IDENTIFICATION OF METALLURGICALSULPHURIC ACID PLANTS PRODUCTION LINE BOTTLENECKS

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Abstract- Sarcheshmeh Copper Smelter in Kerman Province, Iran is equipped with a sulphuric acid plant that treats the smelter off-gases containing low SO_2 concentrations to produce sulphuric acid with single absorption system. There is provision in the design to convert the plant from single to double absorption would allow it to handle higher SO_2 concentrations and produce more sulphuric acid.This study examines various options for handling the off-gas connected with implementing new technology at NICICO's Sarcheshmeh Copper Smelter by steady state simulation of the sulphuric acid plant by ASPEN PLUS V.8 process simulation software and Plant data extracted from DCS (Distributed Control System) employed for validation of the model.The modeling results agree very well with the real plant data.There are two ways to increase production capacity in sulphuric acid plants: increase SO_2-laden gas flow rate and increase SO_2 concentration. In obedience to the plant design basis, gas flow limited by the plant blower. Increase SO_2 concentration, increases converter first bed temperature which is harmful for catalysts. Also heat capacity of gas-gas heat exchanger for decrease 1st bed outlet temperature is another obstacle to increase SO_2 concentration boundlessly. According to simulation results, via minor changes in available equipment, it is possible to increase production capacity about 50% rather to main design by increase SO_2 concentration about 50% under strict environmental regulations. Beside increase production rate, SOx emissions from the plant keep under environmental regulations, less than 300 ppm.Besides controllability, operability and optimization studies the plant model is also useful for operator training and various scenario assessments.

Keywords- Sulphuric acid, Metallurgical, Simulation, Debottlenecking, Double Absorption.

I. INTRODUCTION

Around 200 million metric tons of sulphuric acid is manufactured per year- Most of it from strong SO_2 (~12%) gas. SO_2 in smelting and roasting gas accounts for about 30% of sulfuric acid production. Two and a half to four tonnes of sulphuric acid are produced for every tonne of copper smelted from sulphide concentrates [5]. Smelting copper from sulphide concentrates involves oxidation. Significant by-products are iron oxide and sulphur dioxide. The iron oxide is combined with flux to form molten slag, which is processed for copper recovery, then discarded. The sulphur dioxide gas is made into sulphuric acid. The National Iranian Copper Industries Company (NICICO) operates the Sarcheshmeh Copper Smelter in Kerman Province, Iran. The smelter is equipped with a sulphuric acid plant that treats the pierce smith converter furnaces off-gases to produce sulphuric acid.The sulphuric acid plant is a single absorption plant designed for initial production capacity of 100,000 TPA of H_2SO_4 expressed as 100% H_2SO_4, to treat off-gases containing low SO_2 concentrations. The feed gas to the existing plant is taking from the Pierce Smith (P.S) converters after cooling and dedusting in the existing hot dust precipitators. The plan was that when upgrades to the smelter were implemented, the sulphuric acid plant could be converted to a double absorption plant that would allow it to handle higher SO_2 concentrations and produce more sulphuric acid.The acid plant has been designed based on existing converter off-gas characteristics for a future capacity of at least 300,000 TPA.

II. ASSUMPTIONS

The following assumptions have been made for this study:

- Minimum O_2 to SO_2 ratio for conversion is 0.8.
- The effluent treatment system is assumed to be adequately sized.

III. THE METALLURGICAL SULPHURIC ACID PLANTS

The metallurgical sulphuric plant is physically the most complex type of sulphuric acid plants, and hence the most expensive in terms of fixed capital investment and manufacturing expenses.
The manufacture of sulphuric acid in metallurgical sulphuric acid plants involves three basic steps:
1) Purify and dry the SO_2-laden gas
2) Conversion of SO_2 to SO_3
3) Absorption of SO_3 in water solution to form H_2SO_4.
The 3D plan of main equipment of a typical metallurgical sulfuric acid plant shown in Figure 1.

