



Integrated production of liquid sulphur dioxide and sulphuric acid via a low-temperature cryogenic process

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Synopsis

The paper describes the design options available for the simultaneous production of liquid sulphur dioxide, via cryogenic condensation, and sulphuric acid in a sulphur-burning sulphuric acid plant. The impact of the operating conditions of the cryogenic condensation on plant capital and operating costs are discussed, with the main focus on the optimization of the most important economic and operative drivers of the non-ferrous mining industry, such as energy efficiency, reliability, and availability. A case history relevant to an integrated sulphur-burning plant producing liquid sulphur dioxide and sulphuric acid, recently started up in the Democratic Republic of Congo, is described.

Keywords

sulphur burning, sulphuric acid, liquid SO₂, cryogenic SO₂ condensation, liquid sulphur dioxide, sulphur dioxide.

Introduction

The production of liquid sulphur dioxide from elemental sulphur, by cryogenic condensation from a gaseous stream, can be easily integrated or combined with a sulphuric acid production plant. A portion of the SO₂-bearing gas that is fed to the first stage of the SO₂-SO₃ catalytic converter can be diverted to a unit dedicated to the condensation of SO₂ at low temperature. The off-gas leaving this unit after condensation still holds a residual amount of SO₂, which needs to be removed before release to the atmosphere. SO₂ removal is conveniently effected by returning the off-gas to the first stage of the catalytic converter, and thereby producing sulphuric acid. When a new plant is designed, once the required liquid SO₂ production capacity has been fixed, the amount of sulphuric acid that can be co-produced varies from a minimum inevitable production that is necessary to allow the operation of an acid plant, up to a large-capacity modern plant. The liquid SO₂ unit is a stand-alone package, which can also be integrated into an existing sulphuric acid production plant with minor modifications subject to a revamping study.

Selection of cryogenic unit design parameters

This section focuses on the identification of the most effective design parameters for the SO₂ cryogenic condensation unit, which can be integrated with a sulphur-burning acid plant having the typical capacity requirements for a copper/cobalt mining operation.

The cryogenic process is based on the condensation of SO₂ vapours, and is thus related to the vapour/liquid equilibrium behaviour of SO₂. The SO₂ condenser operating temperature and pressure can have a strong impact on both capital and operating costs of the unit, and therefore need to be selected through an optimization exercise following the conceptual design phase.

Design basis

The cryogenic unit will be fed with a portion of the gaseous stream from the sulphur-burning section of an acid plant. We are considering a standard sulphur furnace capable of operating within an SO₂ concentration range of 10–13% by volume.

The higher the SO₂ concentration in the feed gas to the SO₂ unit, the lower the energy consumption and the better the efficiency of the unit. However, in practice, integration with a sulphuric acid plant limits the SO₂ concentration to 14% by volume with standard sulphur furnace designs. Concentrations up to 18% are possible with major upgrades in the furnace design, although with such a high SO₂ concentration, NO_x production could be high and post-dilution with dry air could be necessary to achieve the optimal oxygen level at the converter inlet.

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Given a required SO₂ production capacity, the amount of gas fed to the cryogenic unit is related to the SO₂ removal capacity of the cryogenic condenser. Taking advantage of the integration with an acid plant, the exhaust gas is returned to the first pass of the SO₂- SO₃ catalytic converter. Since the uncondensed SO₂ is not vented to the atmosphere, a very low SO₂ residual concentration (parts per volume) in the exhaust gas is not required.

We found that 4% by volume residual SO₂ concentration is an optimum value, since it allows the use of operating conditions that do not require sophisticated equipment and provides the most effective operating cost.

Selection of condensation temperature and pressure

The SO₂ condensation temperature is a key parameter which has a strong impact on the design of the cryogenic unit. According to our optimization, this temperature shall be minimized. In fact, we select to condense SO₂ vapours at -65°C inside the tubes of a heat exchanger, which are submerged by a refrigerant evaporating at constant temperature slightly above the SO₂ freezing point (-75.5°C).

The condensation at -65°C requires the use of a two-stage (high- and low-pressure) cryogenic package, working with two fluids (R23 and NH₃ for the separate low- and high-temperature circuits.

This is a standard package available from different vendors in the refrigeration business. The minimized working temperature has a minor impact on capital expenditure and power consumption, as can be seen from Table I, which compares the performance at two different condensing temperatures.

We can operate the condenser at -65°C and about 0.3 bar (gauge) pressure, in order to achieve 4% uncondensed SO₂ inside the exhaust gas.

