

# Innovative Path-Breaking “Cold Process” to Manufacture Sulphonating Agents and Sulphur-Based Chemicals

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## Abstract

Manufacture of Sulphuric acid and Sulphonating agents underwent revolutionary change as a result of the inventive contact process using Vanadium Pentoxide catalyst in the 1950's.

The “Single-Contact Single-Absorption” process was widely used until the 1970's. The conversion efficiency of  $\text{SO}_2$  to  $\text{SO}_3$  was restricted to 96.5% resulting in stack emissions of 16 to 20 Kgs of Sulphur dioxide per ton of acid produced.

Global warming and environmental concern prompted further improvement by introducing DCDA, Double-Contact Double-Absorption process. In the DCDA process the product  $\text{SO}_3$  was absorbed by introduction of Inter-Pass Absorption Tower (IPAT) keeping  $\text{V}_2\text{O}_5$  contact process unchanged. Thus, the overall conversion efficiency was raised to 99.5-99.7 %, thereby reducing Sulphur dioxide emissions to below 4 Kgs per ton of acid produced. This is today taken as an International Standard as recommended by Environmental Protection Agency of USA.

Even so, at the current production level of over 150 million tons of Sulphuric acid per annum, this results into over one million tons of acid rain per year! This acid rain has serious impact on flora and fauna as well as aquatic life.

The path-breaking “Cold Process” invented by Navdeep Enviro and Technical Service Pvt. Ltd, Mumbai (India), and for which a patent has been applied at the International Patent Agency in Geneva, is designed to produce Sulphuric acid and Sulphonating agents with zero emission of Sulphur dioxide, which totally eliminates acid rain. This paper outlines the techno economic features of the process, giving cost effectiveness of reduced plant area, lower maintenance costs, and higher cogeneration of steam with lower utility consumption.

## Introduction

For over a century, most industrial products have needed the use of Sulphuric Acid at one stage or another of their manufacture. Included are universally used products such as steel, paper, textile, drugs, dyes, paints, fertilisers, non-ferrous metals, petroleum products, computer products etc. This is the reason why Sulphuric Acid is known as King of Chemicals. The manufacture of Sulphuric acid and Sulphonating agents underwent revolutionary change as a result of the inventive contact process using Vanadium Pentoxide catalyst in the 1950's.

The SCSA (“single-contact single-absorption”) process was widely used until the 1970's. The conversion efficiency of  $\text{SO}_2$  to  $\text{SO}_3$  was restricted to 96.5% resulting in stack emissions of 16 to 20 Kgs of Sulphur dioxide per ton of acid produced.

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Even so, at the current production level of over 150 million tons of Sulphuric acid per annum, the DCDA process results into over one million tons of acid rain per year! This acid rain has serious impact on flora and fauna as well as aquatic life.

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“Intentional Wisdom” has been the guiding principle for over 150 years at MIT, Cambridge, USA. The author completed his Post-graduation in Chemical Engineering at MIT in 1958, taking MIT’s guiding principle to heart. On his return to India in 1961, after serving as a faculty member at MIT, joined M/s. Dharamsi Morarji Chemical Company Ltd. (DMCC).

DMCC produced phosphatic fertilisers requiring Sulphuric Acid. From a modest beginning of an SCSA 50 TPD Sulphuric Acid plant, over the period of 27 years, DMCC designed and operated a DCDA 800 TPD plant, which was a considerable achievement. On retirement from DMCC in 1987, the author founded an innovative consultancy company namely Navdeep Enviro and Technical Services Pvt. Ltd. (NEAT) as Managing Director. Over the past 30 years, NEAT has undertaken more than 100 projects in the manufacture of Sulphuric Acid and Sulphonating agents, which have been cost effective and environment friendly.

The latest innovation, “The Cold Process”, is the subject of this paper. It is envisaged that by adopting this path-breaking technology, the costs of chemicals based on Sulphuric Acid and Sulphonating Agents will be reduced considerably and would eliminate totally the emission of SO<sub>2</sub>.

## Historical Background History of Sulphuric Acid

Sulphuric acid was known to medieval alchemists under a variety of names, including oil of *vitriol* and *spirit of vitriol*. These substances were produced by the dry distillation of minerals including iron (bivalent) sulphate heptahydrate, FeSO<sub>4</sub>·7H<sub>2</sub>O known as green vitriol, and copper (bivalent) sulphate pentahydrate, CuSO<sub>4</sub>·5H<sub>2</sub>O known as blue vitriol. When heated, these compounds decompose into iron and copper oxides, respectively, giving off water and Sulphur trioxide, the two of which combine to produce a dilute solution of Sulphuric Acid. Preparations like these have been ascribed to alchemists, including the 12<sup>th</sup> century Arab Abou Bakr al-Rhases and the 13<sup>th</sup> century German Albertus Magnus.

In the 17<sup>th</sup> century the German-Dutch chemist Johann Glauber prepared Sulphuric acid by burning Sulphur together with saltpeter (potassium nitrate, KNO<sub>3</sub>) in the presence of Steam. As the saltpeter decomposes, it oxidises the Sulphur to SO<sub>3</sub>, which combines with water to produce H<sub>2</sub>SO<sub>4</sub>. In 1736, Joshua Ward, a London pharmacist, used this method to begin the first large-scale production of Sulphuric Acid.

In 1746, in Birmingham, John Roebuck began producing Sulphuric acid this way in lead lined chambers, which were stronger, less expensive and could be made larger than the glass containers which had been used previously. This *lead chamber process* allowed the effective industrialization of Sulphuric acid production, and with several refinements remained the standard method of production for almost 2 centuries.