1.1. FEED GAS

The primary purpose of metallurgical operations with sulphide ores is the production of base metal, such as copper. Smelting process involves melting sulphide concentrates in a furnace at 1500K in an oxidizing atmosphere. The overall reaction is:

$$CuFeS_2(s) + O_2 \rightarrow Cu - Fe - S(l) + FeO(l) + SO_2(g)$$

Production of sulphuric acid is carried out mainly as a means of limiting the emission of sulphur dioxide

(SO_2) to the atmosphere from these operations. The acid thus obtained becomes a saleable by-product.

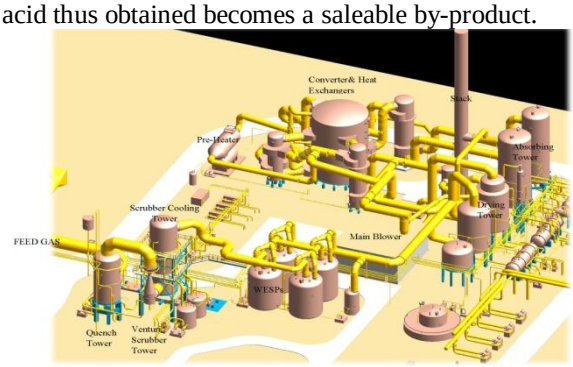


Figure 1: 3D plan of Gas cleaning unit and contact section of a metallurgical sulphuric acid plant

The concentration of SO_2 in gas derived from metallurgical sources has traditionally been lower than in gas derived from sulphur burning (although the difference is becoming less with the adaptation of modern flash smelting techniques). Therefore, for a given quantity of SO_2 processed, the total volume of gas is often greater for a metallurgical plant. This results in larger and more expensive equipment.

1.2. FEED Gas Cooling And Purification

SO_2 gas generated from metallic ores contains fine solids, metallic vapours, acid mist and water vapour which must be removed by scrubbing and cooling in a wet purification system. Because of their solids content, ore gases are the most difficult to clean. The gas entering dehydration must be dust free (0.001 to 0.01 g/Nm^3 of gas) to avoid plugging downstream SO_2-oxidation catalyst [8]. Cleaning and cooling of the gas is accomplished by scrubbing with a weak acid solution. The acid strength and solids build-up are controlled by purging and water addition. The temperature is controlled either by cooling the circulating weak acid. The saturated gas then flows through electrostatic precipitators where acid mist and residual dust are removed.

1.3. Heat Removal And Recovery

In a sulphuric acid plant, virtually all the steps - raw material combustion, SO_2 conversion, drying, SO_3 absorption, and acid dilution are exothermic. Large amounts of heat are liberated, and the surplus must be removed in order to maintain proper thermal control in the process. The amount of excess heat available is generally a function of the SO_2 gas concentration. Therefore heat recovery has become more common in metallurgical plants.

1.4. Conversion System

Dry SO_2 gas at approximately 425^{o}C in the presence of excess O_2 is oxidized to SO_3 by contact with vanadium catalyst.

$$SO_2 + 2V^{5+} + O^{2-} \rightarrow 2V^{4+} + SO_3 \quad (1)$$

$$^1/_2\, O_2 + 2V^{4+} \rightarrow 2V^{5+} + O^{2-} \quad (2)$$

Overall reaction:

$$SO_2 + {}^1/_2\, O_2 \rightarrow SO_3 \quad (3)$$

Since the reaction is exothermic, the gas becomes heated adiabatically and its temperature rises until the SO_2-SO_3 equilibrium is approached. The vanadium catalyst must be molten for Reactions (1) and (2) to occur. It typically melts around 680K, slightly cooler when it contains caesium ions.

The gas is cooled again to about 425^{o}C by heat exchanger and passed through another conversion stage. The process is repeated for a total of 3 or 4 stages wherein most of the initial SO_2 is converted to SO_3.

