



Cansolv® SO₂ Scrubbing System: review of commercial applications for smelter SO₂ emissions control

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Synopsis

As new legislation drives metallurgical plants to lower SO₂ emissions, plant managers face the challenge of keeping their costs under control. The Cansolv® SO₂ Scrubbing System has been broadly adopted in the non-ferrous industry as a cost-effective solution for smelter operators to meet the new SO₂ emissions targets.

The Cansolv® SO₂ Scrubbing System is an amine-based regenerable process that selectively absorbs SO₂ from a variety of gases, including dilute smelter gases, such as furnace and converter gases. The system produces a pure, water-saturated SO₂ by-product stream, which can then be directed to the front end of a sulphuric acid plant for conversion to sulphuric acid. When deployed in a smelter complex, the Cansolv® SO₂ Scrubbing System may also be used to process acid plant tail gas, allowing single absorption sulphuric acid plants to achieve emissions an order of magnitude lower than that of a double absorption acid plant with a lower capital investment. Depending on inlet gas temperature, SO₂ emissions in the treated gas can be controlled to as low as 55 mg/Nm³.

This paper will describe some of the applications where customers have or are planning to use the Cansolv® SO₂ Scrubbing System, as well as which features and cost advantages for the treatment of smelter gases were important in the technology choice.

Introduction

Cansolv Technologies Inc. (CTI) was formed in 1997 to commercialize the Cansolv® SO₂ Scrubbing System. In 2008, CTI was acquired by Shell Global Solutions International B.V. (SGSI) and the company now operates as a wholly owned subsidiary of SGSI. CTI is an innovative, technology-centred company with a commitment to provide custom designed economic solutions to clients' environmental problems.

The Cansolv® SO₂ Scrubbing System was originally developed 20 years ago for the utility flue gas desulphurization (FGD) market to compete with the dominant wet limestone scrubbing technology. Because of the very substantial barriers to entry in this market, the process was instead first commercialized on smaller process applications including sulphur plant tail gases, acid plant tail gases and smelter off-gases. In the ten years since the first technology license was signed, adoption

of the Cansolv SO₂ technology has been most intense in the non-ferrous smelting/acid plant tail gas applications where it has been applied to gases which were unsuitable for conversion to acid due to low or variable concentrations. Today, half of the users of the Cansolv process are in the non-ferrous sector, a trend which is forecast to continue for most of the next decade.

At this time, ten commercial Cansolv® SO₂ Scrubbing Systems are in operation, four are scheduled for start-up in 2009 and several more are in the detailed engineering or procurement phase. In 2009, the first Cansolv SO₂ coal combustion gas scrubber will also be commissioned.

Specifically to the metallurgical industry, some sources are particularly challenging including SO₂ from gases that are highly variable in nature, such as gases from Pierce-Smith converters and batch smelters. These gases are either too dilute or variable in SO₂ concentration to be suitable for direct feed to an acid plant. By varying inventories of lean and rich absorbents, the Cansolv® SO₂ Scrubbing System has been engineered to uncouple absorption and regeneration processes. In operation, the lean absorbent flow to the absorber is modulated according to inlet concentration while the rich amine is pumped to the regenerator at a constant flowrate, creating a steady stream of pure SO₂ from a variable or dilute stream of SO₂ laden gas. The pure concentrated SO₂ can be converted to sulphuric acid (without further gas cleaning), dried and liquefied or in some cases, reduced to elemental sulphur.

New metallurgical processes are currently being deployed that make use of SO₂ as a

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reagent directly. In such cases, neither drying nor liquefaction is necessarily required and gaseous water saturated product can be compressed to the process pressure. This is of particular relevance to the African market where cobalt and uranium processing are set for long-term growth.

As new legislation is coming into effect in Africa, smelters will have to reduce SO₂ emissions. This paper will address the advantages to integrating the Cansolv® SO₂ Scrubbing System to manage smelter SO₂ emissions.

Cansolv® SO₂ Scrubbing System description

The Cansolv® SO₂ Scrubbing System is a patented technology that uses an aqueous amine solution to achieve high efficiency selective absorption of SO₂. The scrubbing by-product is pure, water saturated SO₂ gas recovered by steam stripping using low quality heat. The process is regenerable, meaning the chemical absorbent is not consumed. The high costs of consumable reagents are thus eliminated and effluents are reduced to a minimum. Furthermore, the high capacity and selectivity of the absorbent reduce capital costs.

