Comparative Study of Techno-Economic Evaluation of the Production of Liquid Sulphur Di Oxide

Economical ~ Safe ~ Environment Friendly

Navinchandra. G. Ashar,

MS (Chem Engg, MIT, USA)

Mumbai, India

NAVDEEP ENVIRO AND TECHNICAL SERVICES PVT. LTD.

: Mumbai office :
Behramji Mansion, Fourth Floor, Sir P.M. Road
Fort, Mumbai 400 001 INDIA
Tel: 022 -2262 2023, 022 -3293 1834

Email : navdeepenviro@gmail.com

: Design office :
Plot 257, "Lumbini", Kansai Section
Ambarnath (East) 421 501, Dist. Thane
Tel: 0251-2602269

Executive Summary

Sulphur di-oxide – The King of Chemicals

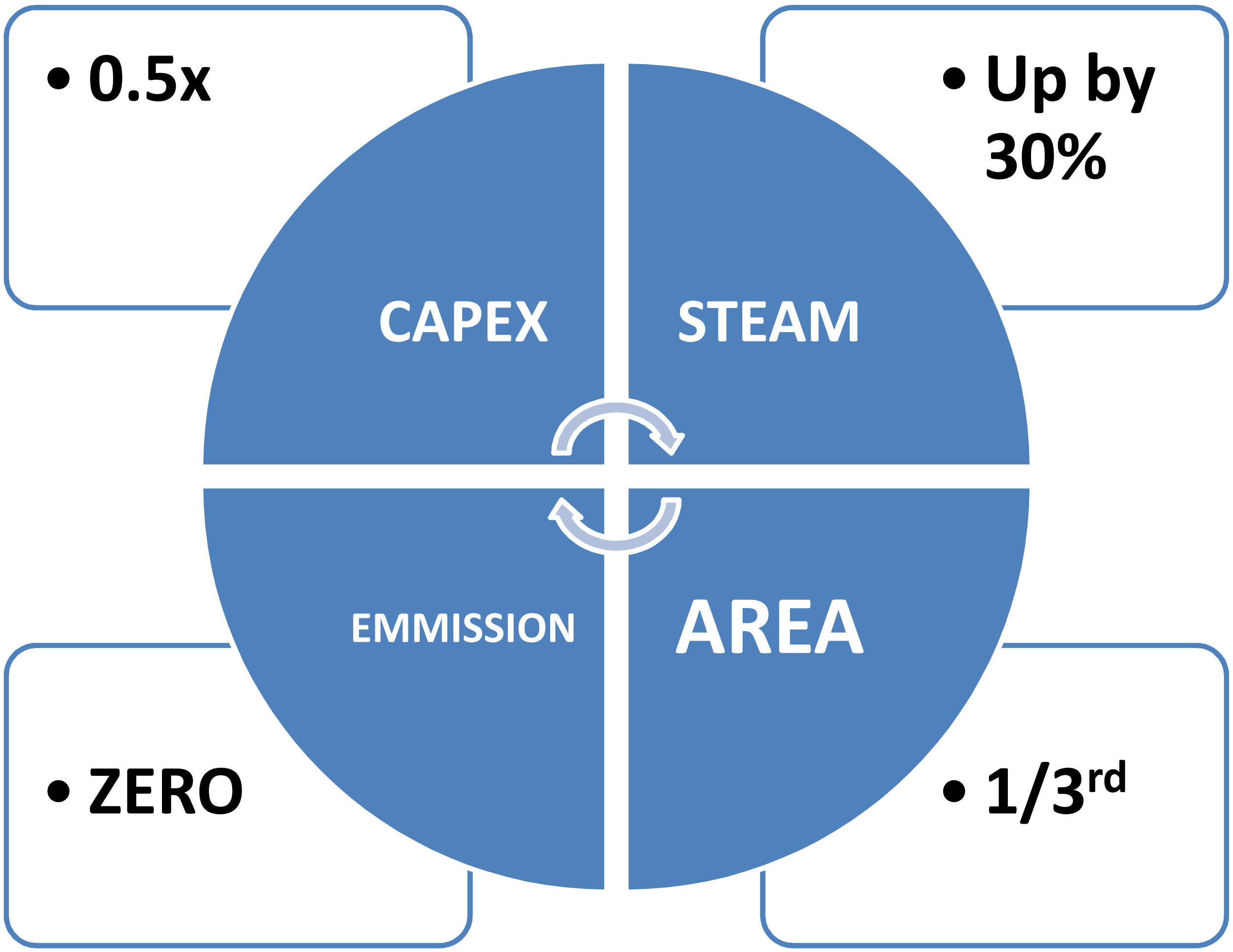
Sulphuric Acid – Liquid Sulphur di Oxide – Oleums – Liquid Sulphur tri-oxide

Uncertainty of the price of oil, the field has become very competitive. Technologies established over several decades have to be re-evaluated for making the production economical, environment friendly & safe operation.