A standard blower is used to circulate the gas through the liquid SO₂ unit. The blower head is set to the minimum amount required to withstand the pressure drops in the gas circuit, providing an optimized total electrical power consumption for the liquid SO₂ unit.

Understanding the parameters optimization

Figure 1 shows the behaviour of the SO₂ vapour/liquid equilibrium, providing the calculated amount of uncondensed SO₂ in the exhaust gas as a function of the condenser pressure at three different condensation temperatures.

A temperature increase from -65°C to -45°C requires the use of a two-stage cryogenic package, which can be optimized to use NH₃ as a single fluid and to require a slightly lower electrical power consumption and capital expenditure.

Table I

Comparison of two liquid SO₂ packages operating at -65°C and -45°C

Package	A	B
<i>Characteristics of machinery</i>		
Condensation temperature	-65°C	-45°C
Condenser pressure	0.3 bar (g)	3.2 bar (g)
Cryogenic package	Two stages (cascade) system, with Separate fluids NH ₃ , R23. (see Figure 2)	Two stages (cascade) system, with NH ₃ as mono fluid.(see Figure 3)
HP and LP compressors	Screw-type, oil-injected HP stage compression ratio:8.2 LP stage compression ratio:12.2	Screw-type,oil-injected HP stage compression ratio: 6.2 LP stage compression ratio:4.5
SO ₂ gas booster	Single stage, centrifugal blower (see Figure 4) Head: 0.2 bar LV motor	Two stages, integrally geared gas compressor with inter-refrigeration. (see Figure 5) Head: 3.5 bar HV motor
<i>Major utilities consumption</i>		
Water for cooling	1 710 000 kcal/h	2 940 000 kcal/h
Electrical power		
Cryogenic package HP stage	513 kW(LV)	372 kW(LV)
Cryogenic Package LP stage	513 kW(LV)	240 kW(LV)
Gas booster	160 kW(LV)	1950 kW(HV)
Total power	1186 kW	2562 kW
<i>Pros and cons</i>		
Operation	A variable-frequency driver is used to manage the gas flow variations, allowing energy savings	The multistage, engineered gas compressor requires a gas bypass to manage the flow variation which may be required by the process
Maintenance	Two fluids shall be managed as refrigerants	The gas compressor requires more maintenance and specialized technical service
Capital (based on machinery cost, not installed)	Baseline	30% more expensive (mostly due to the gas compressor)

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The SO₂ condenser shall be operated either at -45°C and 4 bar (a) or -25°C and 12 bar (a) to limit the amount of uncondensed SO₂ in the return gas at 4 vol. %.

Operation at higher uncondensed SO₂ concentration (e.g. 8 vol. %) requires practically doubling the amount of gas in order to match the targeted production capacity.

In this case we still require to condense SO₂ at either -45°C and 2 bar (a) or -25°C and 6 bar (a).

Operation at about atmospheric pressure will not be possible at either -45°C or -25°C with a feed gas with 10–12% SO₂ concentration. Working at temperatures higher than -65°C requires the use of a proper compressor to obtain the required gas compression ratios. This compressor can be very complicated, and the associated costs in terms of capital and power consumption change dramatically from a standard blower.

Table I provides a comprehensive comparison between two liquid SO₂ packages designed for -65°C and -45°C. The data refers to a plant having the following design basis:

- Production capacity: 900 t/day 100% acid plus 100 t/day liquid SO₂
- Standard sulphur furnace operating at 10–12% SO₂ concentration
- Double conversion double absorption (DCDA) plant
- Catalytic SO₂-SO₃ converter with standard V₂O₅ catalyst and 3+1 configuration

