SULPHURIC ACID PLANT INTEGRATION IN NICKEL HYDROMETALLURGICAL FACILITIES

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ABSTRACT

Nearly all base metals hydrometallurgical processes require sulphuric acid. This acid is often produced on-site in one or more conventional double contact double absorption (DCDA) type sulphuric acid plants. On-site production has the key benefit of providing steam and electricity as co-products. This paper provides an overview of sulphuric acid plants used at nickel leaching operations and insight into the challenges faced when balancing acid, steam and electricity demand - especially during transient and turndown operation. CORE-SO2™ technology is presented which has been tailored to specifically meet the industry's need for lower capital cost, decreased tail gas emissions (without effluent generation), maximized energy recovery along with reliable turndown capability and zero CO_2 emissions. CORE-SO2™ plants can produce from 100 t/d up to 13,000 t/d of acid in a single train.

Keywords: Sulphuric acid plants, base metal and nickel hydrometallurgy, emissions

INTRODUCTION

Sulphuric acid is used to leach valuable metals such as nickel, copper, cobalt and rare earth elements. This acid is supplied from an external source or by on-site production from sulphur. A key benefit to on-site production is the acid plant's heat recovery process that generates steam that can be used in the hydrometallurgical plant or for electricity generation. Acid plants can also provide low grade heat as hot water that can be used for process heating or for desalination. Most hydrometallurgical plants are in remote locations where the acid plant's electricity generating capability plays a critical role in maintaining efficient, low-cost operations.

REFERENCE PLANTS

Table 1 shows several nickel and copper hydrometallurgical facilities and their on-site acid plant production capacity along with their associated power generating equipment and its capacity. All the acid plants burn sulphur to produce sulphuric acid and raise high pressure superheated steam. The superheated steam is most often used to generate electricity, but in some cases it is sent to the hydrometallurgical facility for heating purposes.

Some of the world's largest single train acid plants are found at nickel hydrometallurgical facilities which is the focus of this paper. Acid plants are also used at copper leaching operations. The NorAcid plant in Chile is located on the coast and produces acid for use at several copper leaching operations in the region.

Table 1: Operating Acid Plants and Their Power Generating Capacity

Owner	Operation	Metal	Location	Acid Production	Generating Capacity
First Quantum Minerals	Ravensthorpe	Ni	Western Australia	1 x 4400 t/d	3 x 18 MWe STG(1)
Glencore	Minara	Ni	Western Australia	1 x 4500 t/d	2 x 28 MWe STG(2) 1 x 31.5 MWe GT(2)
MCC-JJJ Mining	Ramu	Ni	Papua New Guinea	2 x 1700 t/d	No co-gen(3)
Sumitomo/Komir	Ambatovy	Ni	Madagascar	2 x 2750 t/d	3 x 45 MWe STG(4)
Tsingshan / Eramet	PT Weda Bay Nickel	Ni	Indonesia	2 x 3350 t/d	70 MWe(5)
CMOC	Tenke Fungurume	Cu	DR Congo, Africa	1 x 825 t/d 1 x 1400 t/d	1 x 6 MWe STG 1 x 20 MWe STG(6)
Freeport McMoRan	Safford	Cu	Arizona, USA	1 x 1550 t/d	1 x 17 MWe STG(7)
NorAcid S.A.	Mejillones	Cu	Chile	1 x 2060 t/d	1 x 24 MWe STG(8)

*GT = Gas Turbine Generator, STG = Steam Turbine Generator

HYDROMETALLURGICAL PLANT UTILITY CONFIGURATIONS

Overview

Many options are available to the designer when integrating a sulphuric acid plant into a remote hydrometallurgical facility. The term remote in this case means that the facility is located where a connection to an electrical grid is not available. Electricity cannot be imported or exported and must be generated on-site. The remoteness of the site also prevents sulphuric acid from being exported to external customers.

The demand for acid, steam and electricity at steady state and at turndown conditions must be considered and appropriate supplemental systems installed to manage varying operating conditions. Start-up electrical and steam generating systems often consist of fuel fired diesel generators and fuel fired package boilers. These systems must be installed to ensure the acid plant can be preheated and commence operation after construction and after subsequent cold shutdowns.

The next few sections provide example configurations for hydrometallurgical facilities based on their acid, steam and electricity requirements. In the figures that follow:

- Medium pressure (MP) steam (7 bar(g), saturated) is used to indirectly melt sulphur and is also supplied to the acid plant for use in the deaerator. The deaerator conditions the boiler feed water prior to it being pumped to the acid plant economizers and steam generating system. Additional steam pressure let down to 3 - 5 bar(g) occurs prior to some users (filters, tanks, jacketing, etc.) in the sulphur melting area. It should be noted that MP steam can also be 20 bar(g) steam that is sometimes required for the hydrometallurgical plant.