1.5. SO_3 Absorption

The partially cooled SO_3 gas mixture from the conversion system is passed to the absorbing system where SO_3 is absorbed by intimate contact with warm 98-99 percent sulphuric acid flowing counter-current through the tower packing (Eq. 4).

$$SO_3(g) + \underset{\text{In 98.5\% } H_2SO_4}{H_2O(l)} \xrightarrow[@350\text{-}380\ k]{} \underset{\text{strengthened sulfuric acid}}{H_2SO_4(l)} \quad (4)$$

The acid becomes strengthened by SO_3 reaction with free water and increases in temperature by absorption of sensible heat from the gas as well as heat from the SO_3/H_2O reaction. Product acid is drawn from the system. Surplus heat is removed by indirect exchange of circulating acid with cooling water for the drying and final absorbing towers.

1.6. Double Absorption

The technique of double absorption is employed where very low SO_2 emissions are required. The two absorption towers in this system are notable. In a standard single-absorption plant, there will typically be three or four converter stages (for conversion of SO_2 to SO_3) followed by a single absorption stage. These designs typically permit conversion of about 97-98% of the SO_2 to SO_3 [6]. The remainder of SO_2 enters the atmosphere after the absorption tower. Conversions of 99% and higher can be accomplished by employing the double absorption technique. Here the SO_2 that remains after the first absorption stage is further reacted to form additional SO_3. The additional SO_3 so formed is recovered in a second absorber, hence the term double absorption related second absorption tower used in this kind of systems after 4th or 5th beds. Practically, the first stage oxidizes most of the SO_2-in-feed-gas and makes the product SO_3 into strengthened sulphuric acid. It makes about 95% of the plant's new H_2SO_4. The second stage oxidizes almost all the remaining SO_2 and makes its product SO_3 into strengthened sulphuric acid. The final exit gas is very dilute in SO_2 and SO_3.



Figure 2: Double absorption system main Equipment.

IV. STEADY STATE SIMULATION

Block flow diagrams of gas cleaning unit and contact section illustratedrespectively in figures 3 and 4.In another study[1], both gas cleaning unit and contact section simulated in one model and for simulation of all heat exchangers Aspen Exchanger Design and Rating (EDR) has been used.In this way any change in FEED GAS characteristics (Constituents concentration, flow rate and temperature) shows its effects on downstream equipment outlet parameters such as flow, temperature and eventually final product. In this study the steady state model in Aspen Plus implementedfor investigation production increase bottlenecks and debottlenecking the production line of Sarcheshmeh sulphuric acid plant. So the model modified and customizedaccording to Sarcheshmeh sulphuric acid plant design (Figure 5).All major equipment which considered in simulation listed in table 1.

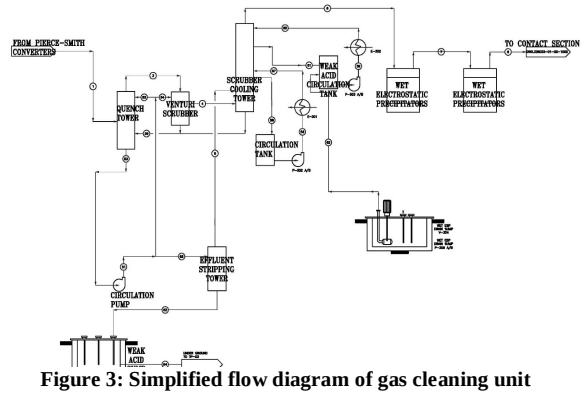


Figure 3: Simplified flow diagram of gas cleaning unit

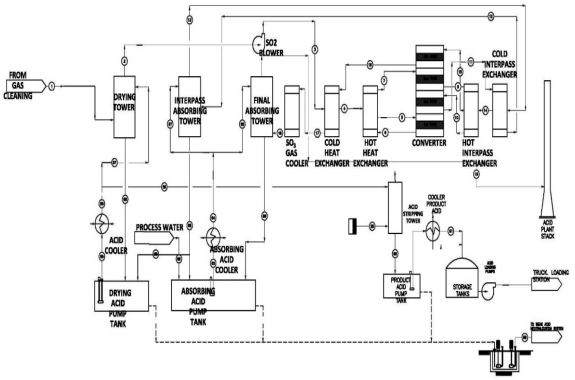


Figure 4: Simplifiedflow diagram of Contact section

[1]Paper title: ASPEN PLUS Simulation of Double Absorption System in a Metallurgical Sulphuric Acid Plant. This article submitted for publication by authors of current paper. In this paper a simulation model for metallurgical sulfuric acid plants developed and discussed in detail.