The following outlines the process description for the Cansolv® SO₂ Scrubbing System. Refer to Figure 1 for the process flow diagram of the Cansolv® SO₂ Scrubbing System as applied to the non-ferrous industry when the SO₂ by-product is converted to sulphuric acid.

► The smelter gas is first treated for bulk dust removal by either a dry electrostatic precipitator or a baghouse filter. Some customers have engineered heat recovery systems such as pressurized hot water closed circuits to send heat recovered from the smelter gas to the Cansolv reboiler. Analyzing the heat recovery potential of the gas is a key element to reduce operating costs when integrating the Cansolv® SO₂ Scrubbing System at a smelter.

- Following treatment for dust removal and heat recovery, the gas must be quenched in a prescrubber tower. Some additional dust or acid mist removal may be warranted so quench solutions can vary in design from simple quench elbows to venturis and in exceptional cases to quench towers with wet ESPs. Because the Cansolv process is tolerant to dust, the complexity of gas quenching/cleaning is normally determined by the compliance obligations with respect to SO₃/acid mist at the emissions point. Occasionally, where the treated gas is hot or high in moisture, gas subcooling is added to a quench.
- Figure 2 shows the Cansolv SO₂ scrubber in a combustion gas application in an aluminium smelter. The gas is quenched directly in a venturi (in the background) which is connected by a wetted elbow to an FRP separator (on left). Off the latter, the gas is ducted to the Cansolv absorber (on right). The absorber is stainless steel lined carbon steel.
- The gas is then contacted with the lean amine solution in a countercurrent SO₂ absorber tower containing structured packing where the SO₂ is absorbed. The treated gas exits the SO₂ absorber tower to atmosphere via a stack with a SO₂ content less than 200 ppmv. The SO₂ laden rich amine from the absorber tower is pumped to the SO₂ stripper tower.
- The amine solution is regenerated by indirect steam stripping and the SO₂ gas is recovered as a pure, water saturated product. Various heat sources may be used in the reboiler, such as low pressure steam or pressurized hot water. Also, heat recovery options internal to the Cansolv® SO₂ Scrubbing System such as mechanical vapour recompression or double effect split flow may reduce heat requirements by as much as 55%.

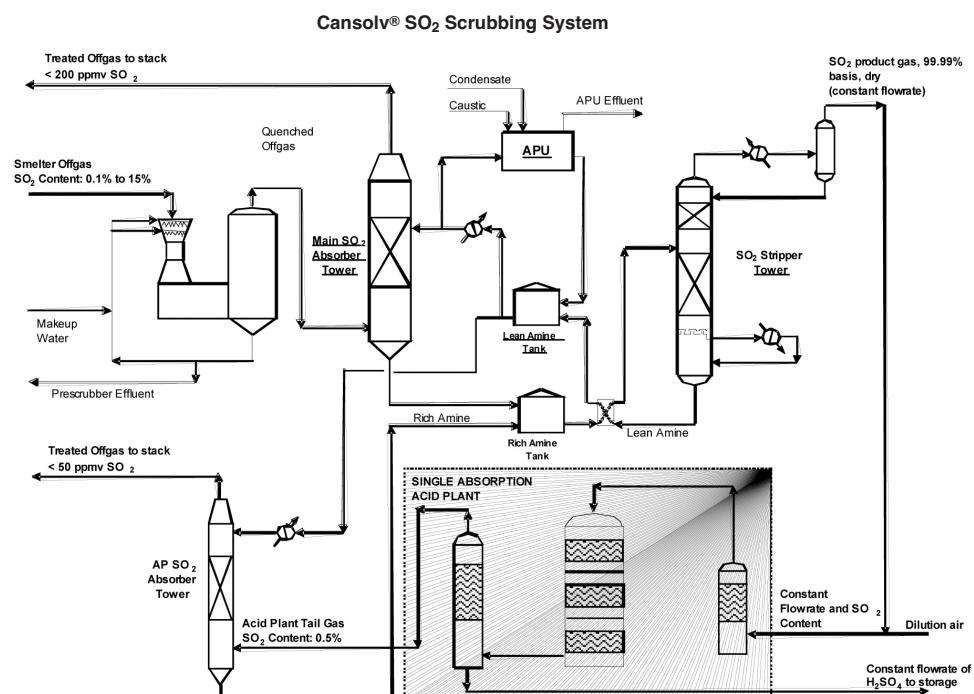


Figure 1—Integrated Cansolv® SO₂ Scrubbing System with conversion of SO₂ by-product to sulphuric acid

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Figure 2—Cansolv SO₂ scrubber

- The lean amine leaves the reboiler and is pumped to each SO₂ absorber tower via the lean-rich amine heat exchanger, the lean amine tank and the lean amine cooler.
- A slipstream of the amine is treated for heat stable salts (HSS) and dust removal in the amine purification Unit (APU).
- When a new acid plant is required to convert the SO₂ by-product to acid, clients have maximized the value of the Cansolv® SO₂ Scrubbing System by installing a single absorption sulphuric acid plant. The tail gas from the acid plant is then directed to a second SO₂ absorber tower and emissions as low as 20 ppmv SO₂ are achieved. The rich amine from the AP SO₂ absorber tower is directed to the common SO₂ stripper tower for regeneration.