- High pressure (HP) steam is usually specified as 40 bar(g) or 60 bar(g) steam. Superheated steam is supplied to the steam turbine generator (STG) and is typically 400°C for 40 bar(g) systems and 500°C for 60 bar(g) systems. Conventional double contact double absorption (DCDA) type sulphur burning acid plants produce 1.2 – 1.4 t superheated HP steam (60 bar(g) / 500°C) per t acid (100% H_2SO_4 basis).

- The hydrometallurgical plant may need HP steam for its process (usually high-pressure acid leach (HPAL) autoclaves) or MP steam for process heating. Both are often supplied at saturated or slightly superheated temperatures (i.e., 5 - 10°C above saturation temperature).

- STG MP steam is produced in an extraction port located on the turbine. This is a common design feature that enhances power generation while meeting the acid plant demand for MP steam.

- Unless otherwise noted, the STG's are condensing which maximizes power generating capacity.

High Electricity Consumption

The block flow diagram shown in Figure 1 is for a facility with electricity demand that exceeds what can be produced from acid plant steam. In this example, a gas turbine generator with a HRSG (heat recovery steam generator) provides additional steam to the STG(s). Dashed lines represent intermittent operation. This applies to this figure and all subsequent figures in this paper.

Fuel fired package boilers can be used to increase steam production. This steam is used to generate electricity if the gas turbine generator or acid plant are not supplying sufficent steam. Fuel fired generators (not shown) are used to provide start-up and back-up electricity.

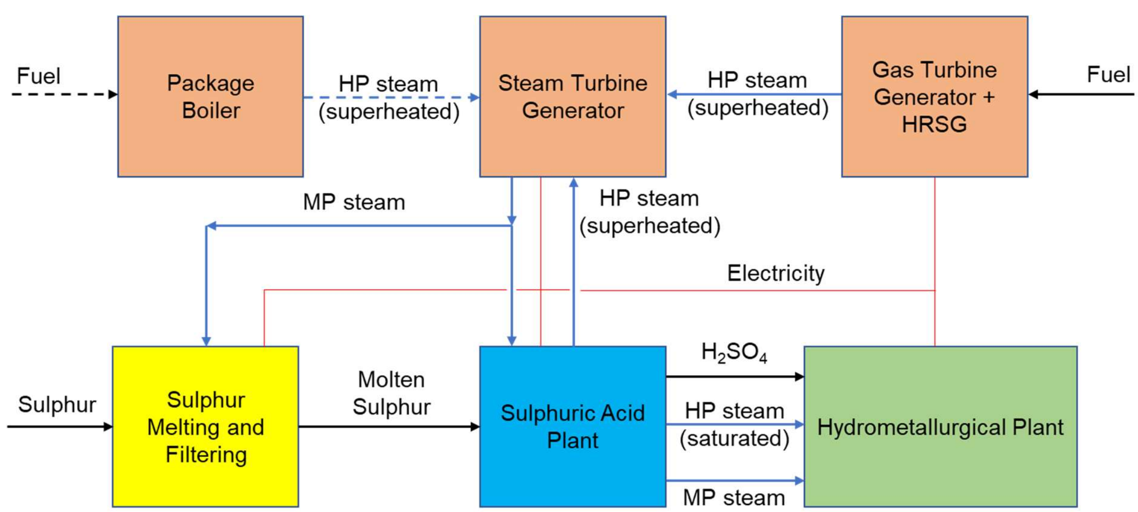

Figure 1: Utility Block Flow Diagram, High Electricity Consumption

In Figure 1, MP steam from the acid plant can be produced by installing an ALPHA™ system in the acid plant that generates steam (5-10 bar(g), 0.55 t steam per t acid (100% H_2SO_4 basis)) from hot, approximately 200°C, concentrated, 99 wt.% H_2SO_4 acid (Figure 2). This system decreases the amount of cooling water required for the acid plant which decreases water consumption if evaporative cooling is used and decreases electricity consumption if indirect air cooling ("fin-fan") is used.

A feature of ALPHA™ is its ability to be turned on and off while maintaining design sulphuric acid production rates from the acid plant. This flexibility allows the MP steam system operation to be optimized to meet hydrometallurgical plant requirements.

