HANDLING OF FLUCTUATING AND LOW-STRENGTH SO\textsubscript{2} GASES 
AN OVERVIEW

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Abstract

Fluctuating SO\textsubscript{2} gas streams represent a difficult task for designers of SO\textsubscript{2} removal systems (with respect to designing the plant), but in spite of the designers great efforts to solve the problems, the operation of such plants requires much care and attention. A fluctuating gas flow usually results from metallurgical smelting processes. Both gas composition and gas flow rate may vary.

The first part of this paper outlines some existing technical solutions and presents the Pros and Cons of the different solutions.

These solutions outline are:
- Sulphuric acid plants operated with a preheater permanent in operation
- Sulphuric acid plants with concentration increase of SO\textsubscript{2} gas either using regenerative SO\textsubscript{2} removal or cryogenic partial condensation of the SO\textsubscript{2}
- Sulphuric acid plants with additional burning of sulfur to increase SO\textsubscript{2} content
- Single-stage sulphuric acid plants followed by a tail gas system (which is) designed for periods of low SO\textsubscript{2} input

In the second part, this paper describes some existing technical solutions for removal of SO\textsubscript{2} at low concentrations (i.e. less than 0.1 - 2 % by volume), which could be used as tail gas treatment system for acid plants. While selecting an appropriate solution, special attention should be given to operating costs, which usually to a large extend depends on the type of absorption agent and the costs for disposal of the sulfur compound produced.

Gas Sources:
The origin of fluctuating gas streams usually is a metallurgical batch process. The conditions of batches are adjusted depending on the oxidation potential of the gas atmosphere. In this way, either the reduction of metal compounds to metal or the oxidation of metal sulfides is achieved. The individual stages of the batch not only produce different gas atmospheres, but also different off-gas flow rates.

Examples for batch-wise operated metallurgical processes are the various lead smelting processes such as Ausmelt, Isasmelt, Kaldo and the Pierce Smith Converters for copper matte that to be converted to blister copper and slag.
Fluctuation:
Fluctuation of the gas flow rates may vary from 100% to 20%. At the same time, the SO$_2$ concentrations of the gas also vary from 20% to 0% (by volume).

In some cases, maximum flow rate and maximum SO$_2$ concentration may occur simultaneously, the same may apply to minimum flow rate and minimum SO$_2$ concentration.

For the operation of an SO$_2$ removal plant, this means that the plant has to be sized for being operated between acid productions of 0% to 100%. Such fluctuation is comparable to the start-up and shutdown conditions of plants. The difference being that the plants have to cope with such conditions more or less on a permanent basis, at least twice a day.

Diagram: Fluctuation of Gases Released from Batch Processes

| Process 1, lead smelter, Source: Outotec | Process 2, lead smelter, Source: Outotec |

The question now is how to treat such gases in order to fulfill the environmental regulations while ensuring a reliable, but also economical operation of the SO$_2$ removal system.

A number of solutions are in use to achieve this goal:

The standard process for removing SO$_2$ from gases showing an SO$_2$ content of more than 4% by volume is a sulphuric acid plant.

Regarding sulphuric acid production, the following technical solutions are in operation:
Firstly we have systems where the fluctuating gases are added to other SO$_2$ containing gas flows. The receiving gas stream should have a significantly higher SO$_2$ amount than that of the added gas stream. In case the joint gas flows show fluctuations of less than 40% to 100% of SO$_2$, a sulphuric acid plant can be designed and operated safely.
This solution is used in copper smelters, where the gas released from the converters (releasing fluctuating flow rates) is added to the gas from the smelter process that releases a continuous flow rate with a high SO\textsubscript{2} content. In addition, efforts are made to keep the fluctuations from the converters as low as possible.

When this solution is not possible due to the lack of a second SO\textsubscript{2} gas flow, the fluctuating gas has to be treated separately. A standard-type sulphuric acid plant will only operate on an auto-thermal basis, when the SO\textsubscript{2} content is above 3 – 7 % by volume. Auto-thermal means that the heat recovered in the process is sufficient for operating the contact process. This means heating the cold gas to the operating temperature of the catalyst layers can be achieved by recuperative heat exchange with the hot gas from the exit of the catalyst layers under consideration of the heat loss in the absorbers. When the SO\textsubscript{2} content is not sufficient for auto-thermal operation, the gas has to be heated to the operating temperature of the catalyst beds by other means, for example by using the acid plant preheater. In order to avoid dilution of the produced acid during periods with low SO\textsubscript{2} content, the installation of a predryer is recommended. (The reason for the dilution is the water removal in the drying tower that dilutes the acid.)