Managing SO₂ in the non-ferrous industry

Most concentrated smelter gases ((SO₂)>5%) produced from sulphide ore roasting are already processed in metallurgical acid plants. The regulatory focus on smelters has therefore shifted to the reduction of SO₂ emissions from lower concentration (0.5%<(SO₂)<5%) or variable concentration gas sources, such as furnaces, converters and sinter machines.

It is useful to analyse the problem as two related ones:

- How to selectively separate SO₂ from the other gas constituents
- How to convert the separated SO₂ into a by-product suitable for sale or disposal.

Separation of SO₂ from smelter gas

Several customers have selected the Cansolv® SO₂ Scrubbing System to treat a variety of smelter gases, from dilute sources, such as furnace off-gas to variable sources, such as Peirce-Smith converter gases. In all applications, the Cansolv® SO₂ Scrubbing System delivers a steady flow rate of pure water-saturated SO₂ gas. Most customers have elected to convert the SO₂ by-product to sulphuric acid.

Customers have also piloted the Cansolv® SO₂ Scrubbing System on gases such as catalyst recovery roaster gas, nickel smelter furnace and Peirce-Smith converter gas, and lead sinter machine gas. The objectives were to demonstrate the suitability of the technology to treat gases with high dust content and that are variable in flow rate and SO₂ concentration. In all cases, the piloting campaigns were deemed successful and have resulted in either a commercial unit or continuation of the project to detailed engineering.

Table I is a partial list of CTI's commercial applications in the non-ferrous industry.

Conversion of SO₂ to marketable by-product

The Cansolv® SO₂ Scrubbing System is a technology designed to solve the first problem by selectively absorbing SO₂ from the off-gas and regenerating it as a pure water saturated product. A key question faced by adopters of the Cansolv® SO₂ Scrubbing System is what to do with the by-product.

Table I

List of CTI's commercial applications in non-ferrous industry

| Application | Location | Flow (Nm ³ /h) | By-product | Feed SO ₂ concentration | SO ₂ emissions | Status |
|--------------------------------|---------------|---------------------------|--------------------------------|------------------------------------|---------------------------|---|
| SARP acid plant tail gas | North America | 40,000 | H ₂ SO ₄ | 5000 ppm | 15 ppm | Operating (s/u 2002) |
| Lead smelter off-gas | Asia | 33,700 | H ₂ SO ₄ | 0.1–12.5% | 90 ppm | Operating (s/u 2005) |
| Anode furnace off-gas | Asia | 43,000 | H ₂ SO ₄ | 900 ppm—2% | 100 ppm | Operating (s/u 2007) |
| Catalyst recovery roaster | North America | 48,000 | Liquid SO ₂ | 9100 ppm | 100 ppm | Operating (s/u 2008) |
| Sinter machine (secondary) | Asia | 350,000 | H ₂ SO ₄ | 2400 ppm | 140 ppm | Construction (s/u 2009) |
| Sinter plant (primary) | Asia | 2 x 510,000 | H ₂ SO ₄ | 800 ppm | 40 ppm | Construction (s/u 2009) |
| Lead smelter off-gas + APTG | Asia | 83,000 | H ₂ SO ₄ | 1000 ppm—8% | 140 ppm | Construction (s/u 2009) |
| Copper smelter furnace off-gas | Asia | 95,000 | Sulphur | 15%–35% | 250 ppm | Engineering |
| Nickel smelter off-gas | North America | 100,000 | H ₂ SO ₄ | 0.1%–3% | 50 ppm | Engineering (completed piloting campaign on furnace and PS converter gas) |
| Lead sinter machine off-gas | Asia-Pacific | 265,000 | H ₂ SO ₄ | 1–2% | 50 ppm | Engineering (completed piloting campaign) |

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In general, where the end user has a sulphur plant or an acid plant with sufficient capacity to reprocess the SO₂ product, this solution is usually retained as it minimizes capital investment. Where this is not the case, customers generally pick a solution optimized for the local by-product market. Customers who have elected to produce acid and did not have existing facilities to produce it build simple single contact acid plants without gas cleaning to reprocess to acid, though there is currently a surge of interest in reduction to sulphur. Acid made from Cansolv SO₂ product is of a very high quality and purity due to the high purity of the inlet SO₂ product.