John Roebuck’s Sulphuric Acid was only about 35-40% Sulphuric Acid. Later refinements in the lead-chamber process by the French chemist Joseph-Louis Gay-Lussac and the British chemist John a Glover improved this to 78%. However, the manufacture of some dyes and other chemical processes require a more concentrated product and throughout the 18<sup>th</sup> century this could only be made by dry distilling minerals in a technique similar to the original alchemical processes. Pyrite (iron disulphide, FeS<sub>2</sub>) was heated in air to yield iron (bivalent) sulphate FeSO<sub>4</sub>, which was oxidised by further heating in air to form iron (trivalent) sulphate Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, which when heated to 480° Celsius, decomposed into iron (trivalent) oxide and Sulphur trioxide, which could be passed through water to yield Sulphuric Acid in any concentration. The expense of this process prevented the large scale use of concentrated Sulphuric acid.

In 1831, the British vinegar merchant Peregrine Philips patented a far more economical process for producing Sulphur trioxide and concentrated Sulphuric acid. In this process, SO<sub>2</sub>, produced by roasting either Sulphur or pyrite in air, is combined with additional air and passed over a platinum catalyst at high temperatures, where it combines with oxygen from the air to produce nearly pure SO<sub>3</sub>. Even so, there was little demand for highly concentrated Sulphuric acid at the time and the first Sulphuric acid plant using this *Contact Process* was not built until 1875 in Freiburg, Germany.

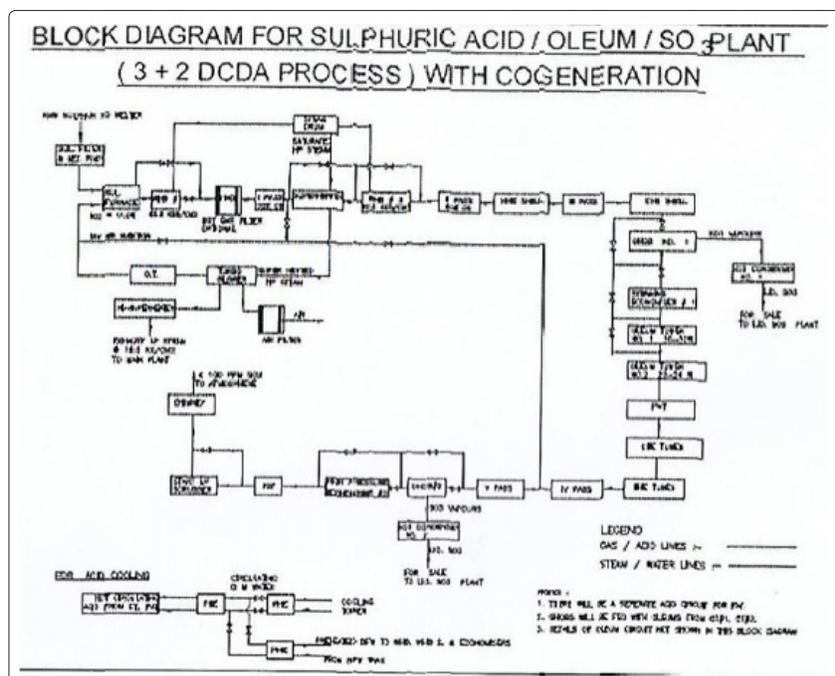
The development of the less expensive and less easily contaminated Vanadium Pentoxide (V<sub>2</sub>O<sub>5</sub>) catalyst by BASF in Germany in 1915, combined with increasing demand for concentrated Sulphuric acid by the chemical industry, led to the gradual replacement of the lead-chamber process by the contact process. In 1930, Sulphuric acid produced by the Contact Process accounted for only 25% of Sulphuric Acid production, while today nearly all Sulphuric acid is manufactured in this way.

The conversion of SO<sub>2</sub> to SO<sub>3</sub> takes place by the reversible, exothermic reaction  
$$2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3 \quad \Delta H = -22.93 \text{ Kcal/g Mole}$$

While the rate of the forward reaction increases with temperature, the equilibrium conversion decreases (thus reducing the yield of SO<sub>3</sub>).

The Contact Process was further modified to the DCDA process, which uses Le Chatelier’s principle. According to this when the SO<sub>3</sub> produced (as a result of conversion of SO<sub>2</sub> by the catalytic process) is absorbed by the intermediate absorption towers, the equilibrium conversion shifts to the right, i.e., more SO<sub>2</sub> is converted to SO<sub>3</sub>. This is accomplished by reheating and then passing the reaction gases through an additional bed of catalyst. The SO<sub>3</sub> produced (additionally) is then absorbed in a second absorption tower.

[See Figure 1 - flow diagram (3+2) DCDA process].



### Unique Properties of Liquid SO<sub>2</sub> and Liquid SO<sub>3</sub>

In order to understand the process involving the production of Sulphur trioxide using a stoichiometric combination of liquid Sulphur and liquid Sulphur dioxide, we need to examine the unique properties of liquid SO<sub>2</sub> and liquid SO<sub>3</sub>.

### Chemical and Physical Properties of Sulphur Dioxide and Sulphur Trioxide

#### Introduction

In order to appreciate the impact of the properties of liquid Sulphur dioxide and liquid trioxide on future technology, it is important that an in-depth analysis of their properties be understood.

Though the data given in this chapter as available in literature, the practical application of the remarkable physical as well as chemical properties of Sulphur dioxide and Sulphur trioxide has been experienced and applied on large scale only recently.

