CANSOLV® SO₂ SCRUBBING SYSTEM: REVIEW OF COMMERCIAL APPLICATIONS FOR SMELTER SO₂ EMISSIONS CONTROL

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ABSTRACT

As new legislation drives to lower SO₂ emissions from metallurgical plants, 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 byproduct stream, which can then be directed to the front end of a sulfuric acid plant for conversion to sulfuric 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 sulfuric 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 and what as well as which features and cost advantages for the treatment of smelter gases were key to the technology choice.

1. 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-centered 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 desulfurization (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 sulfur
plant tail gases, acid plant tail gases and smel ter off-gases. In the ten years since the first technology license was signed, adoption of the Cansolv SO$_2$ 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® SO$_2$ Scrubbing Systems are in operation, four are scheduled for startup in 2009 and several more are in the detailed engineering or procurement phase. In 2009, the first Cansolv SO$_2$ coal combustion gas scrubber will also be commissioned.

Specifically to the metallurgical industry, some sources are particularly challenging including SO$_2$ 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 SO$_2$ concentration to be suitable for direct feed to an acid plant. By varying inventories of lean and rich absorbents, the Cansolv® SO$_2$ 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 SO$_2$ from a variable or dilute stream of SO$_2$ laden gas. The pure concentrated SO$_2$ can be converted to sulphuric acid (without further gas cleaning), dried and liquefied or in some cases, reduced to elemental sulfur.

New metallurgical processes are currently being deployed that make use of SO$_2$ as a reagent directly. In such cases, neither drying nor liquefaction is necessarily required and gaseous water saturated process gas 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 SO$_2$ emissions. This paper will address the advantages to integrating the Cansolv® SO$_2$ Scrubbing System to manage smelter SO$_2$ emissions.

2. **Cansolv® SO$_2$ Scrubbing System Description**

The Cansolv® SO$_2$ Scrubbing System is a patented technology that uses an aqueous amine solution to achieve high efficiency selective absorption of SO$_2$. The scrubbing by-product is pure, water saturated SO$_2$ 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® SO$_2$ Scrubbing System.

Refer to figure 1 for the process flow diagram of the Cansolv® SO$_2$ Scrubbing System as
applied to the non-ferrous industry when the SO₂ by-product is converted to sulfuric 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 sub cooling is added to a quench.

- The photo on the left shows Cansolv SO₂ scrubber on a combustion gas application in an aluminum 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 counter-current 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%.

- 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 sulfuric 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.

Figure 1: Integrated Cansolv® SO₂ Scrubbing System with conversion of SO₂ by-product to sulfuric acid
3. Managing SO₂ in the Non-Ferrous Industry

Most concentrated smelter gases ([SO₂]>5%) produced from sulfide 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 analyze the problem as two related ones:
- How to selectively separate SO₂ from the other gas constituents
- How to convert the separated SO₂ into a byproduct suitable for sale or disposal.

3.1 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 offgas to variable sources, such as Peirce-Smith converter gases. In all applications, the Cansolv® SO₂ Scrubbing System delivers a steady flowrate of pure water-saturated SO₂ gas. Most customers have elected to convert the SO₂ by-product to sulfuric 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. Objectives were to demonstrate the suitability of the technology to treat gases with high dust content and that are variable in flowrate 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.

The table below is a partial list of CTI’s commercial applications in the non-ferrous industry.