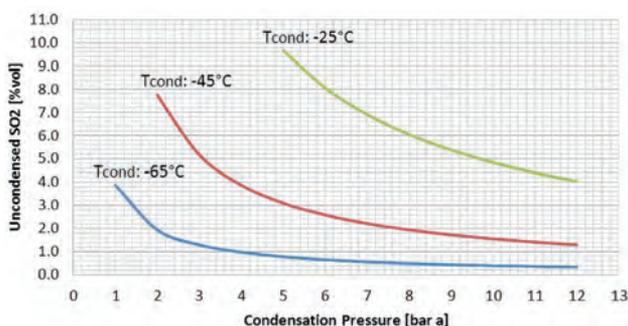


Figure 1—SO₂ vapour/liquid equilibrium as a function of the condenser pressure

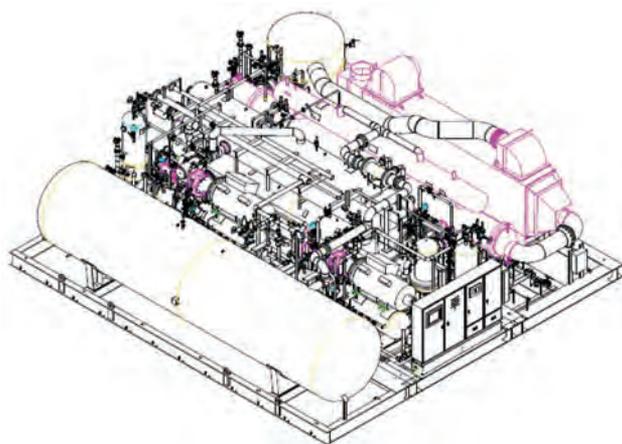


Figure 2—Two-stage cryogenic package, separate NH₃, R23 fluids

- Standard interpass absorption tower with common pump tank
- Liquid SO₂ cryogenic unit, capable of running from a minimum to a maximum capacity without affecting the acid production.

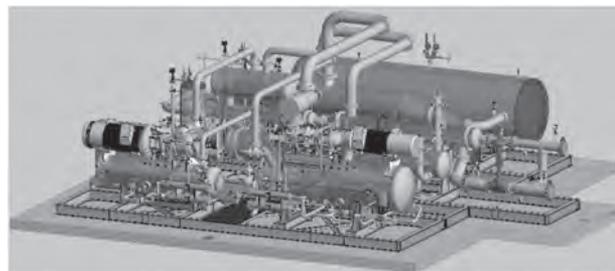


Figure 3—Two-stage cryogenic package, NH₃ monofluid

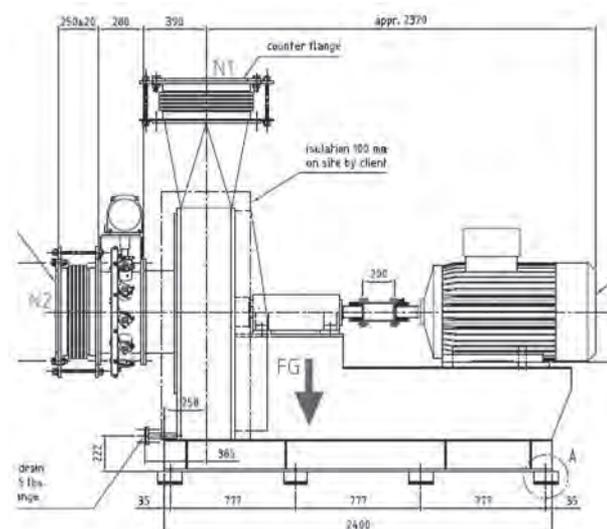


Figure 4—SO₂ gas booster - single-stage, centrifugal blower

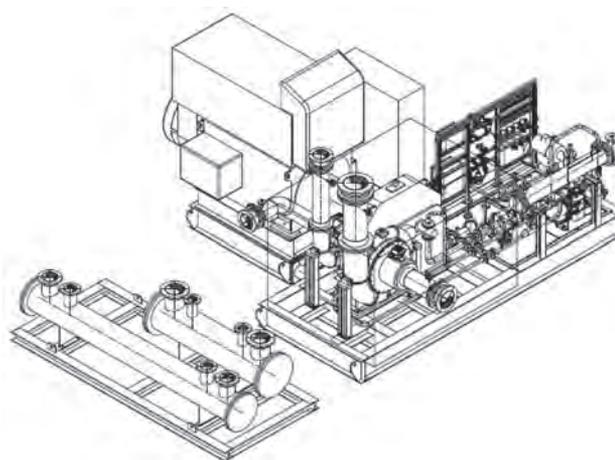


Figure 5—SO₂ gas booster - two stages, integrally geared gas compressor with inter-refrigeration

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The design case 'A' provides not only an important capital saving but allows about 1400 kW less power consumption, 70% lower cooling duty, and provides a more flexible operation and lower maintenance.

Plant configuration for integrated production of sulphuric acid and liquid SO₂

SO₂ cryogenic unit – process description

The process flow diagram of the unit is depicted in Figure 6.

A portion of the SO₂ gas leaving the waste heat boiler of the acid plant (see Figure 7) is diverted to the SO₂ plant. The gas is cooled in the hot reheat exchanger, preheating the exhaust SO₂ gas returning to the acid plant.