The three main features of these two important chemicals are:

- High solubility of Sulphur trioxide in liquid Sulphur dioxide
- Reaction of liquid Sulphur trioxide with liquid Sulphur in stoichiometric proportions instantaneously to produce Sulphur dioxide:  $S + 2SO_3 = 3 SO_2$
- Liquefaction of pure Sulphur dioxide at room temperatures under moderate pressures of 5-6 kg/cm<sup>2</sup> (Please see Figure 2.1)

The current Sulphonation techniques involves Sulphonating agents such as Sulphuric acid, 25 % oleum, 65 % oleum and Sulphur trioxide, and high temperature reactions due to exothermic nature of Sulphonation. The current techniques of Sulphonation further require elaborate chilling and cooling systems, and are generally batch operations and hence require a battery of reactors having varying time cycles.

### Sulphur Dioxide Physical Properties

Sulphur dioxide SO<sub>2</sub> is a colourless, non-inflammable, toxic gas

with a characteristic pungent smell and acidic taste. (Table 2.1)

### Vaporisation of SO<sub>2</sub>

It is important to analyse the physical property of condensation points at various pressures and concentrations of SO<sub>2</sub>

Table 2.1 Physical properties of Sulphur dioxide

It can be observed from the attached Fig. 1.2 that for 100 % liquid SO<sub>2</sub>, moderate pressures are required to liquefy SO<sub>2</sub> at ambient temperatures between 30 and 40° C.

### The Solubility of SO<sub>2</sub> in Sulphuric Acid

The solubility of Sulphur dioxide in Sulphuric acid (see Fig. 1.3) rises in proportion to the SO<sub>2</sub> partial pressure in good conformity with Henry's law, and is increased by lowering the temperature, as represented graphically in Fig. 1.2. In the solution, Sulphur dioxide is present mainly as SO<sub>2</sub> molecules, but Raman spectroscopy confirms the presence in minor proportions of the species HSO<sub>3</sub>, S<sub>2</sub>O<sub>5</sub> and H<sub>2</sub>SO<sub>3</sub>.

The last of these, Sulphurous acid (the anhydride of which is Sulphur dioxide), exists only in aqueous solution. Aqueous solution of alkaline compounds will absorb much more Sulphur dioxide than pure water (Please see Fig. 2.2) because of the formation of hydrogen sulphite (bisulphite) and sulphite ions.

### Solubility of Sulphur Dioxide Water

It can be observed from Fig 2.2 that the solubility of Sulphur dioxide in g/kg H<sub>2</sub>O increases with pressure and reduces with temperature.

This property is of importance in industrial applications in scrubbing of Sulphur dioxide in tail gases.

### Chemical Properties of Sulphur Dioxide

Sulphur dioxide is very stable; thermal dissociation becomes

significant only above 2,000 °C. It can be decomposed by shock waves, irradiation with ultraviolet or X-rays, or by electric discharges.

The reaction of Sulphur dioxide with oxygen to form Sulphur trioxide is industrially the most significant of all its reaction because of its importance in Sulphuric acid production. In the gas phase, it will only take place at elevated temperatures and, for a satisfactory yield of Sulphur trioxide, it requires the presence of a catalyst. In aqueous solution Sulphur dioxide is oxidized to Sulphuric acid at low temperatures by air in the presence of activate coke or nitrous gases or by oxidizing agents like hydrogen peroxide.

The reduction of Sulphur dioxide with hydrogen, carbon or carbon compounds such as methane or carbon monoxide is also of industrial interest. These reactions require high temperature or catalysts or both. They result in mixtures of elemental Sulphur with hydrogen sulphide. If carbon or a carbon compound has been used as the reducing agent, carbon-containing species such as carbon dioxide, carbonyl sulphide and carbon disulphide will be formed as well.

Sulphur dioxide will normally oxidize metals at elevated temperatures, simultaneously forming metal sulphides and oxides. Liquid Sulphur dioxide is a relatively efficient solvent with some water-like properties. Polar inorganic compounds are usually insoluble or only sparingly soluble in liquid Sulphur dioxide, whereas covalent inorganic and organic compounds are often dissolved, mostly forming stable solutions. The fact that aromatic hydrocarbons will dissolve more readily than aliphatic in Sulphur dioxide is exploited on an industrial scale for the extraction of aromatics from crude oil according to the Edeleanu process.

### Physical Properties of Sulphur Trioxide

Sulphur trioxide is produced by catalytic oxidation of Sulphur dioxide in concentrations of 12-15 % in gaseous form. To produce pure Sulphur trioxide the plant gases are passed through oleum towers to produce 25-30 % free SO<sub>3</sub> oleums.

These oleums are boiled in steam heated or gas heated heat exchangers to produce pure Sulphur trioxide.

This is then sent to condensers to produce liquid Sulphur trioxide.

### General Properties of Liquid Sulphur Trioxide

#### Properties of Liquid Sulphur Trioxide

See Fig. 2.3

#### Viscosity of Liquid Sulphur Trioxide

See Fig. 2.4

#### Specific Gravity of Sulphur Trioxide

See Fig. 2.5

#### Vapour Pressure of Liquid Sulphur Trioxide

See Fig. 2.6

#### Molar Heat Capacity of Liquid Sulphur Trioxide

See Fig. 2.7

#### Vaporisation Curves for Sulphur Dioxide

See Fig. 2.1

#### Enthalpy of Sulphur Trioxide Gas

See Fig. 2.8

### Chemical Properties of Sulphur Trioxide

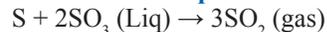
Commercially, Sulphur Trioxide is produced by converting 10-12 % SO<sub>2</sub> by Catalytic Conversion at Temperatures Between 360-600 °C in Multipass Converter of Sulphuric Acid Plant.