The following pie charts (Figure 3) describe by-product solutions adopted by Cansolv licensees:

As indicated in Figure 3, about 1/3 of the adopters of the Cansolv® SO₂ Scrubbing System have to build a new processing facility. These include acid converters, SO₂ drying and liquefaction. One recent smelter located in Asia has also completed a Cansolv plant design with an SO₂ reduction plant to convert product SO₂ to sulphur. Some current adopters are also looking at sodium hydrosulphite facilities to serve local pulp and paper markets. Because the by-product conversion sub-units tend to be relatively low cost features to add to a Cansolv unit, one user has built a system with a SO₂ dryer/liquefaction unit and a hydrosulphite unit for the dual purpose of redundancy and maximizing earnings from by-products.

Key features of integrated smelter SO₂ emissions management

Clients have identified the key advantages of integrating the Cansolv® SO₂ Scrubbing System to manage smelter SO₂ emissions to be the following:

- the ability to treat dilute and variable smelter gases
- less gas cleaning requirements
- simple acid plant design.

Treat dilute and variable smelter gases

One direct consequence of the new legislation to reduce SO₂ emissions is that smelters will need to either increase their existing sulphuric acid production rates or install new sulphuric acid plants if it is desired to convert the recovered SO₂ to sulphuric acid. However, the nature of most smelter gases render them unsuitable for direct feed to a sulphuric acid plant, either because they are too dilute (less than 5% SO₂) or too variable (swings in SO₂ concentration from 0.1% to more than 10% SO₂). Methods have been developed to counter the difficulty in feeding secondary smelter gases to acid plants. Burning sulphur and liquefying the SO₂ from the sulphur burner off-gas to then spike dilute smelter gases to an SO₂ concentration suitable for feed to an acid plant is one method. Another involves varying sulphuric acid production rates as the SO₂ content in the smelter gas varies and keeping the sulphuric acid plant on hot standby by gas combustion. Both of these methods are costly to operate and require the installation of excessive sulphuric acid plant capacity.

The Cansolv® SO₂ Scrubbing System acts as a buffer between the smelter and the sulphuric acid plant by treating a dilute and/or variable gas and producing a constant steady flow rate of pure SO₂ gas. The benefits of this are:

- Eliminates requirement to intermittently or constantly spike the smelter gas with pure SO₂ to render suitable for feed to the acid plant
- Optimization of the required sulphuric acid production capacity
- Constant, steady sulphuric acid production rate
- Simpler operation.

Minimize gas cleaning requirements

The performance of the Cansolv® SO₂ Scrubbing System is not affected by the presence of SO₃ and dust in the feed gas. This has been demonstrated during several piloting campaigns and in the commercial units. The amine purification unit, however, needs to be sized appropriately for the steady state rate of ingress of these components.

A key factor in deploying the Cansolv process is to identify the appropriate design criteria for the quench/pre-treatment. In locations that regulate fine particulates and acid mist as well as SO₂, the quench/pretreatment system will have to be designed to achieve appropriate compliance levels at the stack. While a Cansolv absorber will have modest capture efficiency for mist and fines, it may not be sufficient to achieve compliance. If, on the contrary, stack compliance for mist or fine particulates is not a factor, value engineering may be used to determine the optimal balance between gas pretreatment and APU duty.

Several Cansolv® SO₂ Scrubbing Systems are either in operation or under construction in applications with limited gas cleaning in favour of higher APU duties. Tables II and III indicate the concentration of dust and SO₃ in the feed gas to the SO₂ absorber for some plants in operation and under construction.

The impact on the Cansolv design of reducing gas pre-treatment will increase the APU duty with corresponding increases in caustic consumption and effluent blowdown. If significant dust ingress is designed for, the filtration may exceed the threshold where cartridge filters are practical and automatic candle filters may become more appropriate. While candle filters may be more expensive, in general their annualized cost is lower than that of high efficiency gas cleaning systems.

Optimizing the design of the Cansolv® SO₂ Scrubbing System by integrating the gas pretreatment strategy with the APU design, while considering the stack emission constraints, may result in significant cost savings.

Figure 4 shows a large APU constructed for a high SO₃/acid mist ingress application in the non-ferrous industry. The low pressure drop open spray quench prescrubber at this site captures only a small proportion of inlet dust and mist.