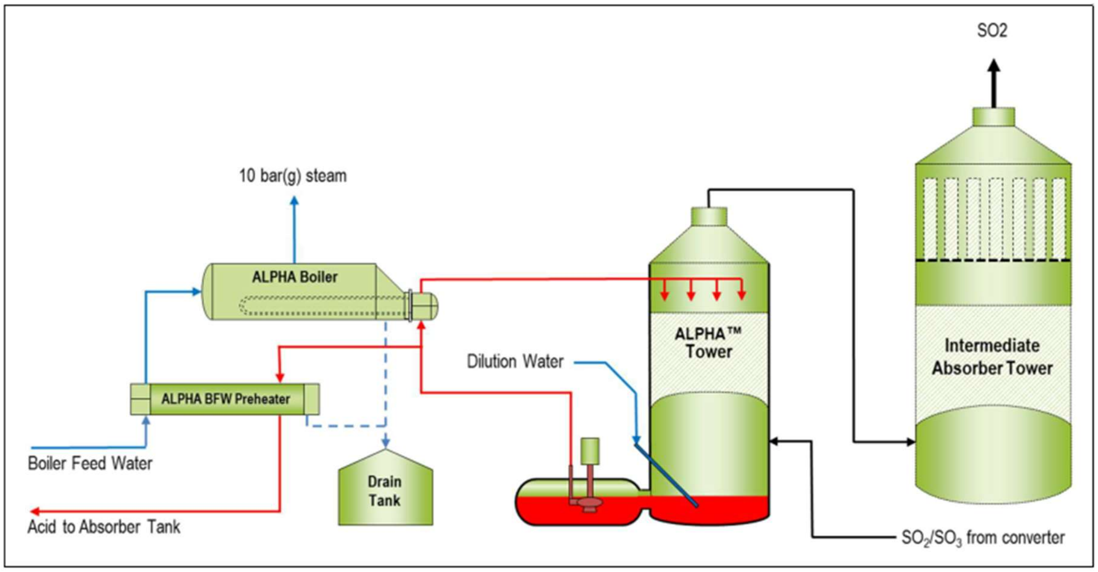

Figure 2: ALPHA™ Process for Producing 10 bar(g) MP Steam from Hot Sulphuric Acid

High Steam Consumption

This configuration is used when MP steam demand in the hydrometallurgical plant is high and the electricity demand is low. A back-pressure steam turbine generator is used to produce electricity and MP steam (typically 20 bar(g)). Less electricity is produced in a back-pressure turbine because the steam is not condensed. MP steam can also be produced in the acid plant by installing a steam turbine driven blower instead of an electric driven blower. Steam turbine driven blowers are commonly used in phosphate fertilizer acid plants where MP steam demand from the fertilizer plant is high.

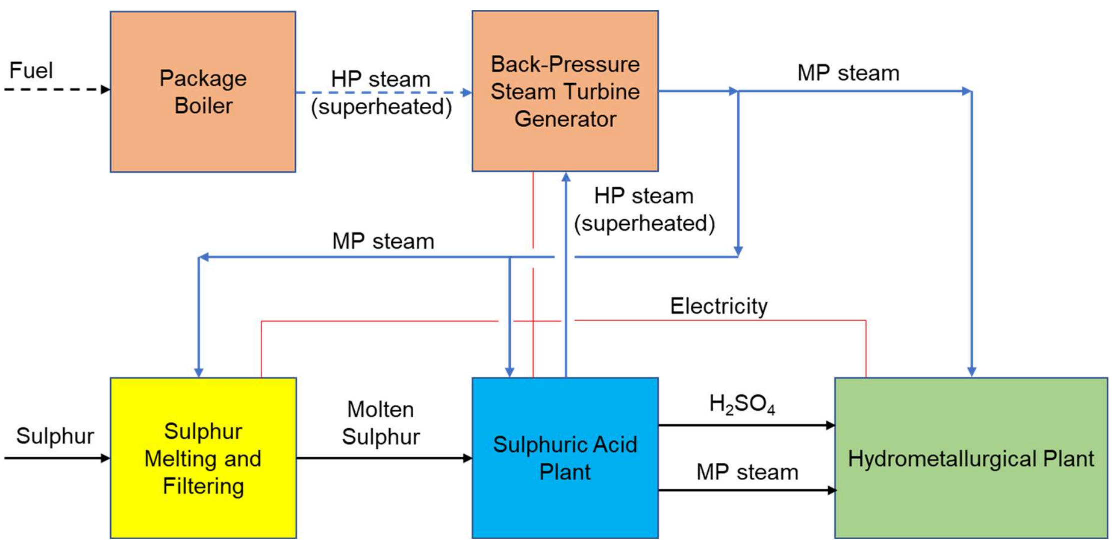

Figure 2: Utility Block Flow Diagram, High Steam Consumption

Hot Water for Desalination

Many metallurgical sites are located where water quality is poor or where seawater is available and can be used for the process. Desalination plants are often installed to produce higher quality water. Low grade heat generated in the acid plant's acid circuit can be recovered as 90°C hot water and sent to the desalination plant where the water is cooled and returned to the acid plant in a closed loop. Figure 3 shows this configuration. Hot water production is maximised and no MP steam is produced in the acid plant.