<table>
<thead>
<tr>
<th>Application</th>
<th>Location</th>
<th>Flow (Nm³/hr)</th>
<th>By-Product</th>
<th>Feed SO₂ Concentration</th>
<th>SO₂ Emissions</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>SARP Acid Plant Tail Gas</td>
<td>North America</td>
<td>40,000</td>
<td>H₂SO₄</td>
<td>5000 ppm</td>
<td>15 ppm</td>
<td>Operating (s/u 2002)</td>
</tr>
<tr>
<td>Lead Smelter Off-Gas</td>
<td>Asia</td>
<td>33,700</td>
<td>H₂SO₄</td>
<td>0.1-12.5%</td>
<td>90 ppm</td>
<td>Operating (s/u 2005)</td>
</tr>
<tr>
<td>Anode Furnace Offgas</td>
<td>Asia</td>
<td>43,000</td>
<td>H₂SO₄</td>
<td>900 ppm-2%</td>
<td>100 ppm</td>
<td>Operating (s/u 2007)</td>
</tr>
<tr>
<td>Catalyst recovery roaster</td>
<td>North America</td>
<td>48,000</td>
<td>Liquid SO₂</td>
<td>9100 ppm</td>
<td>100 ppm</td>
<td>Operating (s/u 2008)</td>
</tr>
<tr>
<td>Sinter Machine (secondary)</td>
<td>Asia</td>
<td>350,000</td>
<td>H₂SO₄</td>
<td>2400 ppm</td>
<td>140 ppm</td>
<td>Construction (s/u 2009)</td>
</tr>
<tr>
<td>Sinter Plant (primary)</td>
<td>Asia</td>
<td>2 x 510,000</td>
<td>H₂SO₄</td>
<td>800 ppm</td>
<td>40 ppm</td>
<td>Construction (s/u 2009)</td>
</tr>
</tbody>
</table>
3.2 Conversion of SO\textsubscript{2} to marketable by-product

The Cansolv\textsuperscript{®} SO\textsubscript{2} Scrubbing System is a technology designed to solve the first problem by selectively absorbing SO\textsubscript{2} from the off-gas and regenerating it as a pure water saturated product. A key question faced by adopters of the Cansolv\textsuperscript{®} SO\textsubscript{2} Scrubbing System is what to do with the byproduct.

In general, where the end user has a sulfur plant or an acid plant with sufficient capacity to reprocess the SO\textsubscript{2} 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 byproduct 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 sulfur. Acid made from Cansolv SO\textsubscript{2} product is very high quality/purity due to the high purity of the inlet SO\textsubscript{2} product.

The following pie charts describe by-product solutions adopted by Cansolv licensees:

![By-Product Profile](image)

*Figure 2: CTI Customer SO\textsubscript{2} By-Product Processing Profile*
As indicated in the graph, 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 & liquefaction. One recent smelter located in Asia has also completed a Cansolv plant design with a SO₂ reduction plant to convert product SO₂ to sulfur. Some current adopters are also looking at sodium hydrosulfite facilities to serve local pulp and paper markets. Because the byproduct 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 hydrosulfite unit for the dual purpose of redundancy and maximizing earnings from byproducts.

4. 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.

4.1 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 sulfuric acid production rates or install new sulfuric acid plants if it is desired to convert the recovered SO₂ to sulfuric acid. However, the nature of most smelter gases render them unsuitable for direct feed to a sulfuric 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 sulfur and liquefying the SO₂ from the sulfur burner offgas to then spike dilute smelter gases to an SO₂ concentration suitable for feed to an acid plant is one method. Another involves varying sulfuric acid production rates as the SO₂ content in the smelter gas varies and keeping the sulfuric acid plant on hot standby by gas combustion. Both of these methods are costly to operate and require the installation of excessive sulfuric acid plant capacity.

The Cansolv® SO₂ Scrubbing System acts as a buffer between the smelter and the sulfuric acid plant by treating a dilute and/or variable gas and producing a constant steady flowrate 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 sulfuric acid production capacity;
- Constant, steady sulfuric acid production rate;
- Simpler operation.
4.2 Minimize gas cleaning requirements

The performance of the Cansolv® SO\textsubscript{2} Scrubbing System is not impacted by the presence of SO\textsubscript{3} 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 which regulate fine particulates and acid mist as well as SO\textsubscript{2}, the quench / pre-treatment 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 pre-treatment and APU duty.

Several Cansolv® SO\textsubscript{2} Scrubbing Systems are either in operation or under construction in applications with limited gas cleaning in favour of higher APU duties. The following tables indicate the concentration of dust and SO\textsubscript{3} in the feed gas to the SO\textsubscript{2} absorber for some plants in operation and under construction.