The gas is further cooled and cleaned from traces of SO₃ inside the SO₂ washing tower, to avoid contamination of the liquid SO₂ product. Gas sensible heat is removed and SO₃ absorbed by countercurrent contact with concentrated acid, circulating through the tower with a dedicated circuit equipped with an acid cooler for temperature control.

A controlled quantity of dilution water is added to the column's tank to maintain the acid concentration at 98.5%. The acid produced by SO₃ absorption is delivered to the sulphuric acid plant.

The SO₂ gas leaving the top of the tower is boosted by a blower, cooled in the cold reheat exchanger by the return gas, and sent to the SO₂ condenser. Inside this unit, part of the SO₂ gas is condensed using a refrigerant. Uncondensed SO₂ is returned to the acid plant with the exhaust gas, after preheating in the cold and hot reheat exchangers.

The design of the unit has been optimized in order to keep the overall pressure drop of the system below 0.2 bar.

The condensed SO₂ is transferred to the liquid storage.

Integration requirements and impact on the sulphuric acid plant performance

The liquid SO₂ unit can be considered as a stand-alone

package, which can be integrated into either an existing or a new sulphur-burning sulphuric acid plant.

The integration has specific requirements, with a slight impact on the performance of a standard sulphuric acid production plant

The sulphur furnace of the acid plant shall be designed for 12–13 vol.% of SO₂ concentration at the outlet. This is feasible using the standard refractory material widely used for sulphur-burning acid plants. The maximum amount of SO₂ that can be condensed from this stream (i.e. the total liquid SO₂ production capacity) is limited by the SO₂/O₂ ratio required by the SO₂-SO₃ converter catalyst.

This ratio shall be within the range of 1.15–1.20, having a residual oxygen content in the stream of about 8–9 vol.%.

The waste heat recovery that can be achieved by an integrated plant is affected by the amount of SO₂ removed from the catalytic converter inlet.

An acid plant designed for medium-pressure saturated steam will produce less steam when liquid SO₂ is operated. An acid plant designed for medium-pressure superheated steam will produce steam at lower superheating temperature when liquid SO₂ is operated. This temperature reduction does not compromise the operation of an electrical power co-generation unit. However, an additional superheater recovering waste heat from the last converter stage could improve the steam superheating temperature, maximizing the efficiency of an eventual power co-generation unit.

As shown in the process flow diagram (Figure 7), the ties-ins between the acid plant and the liquid SO₂ unit are limited to very few lines, which are marked in red.

Case study

Desmet Ballestra completed recently a sulphur-burning, sulphuric acid and liquid SO₂ project, based on DuPont-MECS technology, for a metal mining complex in the Democratic Republic of Congo.

The key plant parameters are summarized in Table II.

The plant was commissioned in mid-2012 with liquid SO₂ production on-stream. Figure 8 shows a photograph of the plant. ♦