The acid cooling circuit design should account for possible fluctuations in demand for hot water from the desalination plant. Additional cooling water system capacity should be designed into the circuit to effectively decouple the acid plant from the desalination plant. This is shown in Figure 4 where the absorbing acid cooler and cooling water tower are sized so that the acid plant design production rate can be maintained with the desalination water heater off-line.

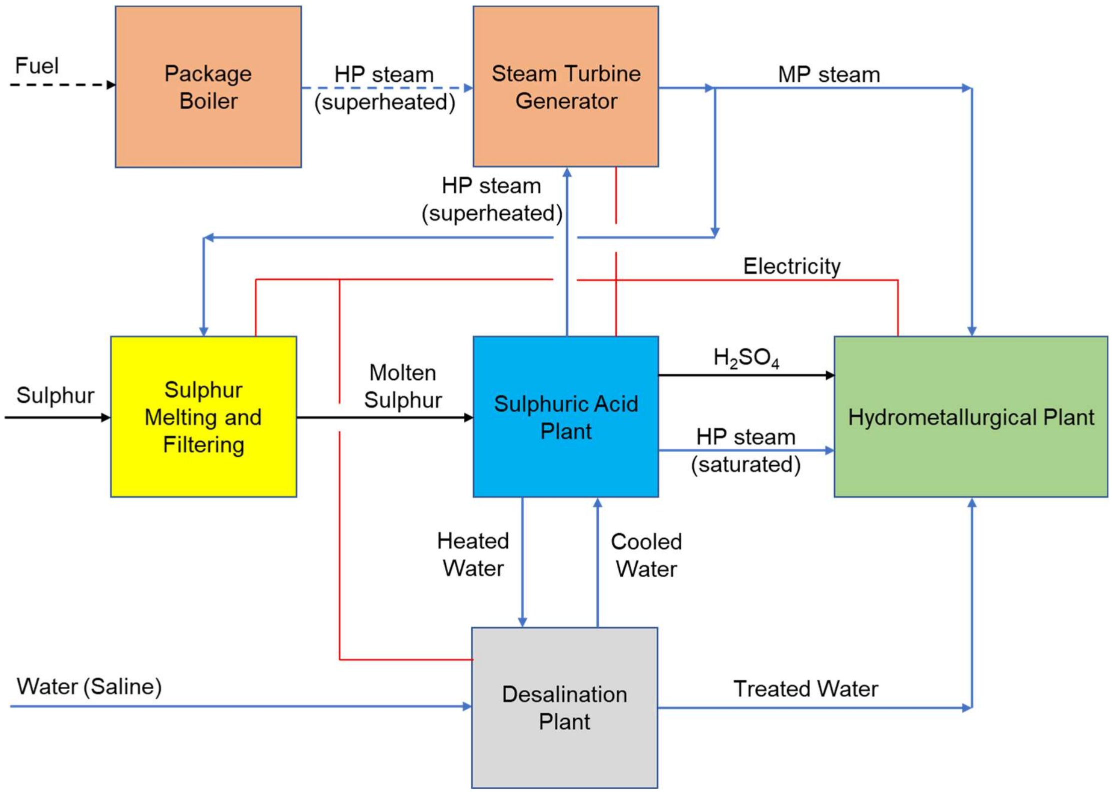

Figure 3: Utility Block Flow Diagram with Desalination Plant

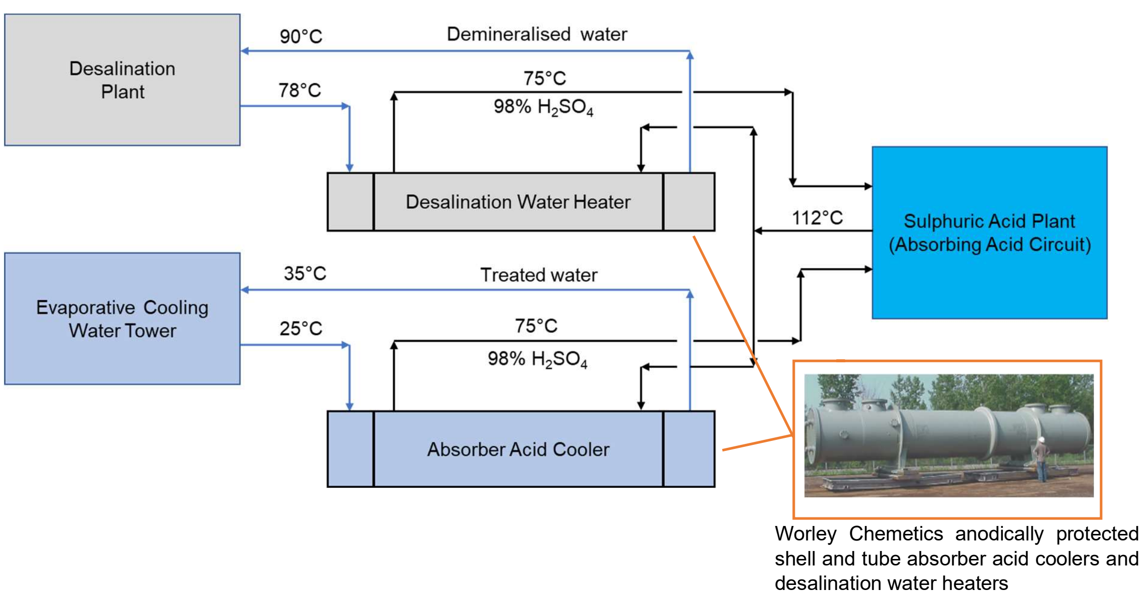

Figure 4: Desalination Plant Hot Water Supply Circuit

ACID, STEAM AND ELECTRICITY BALANCES

Acid

Sulphuric acid is stored at site in large, unlined carbon steel tanks sometimes with anodic protection. Storage quantities are equivalent to between 5 and 10 days of acid production. More acid storage capacity gives the site the ability to operate for longer periods of time with the acid plant off-line. Fortunately, most sulphur burning acid plants have a high availability, often between 98% and 99% and in some cases, approaching 100% outside of major turnarounds.

Major turnarounds are required every 3 to 5 years for catalyst screening and typically last anywhere from 12 to 20 days depending on the scope of repairs required. During this period, the acid plant is cooled to ambient temperature and the vessels opened for inspection and repair. The acid plant is restarted by burning fuel in the sulphur furnace to heat the furnace which is then followed by a series of “dry blows” where dry air is sent through the furnace with the fuel burner turned off to heat the catalyst beds to a temperature above the dew point to prevent catalyst damage during subsequent direct firing. Once all the catalyst bed temperatures are above the dew point temperature, direct firing of the furnace is started and the catalyst beds are heated to around 400°C. The fuel burner is removed and sulphur firing commences.

Most hydrometallurgical facilities will also schedule major maintenance to coincide with the acid plant shutdown because the acid storage capacity is insufficient to provide enough acid to operate at full rates during the outage. In addition, fuel must be burned to generate steam for electricity generation that would normally be provided by the acid plant which increases operating costs for this period.