It's the beginning of **Cold process** of manufacturing Sulphuric acid.

This paper will highlight positives and negatives of the prevalent manufacturing facilities of liquid sulphur di-oxide.

Benefits of Cold Process



Introduction

- Sulphur di-oxide known for its disinfecting and bleaching quality. Since late early 20th century, it has been used for Industrial refrigeration plants; widely used for producing quality paper by preparing Sulphite pulp; quality pulp produced is taken as a raw material for producing viscose rayon.
- Lately Sulphur di-oxide has become a major component in petroleum refining and sulphonation reactions..

History

- Since twentieth century Sulphur di-oxide has been manufactured Industrial scales.
- The advent of contact process in the thirties opened the door for new techniques to produce pure Sulphur di-oxide.
- In the late eighties, due to environmental considerations Sulphur recovery from crude oil and flue gas cleaning from combustion of Sulphureous fossil fuels added to the SO_2 recovery systems.
- Following are the main sources of Sulphur di-oxide production:-

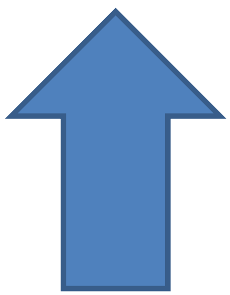
1. Elemental Sulphur
2. Pyrite
3. Sulphide ores of non-ferrous metals
4. Waste Sulphuric acid and Sulphates
5. Gypsum and anhydrite
6. Hydrogen Sulphide-containing waste gases
7. Flue gases from combustion of Sulpherous fossil fuels
8. *Destructive combustion of gypsum and other waste Sulphiric acid containing inorganic or organic salts.

* NEAT has given consultancy services for 200 TPD Sulphuric Acid Plant in Zelzate, Ghent, Belgium.all the plants in Europe manufacturing Dyes, Intermediates, Drugs and other Sulphonated products used this plant for ther waste disposal. This was in 2004-2005 when the plant was to be bought by M/s Madhvani Group of Kenya. NEAT had done the due diligence of the plant and suggested improvements in the operation of the plant.

I. Production From Burning Sulphur By Partial Refrigeration Of Sulphuric Acid Plant Gases

- This process was used by Welmen Lord (USA), Albright and Wilson (UK) and Lurgi (Germany).

- This process requires **high capital cost** and **high utility cost** for refrigeration.



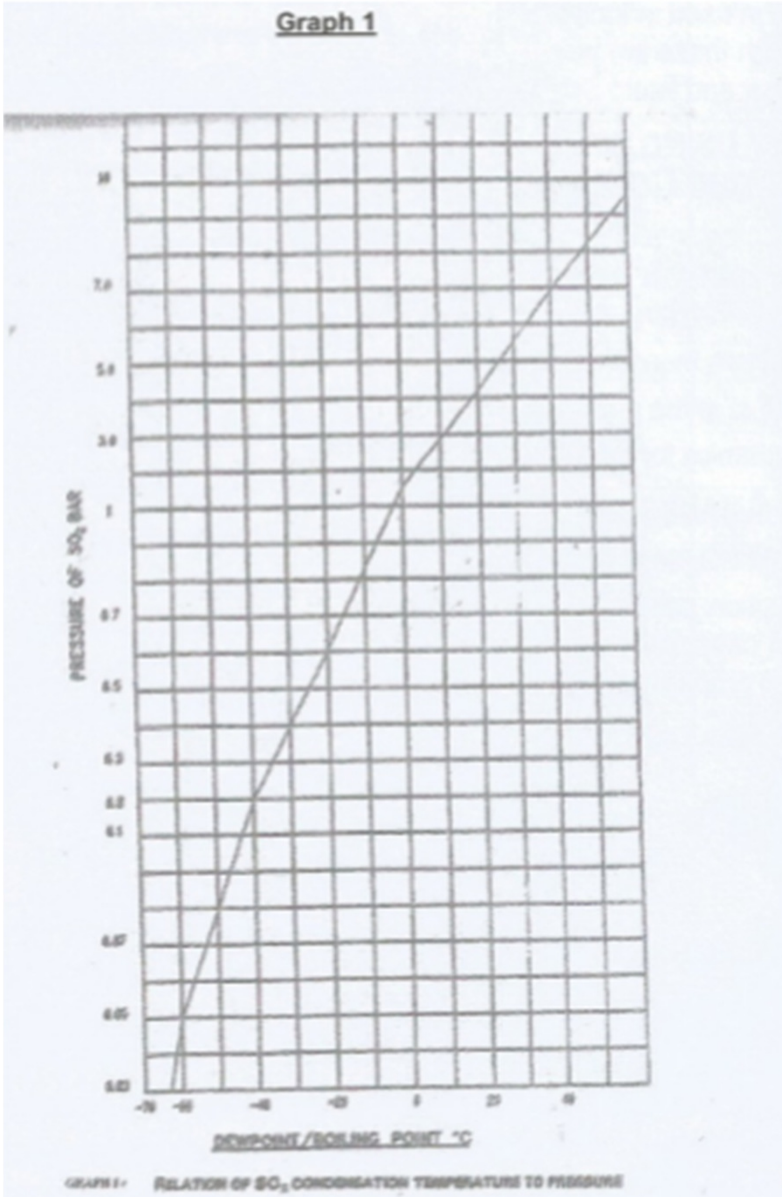
- Due to it being uneconomical, no more industrial units produce liquid Sulphur di-oxide by this process.