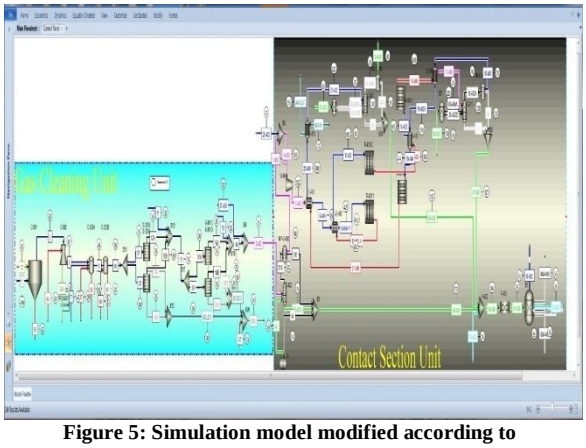


Figure 5: Simulation model modified according to Sarcheshmeh metallurgical Sulphuric Acid Plant design

Table 1: Simulated equipment in model

Tag Number	Equipment	
C-301	Quench tower	Gas Cleaning Unit
C-302	Venturi Scrubber	
C-303A,B	Scrubber cooling towers	
S-301A,B,C,D	Electrostatic Precipitators	
C-402	Secondary drying tower	Contact section Unit
U-401	Main Blower	
E-401	Cold gas-gas heat exchanger	
E-402	Hot gas-gas heat exchanger	
R-401(4 beds)	Catalytic Converter	
E-411	Hot interpass gas-gas heat exchanger	
E-412	Cold interpass gas-gas heat exchanger	
E-413	SO_3 gas cooler	
C-403	Final absorbing tower	
C-411	Interpass absorbing tower	

4.1. Model Validation

In order to examine the model reliability, DCS backup data employed which is appropriate source for validation of simulation. Running simulation for different FEED GAS characteristics, and comparison the results with the plant data shows accuracy of the model. Table 3 illustrates good consistency between simulation results and benchmark data for FEED GAS conditions (Table 2) in single absorption system.

Table 2: FEED GAS

Gas flow: 130,000 $Nm^3/hr.$	SO_2 Concentration(dry basis): 1.8%
Gas flow temperature: 350 °C	1st bed inlet temperature: 435 °C

Table 3: Simulation results and benchmark data

	Plant data	Simulation results
Quench tower outlet temp.(°C)	50	50
Drying tower outlet	40	40

* 2nd bed in single absorption system is empty.

4.2. Identification of Bottlenecks

There are number of different approaches for treating the CF[1] gases utilizing the existing wet gas cleaning system/acid plant and the technologies available for high strength SO_2 gases. Converting the existing acid plant to double absorption is necessary to increase acid production and meet SO_2 emission requirements. But there are several limitations associated with the site (e.g. layout and space restrictions) that will dictate what options should be considered.

A 'conventional' sulphuric acid is able to handle gases containing 12 to 13% SO_2. At higher SO_2 concentrations, the heat generated by the reaction of SO_2 to SO_3 in the first catalyst bed results in an outlet temperature that is high enough to damage the catalyst. The material of construction of the converter also has a temperature limit that can be exceeded if the SO_2 concentration is too high. There are several technologies available to handle high strength SO_2 gases to avoid the high bed 1 outlet temperature but it is not our purpose in this paper.

Here, we examined various options for handling maximum converters off-gas connected with new technology at NICICO's Sarcheshmeh Copper Smelter. Available facilities and current plant layout considered as design constraints.For identification production line bottlenecks there are two ways: Increase FEED GAS flow rate to maximum amount (Blower capacity) and increase SO_2 Concentration in FEED GAS. In follow both methods investigated in details.