If the predryer acid, usually showing a sulphuric acid concentration of 70 – 80 % cannot be sold as a separate product, strengthening of this predryer acid by adding acid produced in the absorbers (98.5 %) is necessary. Instead of strengthening the acid adding absorber acid, an alternative is the usage of a predryer with a downstream concentrator. The acid concentration that can be achieved by the Predyer Re-Concentrator concept depends on the average SO\textsubscript{2} content and the average gas temperature of the SO\textsubscript{2} gas.

To minimize the amount of predryer acid that is produced, it is recommendable to efficiently cool the SO\textsubscript{2} gas in the wet gas cooling and cleaning system to temperatures below 25 °C and by this minimize the amount of water vapour to be removed in the dryer.

In order to also minimize the amount of heating energy (usually light fuel oil, Diesel) a preheater with a high thermal efficiency should be used. Otherwise the annual energy costs on the basis of today’s fuel oil prices easily may reach the range of 1 million € or more.

It is evident that detailed investigations regarding mass and energy balance are required for each individual application. In the sketch, the principal idea of the Predyer Re-Concentrator idea is outlined.
Another possibility to manage low $\text{SO}_2$ concentration periods is to fill the concentration gap with $\text{SO}_2$ from another source. If there is no other separate source available, $\text{SO}_2$ has to be generated from the system itself, for instance removing part of the $\text{SO}_2$, while it is present at high concentrations and then adding it to the gas stream, when the $\text{SO}_2$ content of the gas is low.

A part of the $\text{SO}_2$ can be removed from the gas stream by cryogenic partial condensation of $\text{SO}_2$ at very low temperatures of approximately minus 50 °C. At this temperature a part of the $\text{SO}_2$ in the gas will condense and can be stored as cold liquid. During periods with low $\text{SO}_2$ content, liquid $\text{SO}_2$ is evaporated and added to the fluctuating $\text{SO}_2$ gas stream. The $\text{SO}_2$ condensation and evaporation system and the attached acid plant have to be designed in a way that auto-thermal operation is ensured.

The disadvantage of this solution is the use of the cryogenic system for $\text{SO}_2$ condensation and the related high electrical energy consumption of this low temperature process.
An alternative solution for converting the fluctuating gas flow into a continuous gas flow is the application of a regenerative SO$_2$ removal system. The fluctuating gas stream is sent to a scrubber where a regenerative absorbent agent removes the SO$_2$. In a stripper, the SO$_2$ is then stripped from the SO$_2$ containing liquid and released as vapor saturated concentrated flow of gaseous SO$_2$.

This SO$_2$ flow is then diluted with air and sent to a downstream sulphuric acid plant or is added to the gas flow of another acid plant. Singh, Roy, Sarlis, Ravary and others have reported about such an application during the Sulphur Conferences in 2004 and 2006.

The disadvantage of regenerative SO$_2$ removal processes is the high consumption of heat, usually consumed as low-pressure steam in a reboiler. Approximately 4 –6 tons of low-pressure steam are needed per ton of SO$_2$.

In the next sketch, the principle of regenerative SO$_2$ removal is shown.
Filling the concentration gap by adding SO₂ from a sulphur incineration system is another solution. The use of sulphur burners adding SO₂ to the converter section of an acid plant is a proven technical application, which usually aims at increasing the production of acid, but can also provide additional SO₂ for gases with low SO₂ content in order to run the acid plant as an auto-thermal process.

Incineration of sulphur not only reduces the amount of fuel required but also ensures the continuous production of the acid with a constant concentration of SO₂. That means, also the above described pre-dryer can be avoided when the SO₂ content is sufficiently high. The idea is outlined in the flow sheet on the next page.

The acid plant is designed for the maximum SO₂ amount. The auto-thermal operation is designed for the minimum amount of SO₂ released from the fluctuating gas source and the incineration of SO₂.

It is self-understanding that the SO₂ gas has to be carefully “cleaned” prior to being treated in a sulphuric acid plant. The picture shows a potential flow sheet for the wet gas cleaning system. Such a system consists of a quencher for adiabatic quench-cooling of the hot gas from the furnace. The gas cooling/vapour condensation system consists of a packed gas-cooling tower with indirect heat transfer for pre-cooling the gas. In a gas cooler/condenser operated with direct heat transfer, the gas is further cooled. This cooling stage can be operated with a chiller, if required. A multi-stage wet electrostatic...
The precipitator system does the final gas cleaning respectively aerosol removal. In case that a mercury-free acid is to be produced, the necessary installations for removing mercury from the gas have to be installed additionally.