This is then further reacted with water to form Sulphuric acid by the equation  $H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$

It is important to note that reaction of Sulphur trioxide gas with water would form micron size droplet and cannot be absorbed to form H<sub>2</sub>SO<sub>4</sub>

Formation of Sulphuric acid from SO<sub>3</sub> gas is exothermic and the absorbing H<sub>2</sub>SO<sub>4</sub> in the absorption towers need to be cooled to maintain efficiency of absorption.

### One of the Special Chemical Properties of SO<sub>3</sub> Which Has Been Safer but not Explored till date



$$\Delta H = -74.3 \text{ kcal/g mole}$$

$$\Delta F = -36.71 \text{ kcal/g mole}$$

Since the free energy change is large negative, the reaction is almost instantaneous. In addition, the reaction generates one additional mole in gaseous form, so there is a pressure increase.

### Sulphur Trioxide Is a Strong Sulphonating Agent for Difficult, Organic and Inorganic Chemicals

#### Treatment of Sulphuric Acid Plant Tail Gas from Final Absorption Tower

The tail gases of Sulphuric acid contact plants consist chiefly of nitrogen and residual oxygen. They also contain Sulphur dioxide in low concentrations which depend on the conversion efficiency attained in the conversion stages. The content of gaseous Sulphur trioxide and Sulphuric acid is essentially a function of the temperature and concentration of the irrigation acid in the final absorber. Under unfavorable operating conditions, as, for example, when the Sulphur dioxide-containing converter feed gases are inadequately dried or contain hydrocarbons, Sulphuric acid mists can be formed which are not removed in the absorption system, even when the concentration and temperature of the absorber acid are at their optimum values. The safest way of removing these acid mists is using a candle type demister. However, this is not very effective in removing excessive Sulphur trioxide concentrations, which may result from poor acid distribution in the absorber

**Note: 3.2.2. – 3.2.16 are given in reference “Advances in Sulphonating Techniques”. (Pg. 9 – 17)**

### Production of Sulphur Trioxide

Though the multistage converters in the plant are generally able to convert more than 99.5% SO<sub>2</sub> to SO<sub>3</sub>, it is practically difficult to condense it as such due to the low concentration of SO<sub>3</sub> in the process gas streams. Hence, the gases are passed through an oleum tower in the plant to absorb the SO<sub>3</sub> in a stream of circulating 25-30% oleum.

A controlled stream of the oleum is then heated (boiled) to release the vapours which contain almost 100% SO<sub>3</sub> with only traces of SO<sub>2</sub>. The vapours are then condensed to obtain liquid SO<sub>3</sub> or are absorbed in oleum to produce 60-65% oleum.

For SO<sub>3</sub> condensers, the falling film type condenser (SO<sub>3</sub> vapours on the shell side and a trickling stream of water on the inside of the tubes) is generally found to be safer as compared to a shell and

tube type unit wherein water is circulated under pressure. However, the latter has a higher heat transfer coefficient due to greater water velocities and needs a lower area for heat transfer. It should be fitted with a pressure release valve with a vent line connected to a scrubber.

Depleted oleum having strength of about 20-22% is returned to the oleum tower to increase its strength again by absorption of SO<sub>3</sub>.

### Oleum Boilers (SO<sub>3</sub> Generators)

These are used for generating SO<sub>3</sub> vapours by boiling 28-32% oleums. The higher the strength of the oleum being boiled the lower the boiling point. Hence it is generally preferred to use higher strengths of oleum coming in to the boilers. There are two distinct variants depending on the heating medium used for boiling oleum. The heating medium is generally in the tubes and the oleum is on the shell side. An entrainment separator is built in or externally provided for separating droplets of oleum from the outgoing SO<sub>3</sub> vapours.

### Steam heated Oleum Boiler – SHOB

The heat transfer rates are high in SHOB due to condensing steam and hence these units are smaller in size. The hold-up of oleum on the shell is also less. These units also need smaller support structures. The plant designer has options available for locating these units since they do not need main process gas duct connections.

Safety issues: A dangerous situation can arise in the case of a tube leak as steam can react violently with oleum. Adequately sized safety valves and the provision of rupture discs is a must. The vent lines from these must be led away from the working area-they can be connected to the gas absorption tower or a suitable gas scrubber. Regular replacement of the tubes every 2 years and pressure tests during annual shutdowns will be found useful.

### Gas heated Oleum Boiler – GHOB

Hot gases from the exit of one or more of the converter passes are used for boiling the oleum. The heat transfer rates are low in GHOB due to process gas being the heating medium and hence these units are bigger in size. The hold-up of oleum on the shell is also greater. These units need bigger and stronger support structures. The plant designer does not have many options available for locating these units since they need main process gas duct connections at inlet and exit.

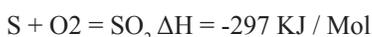
### Manufacture of Liquid SO<sub>2</sub> Historical Background

Liquid Sulphur Dioxide is manufactured for industrial use since past eight decades. The earlier technology required high capital cost involving exotic materials of construction, compression and refrigeration.

During past decade, NEAT has developed and successfully given commercial plants to manufacture Sulphur Dioxide without compression and refrigeration with low capex.

### Manufacture of Liquid Sulphur Dioxide

The conventional method of producing Sulphur dioxide is by combustion of Sulphur followed by absorption-desorption, drying and cryogenic condensation. This process is capital intensive, hazardous, saddled with corrosion and high utility consumption.