II. Production By Burning Sulphur Cooling, Absorption In Alkali And Desorption, Drying By Sulphuric Acid, Compression And Condensation By Refrigeration

- In the late fifties, it was used by plants dedicated totally to produce liquid Sulphur di-oxide.
- Apart from **high cost** of the plant, this process required **special materials of construction** like Hastelloy – C due to heavy corrosion.
- However, for the production of **alkali sulphites** and **bi-sulphites**, this **process is still in operation in certain plants**. This process is still in use for production of Sulphur di-oxide in Canada for metallurgical plants.
- Due to **high capital cost as well as maintenance cost**, this process is now being replaced by **direct reaction of liquid Sulphur with liquid SO_3** as described *later in the paper*.

III. Production By Use Of Organic Solvent From By Product SO_2 Generated in Specific Chemical Reactions

- Sulphur di-oxide is produced as a by-product in the manufacture of petroleum additives, Thionyl chloride, continuous detergent manufacture, etc.
- Sulphur di-oxide dissolved readily in most orgnaic liquids such as methanol, ethanol, benzene, acetone and carbon tetrachloride.
- Sulphur di-oxide is completely miscible even at low temperature with ether, carbon di sulphite, chloroform and glycol.
- The by-product Sulphur di-oxide is absorbed in any of the solvents and then released as pure Sulhur di-oxide recycling the solvents for absorption.
- Depending on pressure at which liquid SO_2 is released from the solvent, the condensation takes place as per **Graph I**.



- It can be observed that if the pressure of desorption tower is maintained between 7 – 10 kg/cm^2, no refrigeration will be required.

- Large quantities of liquid SO_2 are produced by this process as by product.

IV. Production By Use Of Concentrated Oleum (65%) and Solid Sulphur Using Compression And Refrigeration (Batch Process)

- This process is a batch process which was adopted for the production of small quantities of liquid SO_2.
- **Process**: Solid Sulphur is charged in a reactor fitted with agitator and cooling jacket, concentrated Oleum is introduced in stoichiometric proportion to produce concentrated Sulphur di-oxide (97.5%) and free SO_3 (2.5%).
- The gases are led to Sulphuric acid tower to remove unreacted Sulphur tri oxide after passing through demister the pure SO_2 is compressed and chilled to give the final product.
- This process is still used in India in some of existing manufacturing units.
- However, the cost of production being high these are being replaced by latest technique of producing liquid Sulphur di-oxide using molten Sulphur and liquid SO_3.

V. Production By Using Molten Sulphur And Liquid SO_3 Under Pressure Without Compression And Refrigeration (Adopted By NEAT)

- This process is described in detail by the author in the paper presented at British Sulphur conference in 1999 at Calgary, Alberta and, shall also be presented at International Conference organized by Süd-Chemie in Sep 2016 at New Delhi, India.
  - *Paper title: 'Liquid Sulphur Dioxide without Compression or Refrigeration'*
- Currently in India, more than 24,000 TPA of Liquid SO_2 is being produced by the '**NEAT**' process.
- Currently, 4,000 TPA of Liquid SO_2 plant is being built in Kingdom of Saudi Arabia based on '**NEAT**' process.
- As regards the economics for the various plants, it is described in the next section

Comparative Analysis On Techno Economic Considerations

- Manufacture of Liquid SO_2 has gone into a radical change to reduce raw material and utility costs.