A simplified process flow diagram for the wet gas cleaning system can be seen on the next picture.

**Sketch: Wet Gas Cleaning System**

(Remark: The hot gas cooling can be designed as evaporative cooler for gas cooling by water evaporation; alternatively a boiler can be installed.)

In case that the SO$_2$ emission from the acid plant is expected to comply with potential future regulations (perhaps less than 100 ppm of SO$_2$ in the tail-gas???) a double contact – double absorption sulphuric acid plant equipped with 5 catalytic layers is required. 3 of the 5 catalyst layers should be upstream of the intermediate absorber, the other 2 catalyst layers downstream (= 3+2 contact plant).

In such a plant the SO$_2$ gas is heated in several recuperative-type gas-gas heat exchangers to the operating temperature of the catalyst bed. Downstream of each catalyst layer the gas is cooled by means of cold SO$_2$ gas. During low SO$_2$ content periods heat is brought into the system by means of and additional SO$_2$ gas flow from a sulfur incinerator.
The principle idea of operating a metallurgical acid plant with additional sulphur burning is shown on the next sketch.

**Sketch: Flow Sheet - Sulphuric Acid Plant with Sulfur Incineration,**

The sulphur furnace also could be equipped with a downstream boiler for the production of steam. Due to this type of heat recovery, the production of additional sulphuric acid will increase.

The advantage of this technical solution as compared to the above outlined ideas is that the fuel oil for the preheater, respectively the preparation of low pressure steam required for the reboiler is significantly reduced.

The basis of the idea is that over a long period of time the costs for sulphur should at least be covered by the price for sulphuric acid.

In the next table the Pros and Cons of the individual solutions discussed in this paper are outlined.

Any decision about a new installation clearly should consider all costs involved. This does especially refer to the operating costs in terms of energy requirements.
Table: Pros and Cons of the Discussed Solutions

<table>
<thead>
<tr>
<th>Design Challenge</th>
<th>Predryer</th>
<th>Cryogenic</th>
<th>Reg. SO₂ Removal</th>
<th>Sulphur Incineration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluctuating gas flow rates, fluctuating SO₂ content in the gas flow</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solution</td>
<td>Predryer, Preheater in Operation</td>
<td>Condense SO₂ and release during periods of low SO₂</td>
<td>Treat SO₂ Gas in a separate system, produce acid in a sep. system</td>
<td>Produce SO₂ during periods of low SO₂</td>
</tr>
<tr>
<td>Characteristic</td>
<td>Acid plant with Predryer</td>
<td>Acid plant with Cryogenic SO₂ Production stage after Dryer</td>
<td>Gas is treated in a separate SO₂ removal System, concentrated SO₂ gas then converted to sulphuric acid</td>
<td>Acid plant with sulphur incineration</td>
</tr>
<tr>
<td>Technical Feature</td>
<td>Installation of a ReConcentrator will reduce amount of Predryer Acid</td>
<td>SO₂ storage will ensure permanent presence of sufficient SO₂</td>
<td>SO₂ storage will ensure permanent presence of sufficient SO₂</td>
<td>Acid plant to be designed for full range of flow and SO₂</td>
</tr>
<tr>
<td>Potential technical improvement</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Consumption</td>
<td>Cooling Water</td>
<td>high</td>
<td>high</td>
<td>high</td>
</tr>
<tr>
<td>Electricity</td>
<td>average</td>
<td>high, for gas cooling to condense SO₂</td>
<td></td>
<td>average</td>
</tr>
<tr>
<td>Heat Requirement</td>
<td>High, as Light Fuel Oil, Diesel, for Gas heating during low SO₂</td>
<td>Average, as electricity or steam for evaporation of SO₂</td>
<td>Very high, as LP-steam, appr. 4 – 6 kg of steam per kg of SO₂</td>
<td>Very low, as reaction heat of sulphur incineration to SO₂, no other “Heat” – source is required</td>
</tr>
<tr>
<td>(as Fuel Oil, Gas, Steam)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Remark</td>
<td>Non-commercial acid (80 %) is produced</td>
<td>Complex system</td>
<td>High costs for LP steam,</td>
<td>Additional production of H₂SO₄, Price for acid has to cover costs for sulphur</td>
</tr>
</tbody>
</table>

As an alternative to the above-discussed technical solutions, two “separate” plants, each designed for extreme ends of the fluctuations could be applied. This could be for example a sulphuric acid plant for high SO₂ concentrations and a completely separate system for SO₂ removal during low SO₂ content. This separate SO₂ removal system could be used as tail gas treatment system of the acid plant. This idea is outlined in the attached block diagram.
Sketch: Block Diagram Acid Plant and Tail-Gas System

Designing and operating such a 2-stage system will require very much attention. Regarding the fluctuations certain margins allowing for SO$_2$ excess should be provided for. That means the conversion rate of the acid plant and the removal efficiency of the tail gas system should be sufficient to cover all potential deviations.