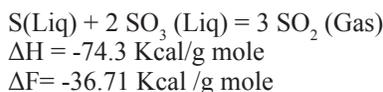
Molten Sulphur at 140 C is fired in an 8-10-meter-long furnace using preheated (80 °C) air. The theoretical temperature achieved by the exit gases is given in Fig. 4.1. For the production of liquid SO<sub>2</sub> high concentrations 16-18 % are necessary. Since the adiabatic temperature in single stage combustion will be high (1600-1800 °C), a twostage combustion system can be used. (Figure. 4.1)

Subsequently pure Sulphur dioxide is produced by chemical reduction of Sulphur trioxide with Sulphur. This route is more direct and attractive due to the fact that process used by IG Farben Industrie of Germany under US patents 3,432,263 and 3,455,652 (1966) is from solid or molten Sulphur to 25 % Oleum at 110 °C giving 98.5 % SO<sub>2</sub> and 1.5 % SO<sub>3</sub>. The excess Sulphur trioxide is further reacted with solid Sulphur in a tower and then traces of Sulphur trioxide are removed by absorbing in 98 % Sulphuric acid prior to compression and condensation.

NEAT's process deals with use of liquid Sulphur and liquid Sulphur trioxide under pressure (8 to 10 kg/cm<sup>2</sup>) to produce pure Sulphur dioxide at relatively low temperature without need for compression of refrigeration.

### Thermodynamic and Kinetic Consideration of the NEAT's Process

It is interesting to note that a highly exothermic nature of Sulphur oxidation in a furnace at about 1000 °C can be carried out at reasonably low temperatures 50-110 °C in a pressurized reactor. This is possible by reaction.



Since the free energy change is large and negative, the reaction is almost instantaneous. In addition, the reaction generates one additional mole in gaseous form. Thus the pressure of the reactor builds up.

If there is a stoichiometric addition of liquid Sulphur trioxide (30 – 40 °C) and molten Sulphur (135-140 °C), under pressure of 8-10 kg/cm<sup>2</sup>, then the Sulphur dioxide (after cleaning) formed (98-99 %) can be liquefied at room temperature. The exothermic heat removal of about 15625 kCal/ton of Sulphur dioxide produced is achieved by circulating cold water through the jacket.

Since the reaction is instantaneous and complete, the reactor volume is very small. However, oleum 25 % is used as a carrier to provide uniform mixing of liquid Sulphur trioxide and liquid Sulphur. Agitation with proper mechanical seal is provided to ensure complete reaction.

The increase in molecules of SO<sub>2</sub> by fifty percent enables build-up of pressure without use of compressor. Fig. 2.1 gives condensation temperature of pure Sulphur dioxide at different pressures. This indicates that if a pressure of 7 to 8 kg/cm<sup>2</sup> is maintained in the system the liquefaction can be done at ambient temperature using water at 35-4 °C, cooling is required at the rate of 1.12 million kCal/ton of product.

The process for the above is shown in block diagram. (Figure. 5.2)

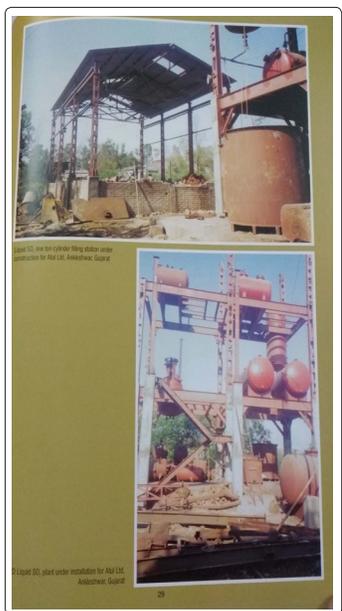
## Process Description

Continuous production of liquid Sulphur dioxide using liquid Sulphur and liquid Sulphur trioxide is economically feasible when it is attached to an existing Sulphuric acid plant producing oleums and liquid SO<sub>3</sub>. A block diagram is given in (Figure. 5.2).

Sulphur trioxide gas is received from the main Sulphuric acid plant by boiling in SO<sub>3</sub> storage tank. Likewise, liquid Sulphur is received in a Day Tank. Molten Sulphur and liquid SO<sub>3</sub> are pumped in the reactor at regulated rates using metering pumps. The reactor is initially charged with 25 % oleum from the overhead tank.

The temperature of the reaction is maintained by circulation of hot/cold water using vessels and pumps respectively. The Sulphur dioxide gases are then reacted to polishing towers in which lumps of solid Sulphur react with the unreacted Sulphur trioxide. The gases then subsequently pass through a Sparger containing Sulphuric Acid for removal of trace Sulphur trioxide. The gases then pass through a Demister and a coke tower to remove the acid mist.

Pure Sulphur dioxide is then condensed in condensers and then received in receivers. These are then sent for loading tankers from which one tonner cylinders or road tankers are filled for sale. (Please see Pictorial view #4 & #5) of 15 TPD liquid SO<sub>2</sub> plant under construction at ATUL/AMAL (Ankleshwar, Gujarat) in 2004.



Picture 1

## Operational Considerations Condensation and Filling Section

It is important that all the gases of SO<sub>3</sub> are absorbed in the Sulphuric Acid Sparger and the Sulphuric Acid mist is removed by cyclone separator as well as mist eliminator and traces are trapped in Coke Tower.

Care should be taken in handling liquid SO<sub>2</sub> under pressure, and protective gear must be available for handling liquid SO<sub>2</sub> leakage or SO<sub>2</sub> vapours. The clean SO<sub>2</sub> gas under pressure between 7 and 8 kg/cm<sup>2</sup> enters the Condenser through a non-return valve and is condensed by water from the Cooling Tower. The quantity

being condensed to be seen through look gas and will be stored alternatively in liquid SO<sub>2</sub> receivers from this it will go to the Filling tank for filling the cylinders together with facility for Weighing Machine generally as per the normal practice of handling liquefied chemical gases under pressure. A scrubbing system for purge is provided using alkali.