Figure 3—CTI customer SO₂ by-product processing profile

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Table II

Scrubbing systems in operation

| Application, location | Dust at wet/dry interface (dust) | Quench/wet dust removal | | | |
|---------------------------|----------------------------------|----------------------------------|--------------------------------|--------------------------------|---------------------------|
| | | Pretreatment | Particulate removal efficiency | Inlet (dust) to Cansolv | APU filtration technology |
| Coal fired co-gen boilers | 200 mg/Nm ³ | Low pressure drop venturi | 85% | 30 mg/Nm ³ >20 kg/h | Automatic candle filters |
| Ferric ball sinter plant | 70 mg/Nm ³ | Open spray quench | 15% | 60 mg/Nm ³ >10 kg/h | Automatic candle filters |
| Oil refinery FCCU | 310 mg/Nm ³ | High press.drop dynamic scrubber | 97% | 10 mg/Nm ³ | Automatic candle filters |
| Oil refinery FCU | 300 mg/Nm ³ | High press.drop dynamic scrubber | 97% | 10 mg/Nm ³ | Automatic candle filters |
| Copper anode furnace | 260 mg/Nm ³ | Low pressure drop venturi | 88% | 30 mg/Nm ³ =1 kg/h | Cartridge filter |
| Steel sinter plant, | 112 mg/Nm ³ | Open spray quench | 30% | 80 mg/Nm ³ >20 kg/h | Automatic candle filters |
| Bitumen-fired boilers | 30 mg/Nm ³ | Open spray quench | 0% | 30 mg/Nm ³ >20 kg/h | Automatic candle filters |

Table III

Scrubbing systems under construction

| Plant | Wet acid mist removal | | | | |
|---|----------------------------|--|------------------------------------|-------------------------------------|------------------|
| | Dry gas (SO ₃) | SO ₃ /mist wet pretreatment | SO ₃ removal efficiency | Inlet (SO ₃) to Cansolv | APU salt removal |
| Coal-fired co-gen boilers | 43 ppmv | None | 0% | 40 ppmv | Ion exchange |
| Oil refinery FCCU | 22 ppmv | High press.drop dynamic scrubber | 88% | 3 ppmv | Electrodialysis |
| Incinerated SRU tail gas | 1500 ppmv | Brownian candle mist eliminators | 99% | 20 ppmv | Electrodialysis |
| Spent acid recovery plant tail gas, USA | 200 ppmv | None | 0% | 200 ppmv | Ion exchange |
| Ferric ball sinter plant, China | 110 ppmv | None | 0% | 110 ppmv | Ion exchange |
| Copper anode furnace, China | 170 ppmv | None | 0% | 170 ppmv | Ion exchange |

Figure 4—APU constructed for a high SO₃/acid mist ingress

Simplified sulphuric acid plant design

The additional SO₂ load from the single absorption sulphuric acid plant is low compared to the SO₂ load from the smelter gases. A dedicated SO₂ absorber tower can be installed to treat the acid plant tail gas. The impact of treating the acid plant tail gas on the regeneration portion of the Cansolv® SO₂ Scrubbing System is minor. This integrated approach to

managing smelter SO₂ emissions reduces the overall investment at the smelter and maximizes the value of the Cansolv® SO₂ Scrubbing System.

For plants that adopt the Cansolv® SO₂ Scrubbing System installed to treat smelter off-gases or fugitive emissions, it is recommended to consider leveraging the investment to control emissions from existing sulphuric acid plant tail gases. The impact of including sulphuric acid plant tail gas on the sizing and cost of the Cansolv® SO₂ Scrubbing System is minimal. The only design modifications involve the installation of a separate SO₂ absorber for the acid plant tail gas. A common regenerator would generally be used. Since the Cansolv® SO₂ Scrubbing System applied to acid plants can reduce SO₂ emissions to 20 ppmv, it is no longer necessary to rely on converter performance to achieve mandated SO₂ emissions. This design feature allows acid plants to be simplified, maximizing the value of the Cansolv® SO₂ Scrubbing System. Several licensees of the Cansolv process have elected to configure their acid plants this way.

Conclusion

Economic circumstances combined with new legislation to reduce SO₂ emissions are putting pressure on smelter operators to complete projects with low capital investment. An increasing number of plants in the non-ferrous industry have adopted the Cansolv® SO₂ Scrubbing System to meet new emissions requirements. In doing so, some have used existing acid plants to reprocess captured SO₂ to produce marginal high quality sulphuric acid, while others have built new by-product processing facilities. ♦