During periods with the acid plant on-line, hydrometallurgical plant maintenance must also occur. A good example is at nickel HPAL operations where one of the autoclaves will be taken off-line and descaled while the other(s) remain on-line. Acid, steam and electricity demand all decrease which needs to be included in the overall facility design.

Steam

Package boilers are used to generate supplemental steam when the acid plant is off-line to ensure electricity generation in the steam turbine generator(s) is maintained. These systems often require the burning of hydrocarbon fuels such as natural gas, LPG, coal, distillate or fuel oil. These fuels can be expensive, especially at remote sites. CO_2 emissions increase.

Excess steam can be sent to a dump condenser to recover valuable boiler feed water. Dump condensers are usually shell and tube exchangers that use cooling water to condense steam. Some sites have dump condensers installed in parallel with their STG’s to ensure acid production remains available even when the STG is off-line. Operating scenarios that require the use of the dump condenser should be minimised to minimise water and/or energy that is required to condense the steam via evaporative cooling towers or fin-fan air coolers.

Electricity

The acid plant produces more electricity than it consumes. The excess electricity is used in the hydrometallurgical plant and other plant wide systems. Fuel fired generators (often diesel) are used to provide acid plant start-up electricity and emergency power when the acid plant is off-line for short durations (a few hours). Electricity demand varies with the demand from the hydrometallurgical plant and the acid plant.

Based on the previous discussion, it’s clear that acid, steam and electricity supply and demand are all interrelated. The next section further illustrates this point.

Operating Scenarios

Table 2 provides a qualitative summary of the effect of varying acid, steam and electricity demand on the operation. “High” represents operation at the design capacity for the plant and “Low” represents operating at the turndown capacity of the plant. In these scenarios, the assumption is that acid cannot be exported to an external customer and electricity cannot be stored in batteries.