Safe Operation of the Liquid SO<sub>2</sub> plant can be ensured by following simple precautions as given below:

- At any time do not allow accumulation of Sulphur in the reactor
- At any time do not allow the temperature of the reactor go beyond 70 °C.
- The purge system must be tested at least once a day.
- Do not allow ingress of water in any section of the plant giving any contact with SO<sub>2</sub>/ SO<sub>3</sub>
- Keep an eye in the pressures, temperatures and ampere of the electric drives.

## Environmental Considerations

Most of the Sulphuric Acid plants world over have the problem of disposal of settled Sulphur sludge. Modern plants have a Sulphur filter, and the filter cake containing 50-70% Sulphur is a sludge disposal problem. This can be converted to SO<sub>2</sub> subsequently converted to 98% Sulphuric acid by the process described in this process with minor modifications. NEAT has applied for an international patent for the same.

From environmental considerations, the storage of Sulphur cake is a fire hazard and a solid waste disposal problem. The leachate being acidic creates liquid effluent problems.

It is suggested that the Sulphur sludge in a slurry/molten form can be pumped into the reactor and be converted to Sulphur dioxide. In case if there is no market for liquid Sulphur dioxide, the reactor can operate at moderate pressures and recycle the Sulphur dioxide thus produced to the Sulphuric acid plant for conversion to SO<sub>3</sub> and Sulphuric acid.

## Conclusion

The use of liquid Sulphur and liquid SO<sub>3</sub> under pressure fed into a reactor to produce liquid Sulphur dioxide has been found to be the most environment friendly, safe and economical option.

## Genesis of the innovative path-breaking “Cold Process” to manufacture Sulphuric Acid and Sulphonating Agents

Since inception of Navdeep Enviro and Technical Services Pvt. Ltd., 1987, NEAT has executed more than 100 projects with innovative technologies for the manufacture of Sulphuric Acid and Sulphonating Agents for the past thirty years.

Lately, NEAT developed a unique process to manufacture Liq. SO<sub>2</sub> reacting stoichiometrically Liq. Sulphur trioxide and Liquid Sulphur in a medium of 25% oleum. The reaction is  $2 \text{SO}_3 + \text{S} = 3\text{SO}_2$

The above reaction is carried out at 50-70° centigrade in a high pressure reactor at 6-8 Kgs/cm<sup>2</sup>.

The reaction is almost 100% conversion and pure SO<sub>2</sub> gas production at 6-8 Kgs/cm<sup>2</sup>\*

Pure SO<sub>2</sub> at high pressure can be liquefied by circulating water from

cooling tower @ 35-40 ° C in a condenser.

The above does not require burning of Sulphur in a furnace. The Sulphur dioxide thus produced can be sent to a catalytic converter to produce Sulphur Trioxide. The above possibility led to the innovative “Cold Process” to manufacture Sulphuric Acid and Sulphonating agents.

The benefits of this process are many.

Conventional DCDA (3+2) described earlier in Fig. 1 can be modified with less than half CAPEX, 1/3rd area and zero emission of Sulphur dioxide.

\*Pure SO<sub>2</sub> can be sent directly to high pressure isothermal converter loaded with cesium activated vanadium pentoxide catalyst operated at 360-380 ° C.

The COLD PROCESS applied to existing H<sub>2</sub>SO<sub>4</sub> plants using DCDA process can utilize NEAT’s technology to produce additional 20-30% H<sub>2</sub>SO<sub>4</sub> without any major capital investment. This process is described in Fig. 2

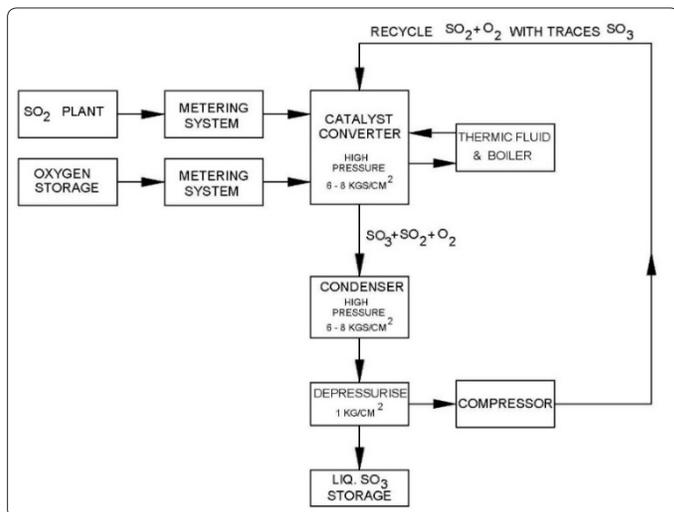


Figure 4: BD for the production of SO<sub>3</sub> using Liq. SO<sub>2</sub> and pure O<sub>2</sub>.

The SO<sub>3</sub> thus produced is converted to H<sub>2</sub>SO<sub>4</sub> by reaction with water. The process is described in Figure. 5.

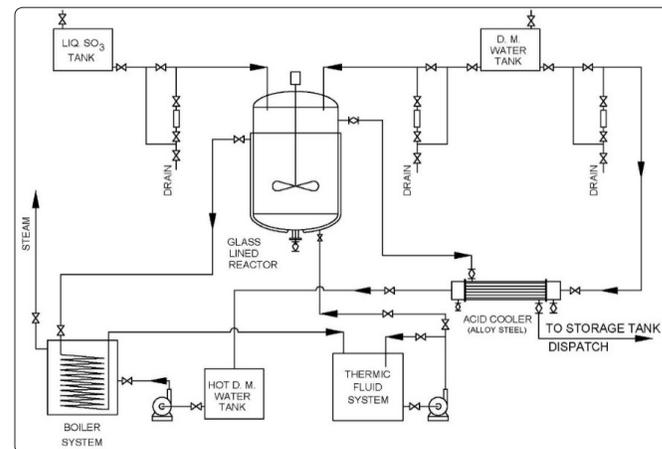


Figure 5: BD for production of H<sub>2</sub>SO<sub>4</sub> with no Stack emissions and acid circulation cum cooling system.