- Comparative production pattern indicates the closing down of Liquid SO_2 plants which were uneconomical and growth of plant capacity using direct process of reacting under pressure liquid Sulphur and Liquid SO_3 under stoichiometric proportion by the reaction

$$S + 2\,SO_3 = 3\,SO_2 \qquad \Delta H = -99 \text{ KJ mole}$$

Production capacities from 1999 to 2010

Table I Sulphur Di-oxide Producers (Merchant) and Capacities ('000 tons)

Table I
Sulphur Di-oxide Producers (Merchant) and Capacities – ('000 tons)

	Producer	Location	1999 Capacity	2010 Capacity
USA	Calabrian Corp	Port Neches, TX	50	180
	Clariant Corp	Bucks, AL	65	NIL
	Marsulex	Copperhill, TN	45	Shutdown
	Marsulex	Cairo, OH	13	20
	PVS Chemical	Chicago, IL	40	36.5
	Republic Group (Olin)	Charleston, TN	45	ND
	Rhodia	Baton Rough, LA	25	DA
	Rhodia	Houston, TX	43	DA
	Thatcher Company	Salt Lake City, UT	10	ND
		Total USA	399	
Canada	Cominco	Trail, BC	88	88
	Marsulex	Timmons, ON	33	Shutdown
	Marsulex	Prince George, BC	33	Shutdown
	Marsulex	Sudbury, ON	110	110
		Total Canada	264	198
India	Transpeck (Batch Process)	Baroda	12	12
	Shree Sulphuric Acid (NEAT)	Ankleshwar	0	06
	Atul Ltd. (NEAT)	Ankleshwar	0	06
	Nath Industries (NEAT)	Vapi	0	06
	Aarti Ltd. (NEAT)	Vapi	0	06
		Total India	12	36

Table II Liquid SO_2 Plants in Europe, Africa and South America

Table II
Liquid SO_2 Plants in Europe, Africa and South America

Company	Location	Capacity	Year	Source
Boliden Harjavalta Oy	Harjavatta, Finland	42,500 MTPA	-	-
Boliden Mineral AB	Skelleftehamn, Sweden	50,000 MTPA	-	Water absorption /strpping followed by drying and liquefication
Calabiran Corporation	Port Neches, Texas, USA	-	-	-
Chemtrade Logistics	Cairo, Ohio, USA	20,000 STPA	-	React Sulphur and sulphur trioxide
Goro Nickel, S.A.S.	New Caledonia	2 x 25 MTPD	-	Sulphur Burning
Grillo-Werke AG	Duidburg, Germany	-	-	Absorption process
Grillo-Werke AG	Frankfurt/Main, Germany	-	-	Condensation process
Marsulex Inc.	Prince George, British Columbia, Canada	90 MTPD	1989	Partial Liquefication of high strength SO2 gas from sulphur burning
Metorex Limited	Ruashi, Congo	65 MTPD	2011	Sulphur Burning
PVS Chem Solutions Inc.	Chicago, Illinois, USA	36,500 STPA	-	Sulphur Burning
Quimetal	Chile	4,000 MTPA 6,000 MTPA	-	Patented process of burnig sulphur in 100% oxygen
Sable Zinc Kabwe	Kabwe, Zambia	6 MTPD	2007	Sulphur Burning
TCP Limited	Phillipines	-	-	-
Teck Cominco	Trail, British Columbia, Canada	-	-	Acidulation of Ammonia from ammonia scrubber bleed
Vale INCO	Sudbury, Ontario, Canada	400 MTPD	-	Compression and liquefication of high stength metallurgical gases from Inco flash furnace
Votorantim Metais	Juiz de Fora, Brazil	35 MTPD	1999	-
Xstrata Copper	Timmins, Ontario, Canada	-	-	Partial Liquefication of high strength SO2 gas from metallurgical gases Shutdown 2010
Xstrata Zinc – Hinojedo Roasting Plant	Spain	-	-	Liquefication

Table III End Use Pattern – 2011 Estimate – Merchant Market Only

Table III **End Use Pattern – 2011 Estimate – Merchant Market Only**			
Derivative	**Percent**	**Derivative**	**Percent**
Chemical Manufacture Precursor to sulfuric acid	40	Agriculture & Food Preservative & Winemaking	15
a) Sodium hydrosulphite Biochemical and biomedical roles b) Other Chemicals c) Reducaing agent	20	Water Treatment Reagent and solvent Miscellaneous	5 5
Pulp & Paper	15		
		Total	100

Key metrics and USP's of the 'NEAT' Process

As regards **raw material** and **utility consumption** by the process adopted by NEAT, the following are **guaranteed** figures per tonne of Liquid SO_2.