Table 2: Operating Scenario Impact on Acid, Electricity and Steam Balance

Demand			Supply		Outcome
Acid	Electricity	Steam	SAP Rate	Fuel	
High	High	High	Design	None	Supply = Demand
High	High	Low	Design	None	Excess steam condensed in dump condenser to recover water
High	Low	Low	Design	None	STG steam by-pass, excess steam to dump condenser
High	Low	High	Design	None	STG steam by-pass, remaining steam to process plant
Low	Low	Low	Turndown	None	Supply = Demand
Low	Low	High	Turndown	Low	Package boiler steam for process plant
Low	High	High	Turndown	High	Package boiler steam for process plant and power generation
Low	High	Low	Turndown	Medium	Package boiler steam for power generation, not process plant

TECHNOLOGICAL ADVANCES IN SULPHURIC ACID MANUFACTURE

Conventional DCDA Plants

The modern contact process has been used for more than 100 years to make concentrated, 98% H_2SO_4, acid. The process reactions are as follows:

(1) $\underset{\text{in air}}{S + O_2} \rightarrow SO_2$ $\qquad \Delta H°_{25°C} = -300$ kJ/mol

(2) $SO_2 + 0.5O_2 \xrightarrow[\text{in catalyst}]{} SO_3$ $\qquad \Delta H°_{25°C} = -99$ kJ/mol

(3) $SO_3 + H_2O \rightarrow H_2SO_4$ $\qquad \Delta H°_{25°C} = -130$ kJ/mol
(in 98.5% H_2SO_4)

Each reaction generates heat which is recovered as steam or rejected to the atmosphere via cooling systems. Figure 5 shows the flowsheet for a modern conventional double contact double absorption (DCDA) type sulphuric acid plant. Reaction (1) takes place in the sulphur furnace where molten sulphur at 140°C is sprayed into a hot, (1150°C) refractory lined furnace where it burns in dry air to generate sulphur dioxide (SO_2). The SO_2 is then sent through three catalyst beds where it oxidises to sulphur trioxide (SO_3) (Reaction (2)).

Heat exchangers and a superheater are located between the catalyst beds to cool and heat the process gas and superheat steam that is sent to the STG. The hot gases leaving the third catalyst bed are cooled in an economizer and superheater prior to entry into the ALPHA™ system and cold absorption system where the SO_3 reacts with H_2O in 98.5% H_2SO_4 to produce H_2SO_4 (Reaction (3)). Dilution water is added to maintain the desired product acid concentration, typically 98.5% H_2SO_4.

The cold gases are then reheated in gas/gas heat exchangers prior to entering the fourth catalyst bed for final SO_2 conversion to SO_3. The gases are then cooled in an economizer prior to entering the final absorption system where SO_3 is reacted with 98.5% H_2SO_4. The gases then leave the final absorption system and are exhausted to the atmosphere via a stack.

Significant improvements to the conventional DCDA design have been made in the past fifty years (nearly all by Worley Chemetics!). These improvements focused on better materials of construction, more efficient heat exchanger designs and improved heat recovery resulting in safer, more reliable and more efficient acid plants. These plants recover more than 99.8% of the feed sulphur to sulphuric acid and can recover more than 93% of the energy generated by the process reactions. However, opportunities exist to further improve the design to address its inherent limitations:

1) Single train capacity: DCDA plants are limited in size to approximately 5,000 t/d for economic reasons (costs increase rapidly at higher capacities) – although technically they can be designed for higher capacities. This capacity limitation requires some sites to install two or more acid plants to meet demand increasing complexity and cost.
2) Emissions: lower tail gas SO_2 concentrations are difficult to achieve without costly scrubbers that use water and expensive reagents (amine, caustic or hydrogen peroxide) and, in some cases, generate waste streams that require disposal
3) Turndown capability is limited to approximately 40% of the design rate
4) Hydrocarbon fuels are required for cold start-up resulting in CO_2 emissions
5) Large equipment, mostly stainless steel, resulting in high capital costs and significant on-site fabrication.