The above reaction involved in The COLD PROCESS are as follows:

1.  $S + O_2 \rightarrow SO_2 - \Delta H = 297 \text{ kJ/mol}$
2.  $SO_2 + \frac{1}{2}O_2 \rightarrow SO_3 - \Delta H = 99 \text{ kJ/mol}$
3.  $SO_3 + H_2O \rightarrow H_2SO_4 - \Delta H = 132 \text{ kJ/mol}$

The Genesis of innovative, path breaking process for manufacture of H<sub>2</sub>SO<sub>4</sub> will have long lasting impact on the H<sub>2</sub>SO<sub>4</sub> plants of the future.

### Thermodynamic and Kinetic aspects of Chemical Reactions Involved

#### Introduction

Prior to our considering chemical reactions, kinetics and environmental concerns, we have to consider three main options namely:

- a) Existing plants using DCDA process.
- b) Manufacture of Sulphonating agents
- c) Grass roots plant with pure oxygen, isothermal reactors and catalyst at 360 °C or lower conversion temperature.

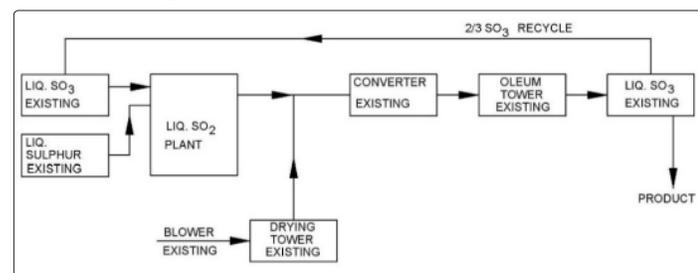


Figure 2: BD for the enhancement of H<sub>2</sub>SO<sub>4</sub> capacity in existing plants.

To clarify the process in Fig. 2, please refer Fig. 3, giving latest state of art to manufacture H<sub>2</sub>SO<sub>4</sub> with use of cesium activated Vanadium Pentoxide Catalyst.

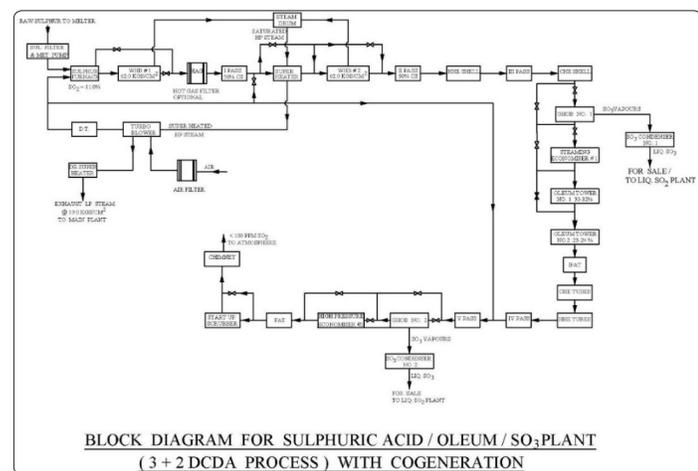


Figure 3

For grassroots plant using “THE COLD PROCESS”, the raw materials are Sulphur and pure oxygen.

Figure 4 describes this process.

### Existing plants using DCDA process

The present world production is over 150 million tons/year Sulphuric Acid and Sulphonating agents; it is unlikely that "The Cold Process" will be adopted across the board. However, these plants can benefit by NEAT's technology to expand their capacity by 20 to 30% with no major capital investment. A block diagram is attached to highlight the process. Chemical reactions involved are unchanged and existing Sulphur burner, WHB, Converter etc. can be adequate with minor modification, if required.

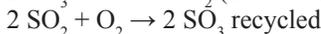
It would be environmentally advantageous to use Cesium activated catalyst as desired stages, replacing conventional potassium activated  $V_2O_5$  catalyst.

### Manufacture of Sulphonating agents

In the existing plants, manufacture of liquid  $SO_3$  is already described earlier.

For manufacture of liquid  $SO_2$  in the existing plants a separate unit using liquid  $SO_3$  and liquid Sulphur need to be provided.

Reactions involved are:



Existing plants can produce with economic benefit merchant liquid  $SO_2$ , depending on market demand.

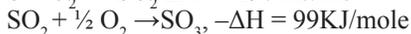
### Grass roots plant with pure oxygen, isothermal reactors and catalyst at 360 °C or lower conversion temperature.

For new plants to manufacture Sulphuric Acid, there are many benefits of using the Cold Process developed by NEAT. This would eliminate burning of Sulphur, drying, interpass and absorption towers, acid cooling system, heat exchangers, mist eliminators and cooling tower. Apart from reducing the CAPEX to less than half and area to less than one third.

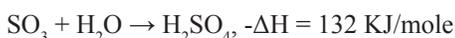
The chemical reactions involved are described earlier for the production of  $SO_2$  using liq. Sulphur and Liq.  $SO_3$ .

The gaseous  $SO_2$  at high pressure will be fed to a catalytic converter cooled by thermic fluid, using Cesium activated Vanadium Pentoxide catalyst, operating at 360 – 380 °C.

The chemical reaction will be



Since the  $SO_3$  thus produced is pure, it can be condensed directly using cooling water from the cooling towers or chilled brine if oxygen is in excess of Stoichiometric requirement. Liq.  $SO_3$  thus produced is partly recycled and balance used for manufacture of Sulphuric Acid by the reaction



The exothermic heat generated can be utilized to produce additional cogeneration of steam.