1. Liquid SO3: 0.841 MT
2. Liquid Sulphur: 0.175 MT
3. Power: 30 kWH
4. Water (for cooling): 1.5 M^3
5. Steam (low pressure): 0.3 MT

Sulphur efficiency is higher than 98%.

Raw material, equivalent sulphur required is 40% of 0.841 = 0.3364 plus 0.175 **i.e. 0.511**. Part of Purged SO2 / SO3 is returned to Sulphuric acid plant.

Cap-ex is low as the MOC is M.S.

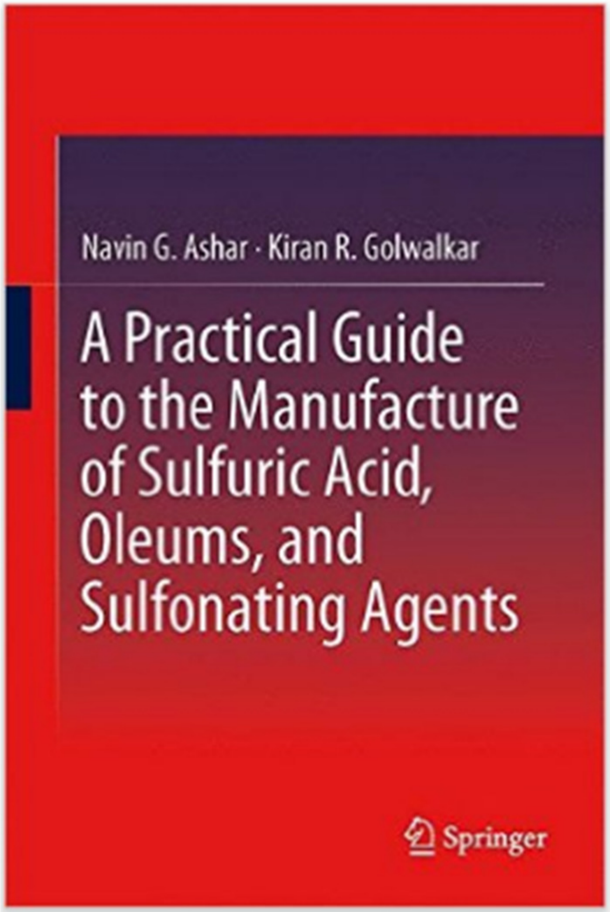
Op-ex is lower due to lack of compression or refrigeration requirements.

Lastly, the process is more Safe & Environment friendly.

Any other process currently in practice is requiring **higher utility costs**.

Conclusion

- A case made here to present comparative study for the manufacture of liquid sulphur di oxide.
- It is demonstrated that direct process of liquid SO_3 with liquid sulphur will be most attractive for future plants.
- However, recovery plants of byproduct SO_2 will also be an attractive economic proposition.



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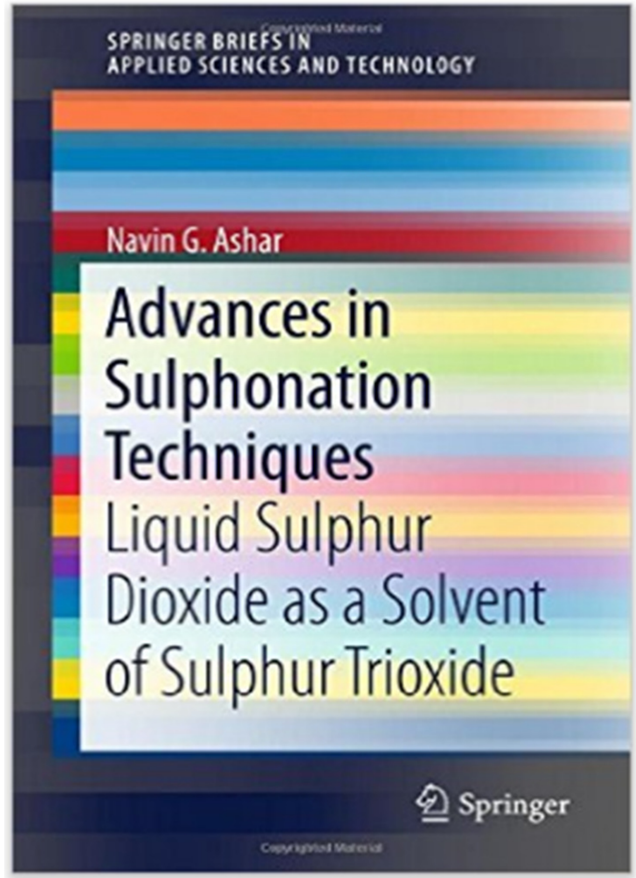

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