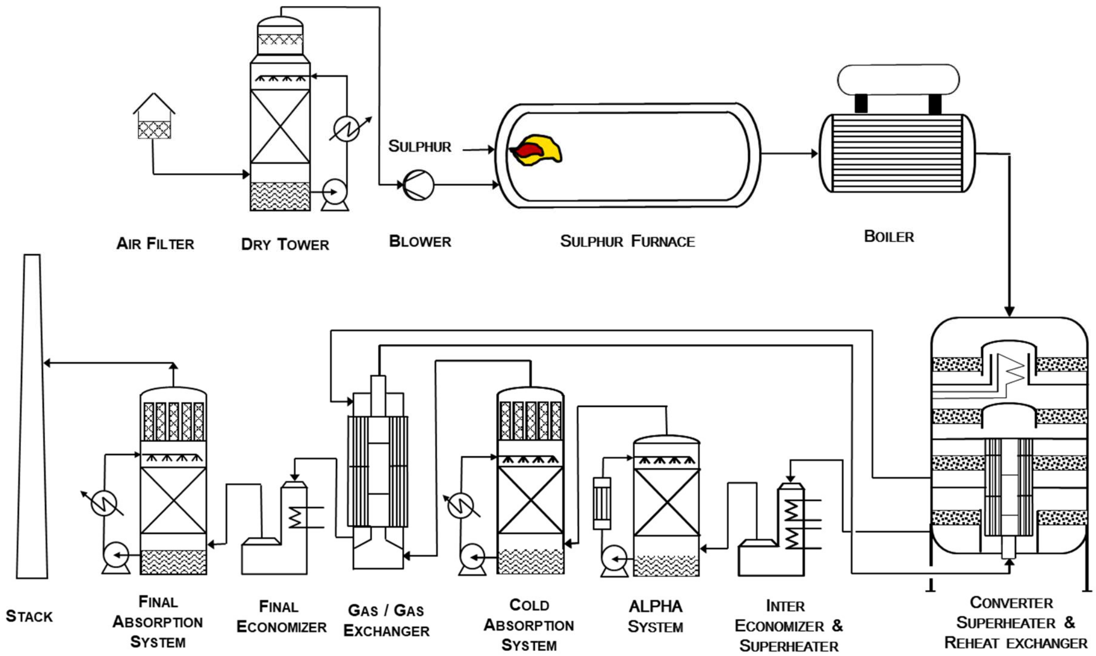

Figure 5: Conventional DCDA Flowsheet with ALPHA™

Worley Chemetics' CORE-SO2™ overcomes these limitations by using industrial oxygen instead of air as shown in Figure 6. The process is discussed further in the next section.

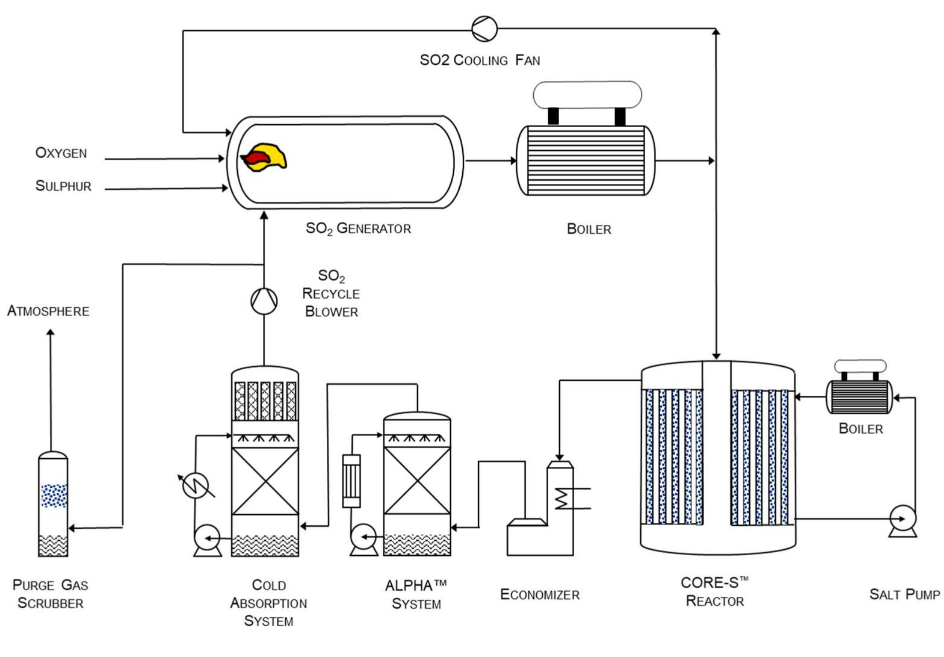

Figure 6: CORE-SO2™ Flowsheet

CORE-SO2™

Process Description

Ambient air is drawn into the oxygen plant (VPSA or cryogenic type depending on capacity) where it is dried and the oxygen and nitrogen are separated to produce a stream of 95 – 98 vol% oxygen which is sent to the SO_2 Generator. In the SO_2 Generator, molten sulphur is reacted with oxygen to form concentrated SO_2 gas (40 vol.% or 60 vol.%). The SO_2 Generator is a proprietary design which allows complete combustion of the sulphur at modest temperature due to recycle of cool SO_2 gas and recycle of gas from the Cold Absorption System. Hot SO_2 gas leaves the SO_2 Generator and is cooled in a boiler where the heat is recovered as high pressure (40 bar(g) or 60 bar(g)) steam. The strong SO_2 gas then flows to the CORE-S™ Reactor.

In the CORE-S™ Reactor, the exothermic conversion of SO_2 to SO_3 takes place as the process gas passes through the catalyst filled tubes. The energy released inside the tubes is transferred to the molten salt coolant flowing on the shell side, resulting in a nearly constant temperature of the process gas enabling high SO_2 conversion rates. The gas leaving the converter is cooled to about 170°C in an Economizer. The cooled gas then enters the (optional) ALPHA™ System and subsequent Cold Absorption System where the SO_3 is absorbed by counter-current contact with circulating 98.5% H_2SO_4 (identical to absorption systems used in DCDA plants). The gases leaving the Cold Absorption System returns to the SO_2 Generator via the SO_2 Recycle Blower.