How could such a tail-gas system be designed?
There are many systems available for removing low concentration SO$_2$. The main applications are in the Power Industry and to a smaller extent in the chemical industry. In the following table, a number of technical solutions is listed. The major consumption figures are given.
For the selection of a potential solution, the most important issue is the operating costs. These usually are the costs for the absorption agent and the costs related to the usage of disposal of the reaction product. In case that a useful product is produced a certain payback may eventually be achieved.
Some reactions result in the formation of slurry. In this case the potential cost for treatment of the slurry should be considered. This does especially refer to the calcium-based reaction products. It should also be remembered that the scrubbers must be designed to withstand the formation of sulphates forming build-up and scaling in the system.
Liquid reaction agents such as caustic soda (diluted NaOH) are easy to handle. If the reaction product can be disposed into a river, this simple technical solution may be an option.
### Table: Processes for Treatment of Low content SO₂ Gases

<table>
<thead>
<tr>
<th>#</th>
<th>Process</th>
<th>Reaction Agent</th>
<th>Reaction Product</th>
<th>Effluent</th>
<th>consumption, Product and Handling</th>
<th>Recommendation for size, Amount of SO₂</th>
<th>Recommendation for plant size, Flow Rate, SO₂ conc.</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sulphuric Acid</td>
<td>none</td>
<td>sulphuric acid</td>
<td>weak acid from wet gas cleaning system, to be treated</td>
<td>electricity, water,</td>
<td>SO₂ = 100 ton/day, Acid = 4 %</td>
<td>Flow Rate = 9500 – 25000 Nm³/h, SO₂ &gt; 3 % by volume</td>
<td>Proven process for SO₂ removal from gases with more than 3 % SO₂ concentration in the gas.</td>
</tr>
<tr>
<td>2</td>
<td>Sodium hydroxide scrubber</td>
<td>NaOH</td>
<td>Sodium sulphate</td>
<td>dissolved neutral salt, often can be disposed in mine</td>
<td>NaOH, water</td>
<td>SO₂ &lt; 30 ton/day, &lt; 2 %, 4 hours</td>
<td>Flow Rate = 50 000 Nm³/h</td>
<td>SO₂ Removal Process is easy to operate, but high need for alkali, agent.</td>
</tr>
<tr>
<td>3</td>
<td>Lime / Limestone Scrubber</td>
<td>CaO/Ca(OH)₂</td>
<td>Calcium sulphate</td>
<td>bleed flow from gypsum washing</td>
<td>Ca(OH)₂, electricity, water</td>
<td>SO₂ &lt; 5 ton/day, &lt; 2 %</td>
<td>Flow Rate = 100 000 Nm³/h, SO₂ &lt; 1 % by volume</td>
<td>If O₂ content in the gas is low, gypsum may have a high SO₂ content, process is in use at all power stations.</td>
</tr>
<tr>
<td>4</td>
<td>Process A</td>
<td>ROCS, Peroside</td>
<td>Sulphuric acid, approx. 50 %</td>
<td>weak acid from wet gas cleaning system, to be treated</td>
<td>H₂SO₄, electricity, water,</td>
<td>SO₂ &lt; 30 ton/day, &lt; 2 %</td>
<td>Flow Rate = 50 000 Nm³/h, SO₂ &lt; 1 % by volume</td>
<td>N₂O₂ is a very expensive reaction agent. Process is economic only if internal use is possible.</td>
</tr>
<tr>
<td>5</td>
<td>Repetitive SO₂ Recovery processes</td>
<td>none</td>
<td>concentrated SO₂</td>
<td>weak acid from wet gas cleaning system, to be treated</td>
<td>Steam, electricity, water, cooling water</td>
<td>Liquid SO₂ is used in some processes</td>
<td>SO₂ &lt; 100 ton/day, &lt; 40 000 kg/year</td>