<table>
<thead>
<tr>
<th>Application, Location</th>
<th>Dust at wet / dry interface [Dust]</th>
<th>Pre-treatment</th>
<th>Particulate Removal Efficiency</th>
<th>Inlet [Dust] to Cansolv</th>
<th>APU Filtration Technology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal fired co-gen boilers</td>
<td>200 mg/Nm\textsuperscript{3}</td>
<td>Low Pressure drop Venturi</td>
<td>85%</td>
<td>30 mg/Nm\textsuperscript{3} &gt;20 kg/hr</td>
<td>Automatic candle filters</td>
</tr>
<tr>
<td>Ferric ball sinter plant</td>
<td>70 mg/Nm\textsuperscript{3}</td>
<td>Open spray quench</td>
<td>15%</td>
<td>60 mg/Nm\textsuperscript{3} &gt;10 kg/hr</td>
<td>Automatic candle filters</td>
</tr>
<tr>
<td>Oil Refinery FCCU</td>
<td>310 mg/Nm\textsuperscript{3}</td>
<td>High press.drop dynamic scrubber</td>
<td>97%</td>
<td>10 mg/Nm\textsuperscript{3}</td>
<td>Automatic candle filters</td>
</tr>
<tr>
<td>Oil Refinery FCU</td>
<td>300 mg/Nm\textsuperscript{3}</td>
<td>High press.drop dynamic scrubber</td>
<td>97%</td>
<td>10 mg/Nm\textsuperscript{3}</td>
<td>Automatic candle filters</td>
</tr>
<tr>
<td>Copper Anode Furnace</td>
<td>260 mg/Nm\textsuperscript{3}</td>
<td>Low Pressure Drop Venturi</td>
<td>88%</td>
<td>30 mg/Nm\textsuperscript{3} =1 kg/hr</td>
<td>Cartridge filter</td>
</tr>
<tr>
<td>Steel sinter plant,</td>
<td>112 mg/Nm\textsuperscript{3}</td>
<td>Open spray quench</td>
<td>30%</td>
<td>80 mg/Nm\textsuperscript{3} &gt;20 kg/hr</td>
<td>Automatic candle filters</td>
</tr>
<tr>
<td>Bitumen-fired boilers</td>
<td>30 mg/Nm\textsuperscript{3}</td>
<td>Open spray quench</td>
<td>0%</td>
<td>30 mg/Nm\textsuperscript{3} &gt;20 kg/hr</td>
<td>Automatic candle filters</td>
</tr>
</tbody>
</table>
Wet acid mist removal

<table>
<thead>
<tr>
<th>Plant</th>
<th>Dry gas [SO₃]</th>
<th>SO₃ / mist wet pre-treatment</th>
<th>SO₃ Removal Efficiency</th>
<th>Inlet [SO₃] to Cansolv</th>
<th>APU Salt Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal-fired co-gen boilers</td>
<td>43 ppmv</td>
<td>None</td>
<td>0%</td>
<td>40 ppmv</td>
<td>Ion Exchange</td>
</tr>
<tr>
<td>Oil Refinery FCCU</td>
<td>22 ppmv</td>
<td>High press.drop dynamic scrubber</td>
<td>88%</td>
<td>3 ppmv</td>
<td>Electrodiagnosis</td>
</tr>
<tr>
<td>Incinerated SRU Tail Gas</td>
<td>1500 ppmv</td>
<td>Brownian candle mist eliminators</td>
<td>99%</td>
<td>20 ppmv</td>
<td>Electrodiagnosis</td>
</tr>
<tr>
<td>Spent Acid Recovery Plant Tail Gas, USA</td>
<td>200 ppmv</td>
<td>None</td>
<td>0%</td>
<td>200 ppmv</td>
<td>Ion Exchange</td>
</tr>
<tr>
<td>Ferric ball sinter plant, China</td>
<td>110 ppmv</td>
<td>None</td>
<td>0%</td>
<td>110 ppmv</td>
<td>Ion Exchange</td>
</tr>
<tr>
<td>Copper Anode furnace, China</td>
<td>170 ppmv</td>
<td>None</td>
<td>0%</td>
<td>170 ppmv</td>
<td>Ion Exchange</td>
</tr>
</tbody>
</table>

The impact to 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 pre-treatment strategy with the APU design, while considering the stack emission constraints, may result in significant cost savings.

The adjacent photo 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.

4.3 Simplified Sulfuric Acid Plant Design

The additional SO₂ load from the single absorption sulfuric 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 sulfuric acid plant tail gases. The impact of including sulfuric 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.

5. 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 sulfuric acid, while others have built new byproduct processing facilities.