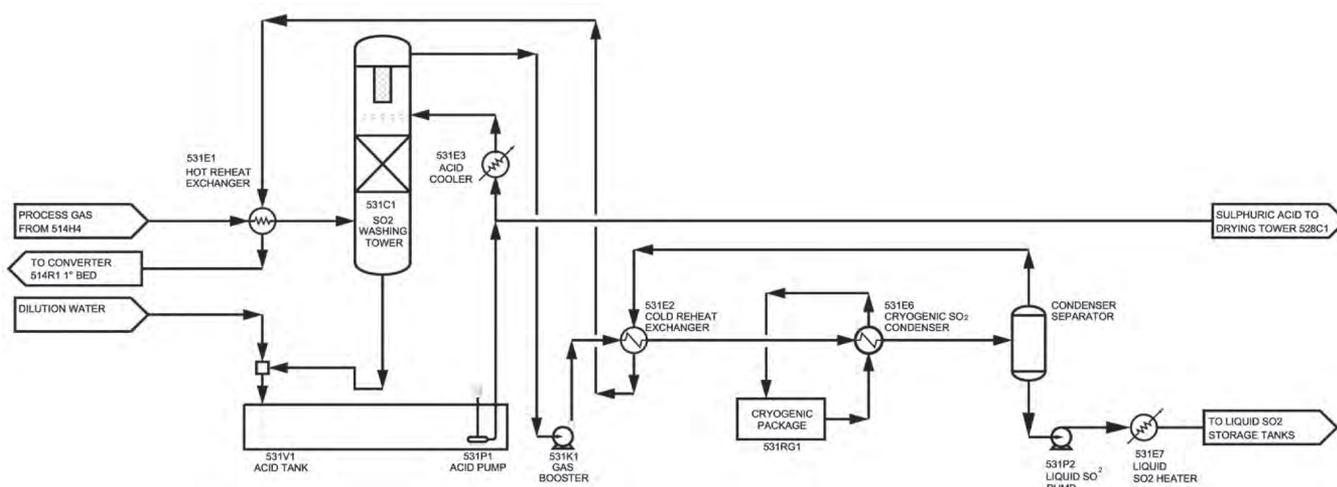


Figure 6—SO₂ cryogenic unit

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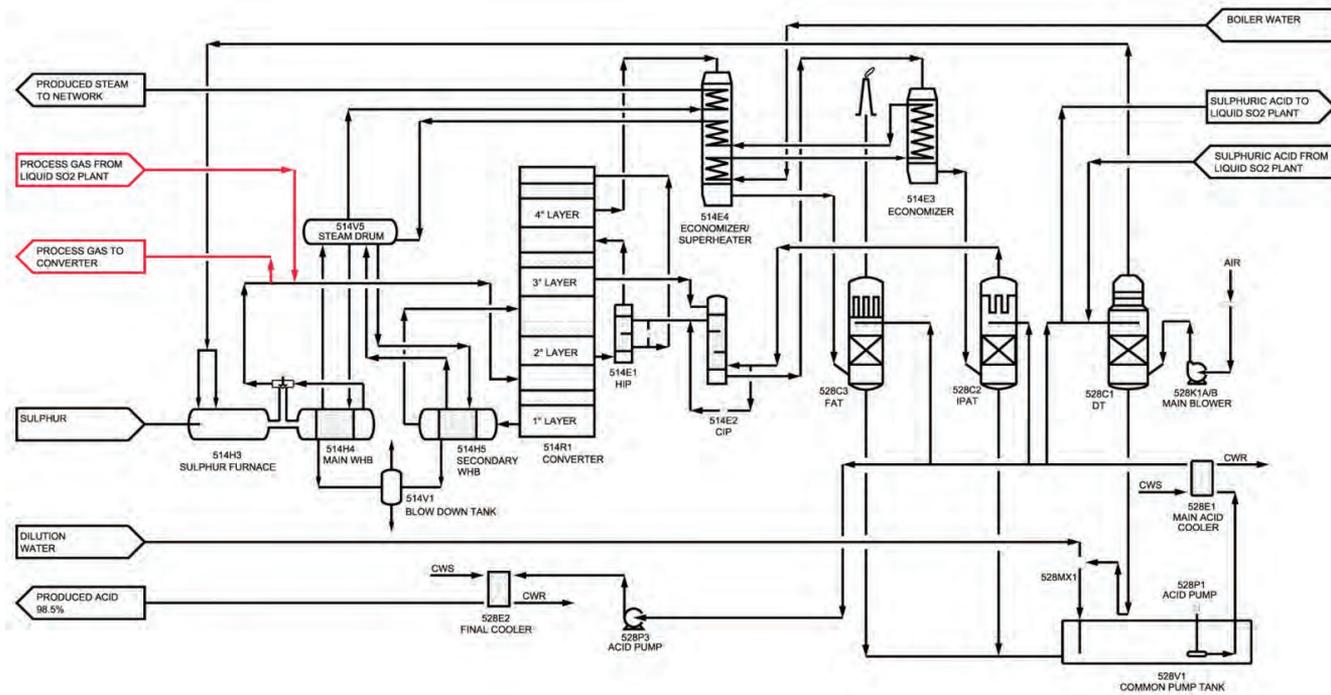


Figure 7—Typical sulphuric acid plant process flow sheet. The tie-ins for liquid SO₂ unit are indicated in red

Table II Case study summary data	
Plant capacity	362 t/d as 100% H ₂ SO ₄ and 90 t/d as liquid SO ₂ or 500 t/d as 100% H ₂ SO ₄
SO ₂ –SO ₃ converter catalyst	V ₂ O ₅ catalyst, DCDA 3+1 configuration, 99.7% conversion
Waste heat recovery system	Co-produced steam at P=25 bar(g), T= 250°C superheated rate: 26.3 t/h when producing liquid SO ₂ rate: 28.4 t/h when producing sulphuric acid only
Liquid SO ₂ unit	Cryogenic condensation at -65°C, atmospheric pressure
Liquid SO ₂ storage	Tank farm having 1000 t total capacity



Figure 8—Sulphuric acid and liquid SO₂ plant in the DRC