4.2.1.Maximum FEED GAS Flow Rate

Maximum FEED GAS flow rate determined by capacity of installed blower on the site. The existing sulphuric acid plant gas cleaning system is designed to treat 130,000 Nm^3/hr. of smelter gas at a temperature of 350 ^oC. Also other existing equipment design were based on the blower suction and discharge capacity, so it is infeasible to replace the blower to increase FEED GAS flow rate.

4.2.2.Maximum SO_2 Concentration

The existing acid plant currently operates as a single absorption plant treating relatively weak SO_2 gas. The plant was designed to be easily converted to double absorption to handle future smelter operating conditions that would result in increased SO_2 concentrations of up to 7% SO_2 at the converter inlet. But it is not maximum SO_2 concentration which can be processed in the plant. Steady state simulation shows that reforming the Existing sulphuric acid plant to a double absorption plant to handle higher SO_2 strengths than 7% SO_2 can be done relatively easily.

Table 4 shows FEED GAS and converter inlet/outlet gas conditions at single and double absorption states and last column shows feed condition forsimulation and its results after optimisation. According to simulation, it is possible to reduce dilution air (decrease O_2 to SO_2 ratio) which makes it possible to process more concentrated off-gas in the sulphuric acid plant.

Table 4: simulation results after optimization operating parameters

		Single Absorption	Double Absorption	Simulation
FEED GAS	Nm^3/h	130,000	119800	119800
SO_2	%	1.8	7	11.5
O_2	%	19	16	11.5
N_2	%	80	77	77
O_2/SO_2	-	10.5	2.2	1
1st bed inlet/outlet temp	°C	435/450	435/607	390/590
2nd bed inlet/outlet temp	°C	420/420	450/491	435/470
3rd bed inlet/outlet temp	°C	420/423	435/441	435/440
4th bed inlet/outlet temp	°C	423/424	425/429	390/394
Acid Production	MTPD	290	950	1400
SO_2 in stack	ppm	250	280	145

4.2.3. Catalyst degradation

The first impact of increase SO_2 Concentration is higher temperature beyond maximum allowable temperature for safe operation in 1st bed of converter which, unfortunately, catalyst begins to lose its catalytic power above about 630 ^oC due to the formation of unreactive vanadate ions and by non-reversible reaction with the silica substrate (Figure 6). This problem is overcome by using catalyst contains caesium ions, which promotes rapid SO_2 oxidation at cool temperatures (~390 ^oC) where equilibrium SO_3 production is efficient. The addition of cesium (Cs) salts to the conventional alkali-vanadium sulphuric acid catalyst formulations has long been known to enhance the low temperature properties of the catalyst [11].So replacing potassium-promoted catalysts with caesium-promoted catalyst, SO_2 oxidation must be done between ~390 and 630 ^oC (Figure 7).It is because we set first bed inlet temperature 390 ^oC to limit outlet temperature in simulation.

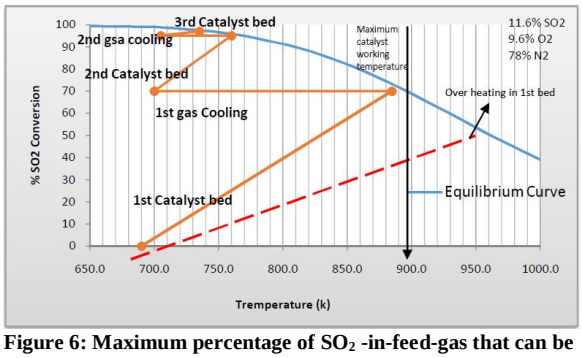


Figure 6: Maximum percentage of SO_2 -in-feed-gas that can be oxidized when equilibrium is attained in a bed.