Thus, instead of 1.0-1.1 tons of steam per ton of acid produced by conventional DCDA process, 'The Cold Process' will produce 1.3-

1.4 tons of steam per ton of Sulphuric Acid produced.

Using Le Chatelier's Principle, higher pressure would give better equilibrium conversion. Also, access of oxygen will give higher conversion due to law of mass action.

### Conclusion

In conclusion, the advantages of the cold process are lower CAPEX and battery limit plant area, higher cogeneration of steam, and zero emission of  $SO_2$  and lower utility consumption.

### Elimination of costly equipment, annual stoppage and high maintenance charges

It is already explained earlier how one can eliminate major equipments required to manufacture Sulphuric acid and Sulphonating agents using conventional DCDA process. The same are outlined in sequential order:

#### Air Blower

For plants up to 500 TPD, positive displacement ROOTs type air compressor can be used. These are driven by electric motors. For large capacity, plants above 500 TPD, centrifugal turbine driven air blower are recommended. The above equipments are very costly and require heavy maintenance. The steam turbine can be seriously damaged if cogenerated steam carries silica.

#### Drying Tower

The compressed air to be fed to Sulphur burner requires removal of moisture due to humidity in the air. Also, carryover of acid mist has to be eliminated. These towers require reclining and are packed by ceramic rings to give adequate mass transfer area. Drying tower required continuous acid circulation and maintenance of optimum temperature for drying. Prior to leaving the drying tower, mist eliminators are introduced to eliminate carryover of Sulphuric Acid.

#### Sulphur Furnace

The Sulphur burner is fed liquid Sulphur from the Sulphur melter after filtration. The dry air is introduced to burn the Sulphur in order to produce 9.5 to 10 % concentration of Sulphur Dioxide.

The adiabatic temperature attained is in the range of 950-1050°C. This require costly refractory high alumina bricks. Also, insulation bricks to prevent loss of heat need to be provided. The burner required costly foundation and provision for thermal expansion.

It is important that once the Sulphur burner is commissioned, it cannot be allowed to cool down without causing damage to the brick lining. During annual stoppage, the brick lining has to be prepared for restarting the plant for smooth operation.

Elimination of Sulphur burner would avoid annual stoppage and thereby the operational time for the Sulphuric Acid plant will be almost full 365 days of the year. This would mean considerable economic benefit and thus reduce the manufacturing cost of Sulphuric Acid.

#### Converter

The conventional DCDA (3+2) requires a multistage converter with intermediate heat exchangers. Since the percentage Sulphur Dioxide is 9.5 to 10 % and the balance being Vair, the diameter has to be provided according to the space velocity recommended by

the supplier of catalyst. Compared to this, in the COLD PROCESS pure oxygen and pure SO<sub>2</sub> are sent to the converter which is kept at constant temperature using thermic fluid. The diameter and the size will be comparatively smaller. The above would mean considerable saving of avoiding requiring in the conventional DCDA process.

### **Interpass and final absorption tower with acid circulation and cooling System**

In order to improve conversion efficiency from 96.5 % to 99.5 %, an intermediate absorption tower is necessary with costly mist eliminators and interpass heat exchangers. They require high maintenance cost due to corrosion or mechanical damage.

Also, the towers are very heavy and require elevated platform and pillars requiring civil foundations.

### **Cooling Towers and plate heat exchangers**

The acid cooling system requires costly plate heat exchangers which are fed with cooling water to remove exothermic heat generated by the reaction of water and Sulphur trioxide. These require regular maintenance which adds to the cost of the final product.

### **Economic and Environmental Advantages of the COLD PROCESS**

We have adequately elaborated earlier, the advantages regarding lower CAPEX, area, maintenance and zero emission of Sulphur Dioxide. We quantify advantage in the outline below.

#### **CAPEX**

It is estimated that for the same capacity of Sulphuric Acid plant, elimination of costly equipment would result into a saving of over 50%. At current prices, a DCDA grassroots plant would cost a minimum of Rs. 1.5 million (\$ 0.025 million) per ton per day capacity of Sulphuric Acid.

#### **Plant Area**

The battery limit for a grassroots Sulphuric Acid plant, using the COLD PROCESS could be approximately 1/3<sup>rd</sup> of that required for a conventional DCDA process. In addition, since there would not be need for annual stoppage, the storage capacity to cater customer demand during annual stoppage for about 3-4 weeks can be eliminated. This would result into a considerable economic advantage using the COLD PROCESS.

#### **Maintenance**

The requirement for maintenance in the COLD PROCESS will be considerable reduced because of elimination of acid circulation pumps, air blower, cooling towers, repairs to Sulphur furnace, etc.

#### **Environmental benefit**

The COLD PROCESS would not need any regulation of Stack emissions since there will be zero emission of SO<sub>2</sub>. This would prevent recurring Acid Rains which currently is to the tune of One million tons per annum.

#### **Cogeneration of Steam**

The COLD PROCESS would produce 0.2-0.3 tons of additional steam per ton of acid produced. Apart from the economic advantage, it will also reduce corresponding pollution due to saving of fuel.

### **Conclusion**

In conclusion, the paper outlines benefits due to the path breaking, innovative COLD process for the production of Sulphuric Acid and Sulphonating agents [1,2].

### **References**

1. Ashar, Navin G, Golwalkar, Kiran R (2013) A Practical Guide to the Manufacture of Sulphuric Acid, Oleums and Sulphonating Agents.
2. Ashar, Navin G (2016) Advances in Sulphonation Techniques.

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