<td>Flow Rate &lt; 50 000 Nm³/h, SO₂ &lt; 1 % by volume</td>
</tr>
<tr>
<td>6</td>
<td>Dry SO₂ processes</td>
<td>Ca(OH)₂, Calcium sulphate and Calcium nitrate</td>
<td>CaSO₄, Ca(NO₃)₂</td>
<td>none</td>
<td>electricity, Ca(OH)₂</td>
<td>SO₂ &lt; 5 ton/day, &lt; 2 %</td>
<td>Flow Rate = 250 000 Nm³/h, SO₂ &lt; 0.8 % by volume</td>
<td>Process is in use at power stations, SO₂ usage &lt; 30 g/h.</td>
</tr>
<tr>
<td>7</td>
<td>Sulphuric acid processes</td>
<td>none</td>
<td>liquid or solidified sulphur</td>
<td>weak acid from wet gas cleaning system, to be treated</td>
<td>electricity, water, natural gas, CH₄</td>
<td>SO₂ &lt; 100 ton/day, &lt; 4 ton/hour</td>
<td>Flow Rate &lt; 100 000</td>
<td>Requires high consumption of natural gas, is only feasible if other processes are not feasible.</td>
</tr>
<tr>
<td>8</td>
<td>Ammonium-sulphate</td>
<td>NH₃, steam</td>
<td>Ammonium-sulphate</td>
<td>depending on further use</td>
<td>NH₃, electricity, water</td>
<td>SO₂ &lt; 100 ton/day (NH₃/VO₂, 25/48)</td>
<td>Flow Rate &lt; 20 000 Nm³/h, SO₂ &lt; 1 %.</td>
<td>NH₃/VO₂ usage as fertilizer. Compost with fertilizer comp. required.</td>
</tr>
<tr>
<td>9</td>
<td>Baffled</td>
<td>none</td>
<td>diluted sulphuric acid (25 – 40 %)</td>
<td>weak acid from wet gas cleaning system, to be treated</td>
<td>electricity, water, concentration, if available</td>
<td>SO₂ &lt; 10 ton/day, &lt; 0.4 ton/hour</td>
<td>Flow Rate &lt; 100 000 Nm³/h, SO₂ &lt; 0.5 %</td>
<td>Process is often applied in pig iron production (TVA)</td>
</tr>
<tr>
<td>10</td>
<td>Ozone-alkaline</td>
<td>Lime, limestone, NaOH</td>
<td>Ozone</td>
<td>ozone, lime, NaOH</td>
<td>SO₂ &lt; 20 ton/day, &lt; 0.5 ton/hour</td>
<td>Flow Rate &lt; 30 000 Nm³/h, SO₂ &lt; 3 %</td>
<td>Process is complicated and difficult to operate</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Desox</td>
<td>ROCS, SO₂, NH₃</td>
<td>ROCS, SO₂, NH₃</td>
<td>none</td>
<td>electricity, (Mg for NO₂ removal.)</td>
<td>SO₂ &lt; 50 ton/day, &lt; 2 ton/hour</td>
<td>Flow Rate &lt; 20 000 Nm³/h, SO₂ &lt; 1 %</td>
<td>For seamless removal of SO₂ and NO₂ in 2 catalytic steps.</td>
</tr>
<tr>
<td>12</td>
<td>ZnO, Zinc Oxide</td>
<td>ZnO, Roaster</td>
<td>ZnSO₄, Zn₂S</td>
<td>weak acid</td>
<td>electricity, water, ZnO</td>
<td>SO₂ &gt; 20 ton/day, &lt; 2 ton/hour</td>
<td>Flow Rate &lt; 100 000 Nm³/h, SO₂ &lt; 0.5 %</td>
<td>Feasible only when ZnO (Roaster agent) and ZnSO₄ can be used in.</td>
</tr>
</tbody>
</table>

Some of the listed solutions may appear rather exotic, but anyway they have been implemented as tailor made solutions for a particular environment in a factory or smelter. And, of course, the list is certainly not complete.
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1988 – 2001
Lurgi, Process Engineer for Gas Cleaning Systems, responsible for process design of gas cleaning systems for off-gases from industrial sources, including smelters, power stations and waste incinerators.

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Outokumpu Technology, now Outotec, Product Manager for Sulphuric Acid Plants and Gas Cleaning Systems, responsible for process design of sulphuric acid plants with upstream wet gas cleaning systems for metallurgical SO2-gases.

„Somehow specialised“ in technical solutions for non-standard technical challenges.