[1] Converter Furnace

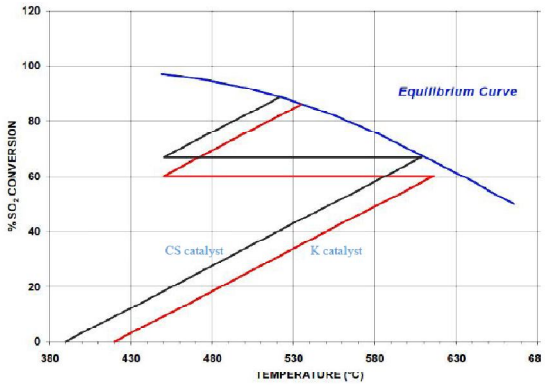


Figure 7: Schematic diagram of 2 different catalysts

4.3. Results and discussion

4.3.1.SOx emissions

A current focus within the sulphuric acid industry is to reduce sulphur dioxide emissions to theatmosphere while maintaining or increasing acid production. The current legislation imposes tighter restrictions in order to reduce the impact of chemical process industry on the environment. The SOx emissions could be significantly reduced by optimizing operating parameters such as converter beds inlet temperatures and flow rates. Through the use of Caesium Promoted Catalyst, it is possible to significantly increasethe SO_2 conversion through a double absorption plant by decreasing 4th bed inlet gas temperature and hence reduce the SO_2 stackemissions.

By appropriate parameter tuning, SOx emissions from the stack can be controlled less than 150 ppm. Installed control system in the plant make it possible to tune all parameter based on simulation results.

4.3.2.Production rate

According to simulation, Increase FEED GAS SO_2 concentration, Increase Production rate about 50%. In this way, it is possible to make the most from available plant facilities and equipment to increase profitability of the plant.

4.3.3.Heat Recovery system

To handle higher gas strengths larger gas – gas exchanger for cooling 1st bed outlet gas and SO_3 gas cooler for cooling final absorbing tower are required. Rigorous simulation of the heat exchanger shows its surface area is big enough to handle required heat load so it does not need any redesign (Table 5).

Table 5: Hot gas-gas exchanger heat loads nad surface area.

	Double Absorption	Simulation
Surface area (m^2)	1798	1798
Heat load(MBTU /hr.)	27	32

But increase surface area of SO_3 gas cooler is inevitable otherwise final absorbing tower inlet gas temperature exceed more than allowable temperature (~250 ^oC) for efficient absorption in the tower(Table 6).

Table 6: SO_3 gas cooler heat exchanger heat loads and surface area.

	Double Absorption	Simulation
Surface area(m^2)	700	850
Heat load (MBTU /hr.)	6.3	7.15 MBUT/hr.

Also the acid circulation system will need be designed to handle higher acid flows and higher heat loads. The Absorbing Acid Cooler will need to be increased in size (i.e. surface area) to handle the higher acid flow and heat load, too.Current acid coolers are Plate heat exchanger type. In order to increase surface area, number of effective plates should increase. But this changes are not so vital and can be done easily.

CONCLUSIONS

In this study, we used modeling technology in debottlenecking existing plant, achieving high production capacity and profitability of the plant, increasing energy recovery, and process analysis to optimize plant operations to meet environmental regulations. Here, we use previously developed model for further study of debottlenecking a metallurgical sulphuric acid plant.The steady state models, implemented in ASPEN PLUS includes a catalytic reactor (four pass converter), heat exchangers such as SO_3 gas cooler and gas-gas heat exchangers, mixers, splitters and absorption columns. The kinetic parameters were fitted to the real plant data, while the remaining model parameters were estimated using classical correlations.

The simulationused to evaluate the behaviour of the plant and detect changes in product quality and capacity, as well as for optimization of the total amount of SOx released in the in the atmosphere. Considering that the sulphuric acid plant is a brownfield site, the study considered available facilities and current plant layout as design constrains. Although in obedience to the plant design basis, gas flow limited by the plant blower and increase gas flow will affect equipmentdimensions.Increase SO_2 Concentration by decreasing dilution air and proper tuning of control parameters, will lead to production increases about 50% while SOx emissionsmeet environmental regulations, too.

ACKNOWLEDGEMENTS

We express our gratitude to all Fanavarn Parsian Company staff for providing some basic information on metallurgical sulphuric acid plants. The support from Dr. Mohammad Naderi, direct manager of FAPCO is also acknowledged.

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