manufacture, Analysis, Control and Optimization*, Elsevier Science, 2005.
2. I. Robinson, N. Van Averbeke, A.J. Harding, J.A.G. Duval, P. Mwape, J.W. Perold, E.J. Roux, *South Africa's Mineral Industry 2003/2004, Department: Minerals and Energy Republic of South Africa*, 2004, pp. 192.
3. <http://www.cansolv.com>
4. <http://www.turbosonic.com>
5. <http://www.dcffm.de>
6. <http://www.outokumpu.com>
7. V. Fattinger and W. Jäger, A Two-Stage Process Combination for the Production of Sulfuric Acid or Oleum with Next to Zero SO<sub>2</sub> Emissions, *Sulphur 98 Conference Preprints Volume 2, British Sulphur*, 1998, pp. 157-170.
8. <http://www.topsøe.com>
9. A. Kristiansen, *Topsøe Wet gas Sulphuric Acid (WSA) Technology for Fixation of SO<sub>2</sub> in Off-gases in the Metallurgical Industry*, 2005, pp. 12.