A small portion of the recycle gas is sent to the Purge Gas Scrubber to control the inert gas concentration in the gas entering the CORE-S™ Reactor. This purge gas consists mainly of the inert gases contained in the oxygen feed.

Strong acid (98.5% H_2SO_4) is produced in the Cold Absorption System and is further cooled to less than 40°C before being sent to storage tanks.

CORE-SO2™ for Hydrometallurgical Facilities

CORE-SO2™ is ideally suited for hydrometallurgical facilities due to its following design features:

1) Ultra-low SO_2 and acid mist emissions, < 0.1 kg SO_2/t H_2SO_4 and <0.005 kg mist / t H_2SO_4 are easily achievable.

2) No CO_2 emissions – ever. Electric heaters are used to start up the acid plant. No waste streams, other than impurities in the sulphur, are produced.

3) Low capital cost, smaller equipment, modular construction, high quality due to shop fabrication instead of field fabrication.

4) Turndown to idle is possible without damaging the equipment. This is important during initial ramp-up after construction when the hydrometallurgical plant is not operating at full capacity. Generally, less acid storage capacity is required which also decreases capital cost.

5) Optimized power production and consumption from the superheated steam generated in the process.

6) High single train production capacity, up to 13,000 t/d, which means multiple trains are not required which decreases initial capital cost and ongoing sustaining capital costs.

7) Nitrogen and other gases, such as argon, can be generated as by-products from the oxygen plant and possibly sold, increasing value.

ENHANCED SUSTAINABILITY WITH CORE-SO2™

The ongoing mission to decrease CO_2 emissions applies to metal producing facilities. A proposed utility block flow diagram for a hydrometallurgical plant based on CORE-SO2™ with zero CO_2 emissions is shown in Figure 7. Electric package boilers are used to provide back-up steam and renewables (wind, solar, and/or hydroelectric) provide supplemental electricity generating capacity.

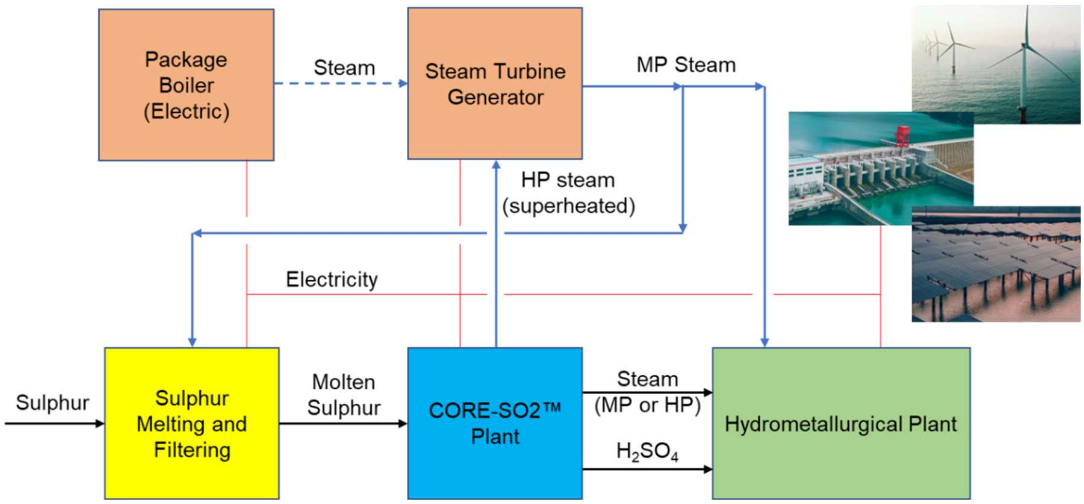

Figure 7. Zero CO_2 Emission Hydrometallurgical Facility

CONCLUSIONS

Sulphuric acid is used at hydrometallurgical facilities to leach valuable metals (Ni, Cu, Co, REE) from ores and concentrates. This acid is commonly produced on-site in conventional DCDA type acid plants. These plants recover energy to produce high pressure superheated steam that is used to generate electricity.

Careful consideration must be given in the design phase to the acid, steam and electricity balances that are required during normal operation. Start-up, transient and turndown operations must be clearly defined and the acid plant and its associated utility systems appropriately designed to cater for these conditions to ensure high efficiency, low-cost operations are maintained.

Hydrometallurgical production of the metals needed for the energy transition can be enhanced by selecting a CORE-SO2™ acid plant which emits no CO_2 and ultra-low quantities of SO_2 and acid mist. Coupling CORE-SO2™ with renewable power results in the possibility of a metal production facility with zero CO_2 emissions.

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