

SO₂ Emission Control in the Aluminium Industry

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Abstract

SO₂ emissions from the aluminium industry are modest on a worldwide and national scale. Large modern smelters using high-sulphur petroleum coke in anodes and smaller smelters with topographical unfavourable locations may, however, be significant sources locally. This has led environmental regulators to again review local legislation. Currently SO₂ emission legislation is in force in Scandinavia and in some parts of the US. The ongoing review of SO₂ emissions may lead to stricter legislation forcing smelters outside these areas to install SO₂ control systems. The electrolysis represents approximately 80% of the released SO₂ for prebake smelters and approximately 95% for Söderberg smelters.

The paper is addressing current SO₂ removal technologies applied within the aluminium industry with focus on investment and operational costs.

Introduction

The increased consumption of sulphur-containing fossil fuels for power generation and heating purposes has led to an increased emission of sulphur dioxide (SO₂). The emissions of SO₂ have proved to cause ecological damage to faunal and vegetal life on land and in lakes. Legislation of SO₂ emissions for large stationary sources is thus being adopted by an increasing number of countries.

The SO₂ emissions from the primary aluminium industry are modest on a worldwide and national scale. A smelter may, however, be a significant source at local and regional level. This is especially valid for large, modern smelters using high-sulphur

petroleum coke for anode production. The same is valid even for smaller smelters provided that topographical or other conditions are unfavourable. This has forced legislation on SO₂ emissions for aluminium smelters in Scandinavia and some states in USA. The issue of introducing SO₂ legislation for aluminium smelters is at present being discussed also outside these countries. National environmental agencies will closely follow the development of SO₂ emissions from the primary aluminium industry.

It is expected that the typical petroleum cokes will contain much higher levels of sulphur in the future than the cokes available just a few years ago. A 4-6% sulphur level is suggested as typical in future coke specifications. A 200,000 ton-per-year smelter may thus under extreme conditions emit more than 1 ton of SO₂ per hour. The possibility that large smelters must implement SO₂ control to prevent deterioration of air quality is hence likely outside Scandinavia and USA⁽¹⁾.

The electrolysis represents approximately 80% of the released SO₂ for aluminium smelters operating with prebake pots and approximately 95% for Söderberg pots. The greatest impact is achieved by treatment of the electrolytic gases – normally downstream of a dry system for HF recovery.

When considering flue gas desulphurisation, most people envisage huge piles of limestone and gypsum. There are, despite this, also other ways of capturing the sulphur^{(2), (3), (4)}.

This paper reviews wet technologies for desulphurisation in commercial operation in aluminium smelters as well as one potential emerging dry SO₂ removal technology.

Wet SO₂ Removal Processes

In the 1960s and 1970s ABB Miljø supplied more than 300 wet scrubbers designed to withstand corrosion and to minimise scaling and clogging. These scrubbers were installed for fluoride removal of gases from Söderberg and prebake pots and were designed as both courtyard and roof scrubbers. The experience gained from these fluoride-removing wet scrubbers was integrated into the design of ABB's modern SO₂ scrubbers.

Single scrubber modules with gas capacities exceeding 1,200,000 m³/h have been built in impregnated pine, steel, reinforced concrete and fibreglass. Various internal linings to protect the concrete or steel from corrosion, such as epoxy and fibre-reinforced polyester (FRP), have been utilised. Rectangular and circular scrubbers made in FRP either single-skin or of sandwich-shell design have been delivered in module sizes up to 285,000 m³/h. Scrubber internals have been made of impregnated pine, thermoplastics, FRP and metal alloys⁽¹⁾.

The principles of the processes with typical examples of recently installed SO₂ scrubbers placed downstream of the dry fluoride recovery system are reviewed in the following sections. In addition cost factors for adding SO₂ removal downstream of existing dry scrubbers are discussed.

Seawater Scrubbing – The Flakt-Hydro Process

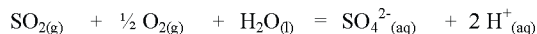
Seawater is naturally alkaline. It contains an excess of calcium and sodium carbonates (like limestone and soda) in solution. These components give seawater a strong capacity to absorb and neutralise acidic gases like SO₂. The carbonate content of the oceans is maintained by the seawater's continuous contact with huge marine and coastal deposits of alkaline sediments. Rivers also continuously transport dissolved alkaline limestone into the sea.

Natural seawater is rich on sulphur. One ton of seawater contains nearly 1 kg of sulphur dissolved as sulphate. The sulphur is a natural and necessary ingredient in the marine environment. The oceans of the world contain more than 10¹⁵ tons of sulphur in the form of sulphate solution. It corresponds to a layer of pure sulphur approximately 1.7 m thick on the surface of all the oceans. It is estimated that all the world's exploitable resources of fossil fuels (coal, oil and gas) contain a magnitude of 10¹¹ tons of sulphur. This corresponds to a paper-thin layer on top of the substantial 1.7 m of natural seawater sulphur.

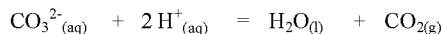
Desulphurisation by seawater is a very simple process. The seawater and gas flow in a once-through operation and the process does not require any addition of chemicals^{(3),(5)}. Removal efficiencies above 90% have been guaranteed and demonstrated on a long-term basis.

Absorption and neutralisation take place according to:

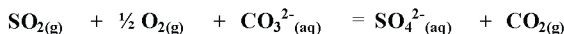
SO₂ absorption:



Carbonate equilibrium:



Overall reaction:



From laboratory testing as well as long-term bioassay testing and recipient follow-up, no significant effects have been detected from the effluent discharged from the Flakt-Hydro system. The Flakt-Hydro process has received international recognition through long-term environmental studies on existing installations, which unanimously have concluded that the environmental impact is negligible. This system is ideal for smelters located in a close proximity to the sea. The system makes use of no reagents, which brings the operating costs to a minimum⁽⁴⁾.

Seawater scrubber experiences

A user of this SO₂ removal technology is the Hydro Aluminium, Karmøy smelter located at the southwestern coast of Norway, with seawater within close distance. A simplified flow diagram of the scrubber is shown in Figure 1.

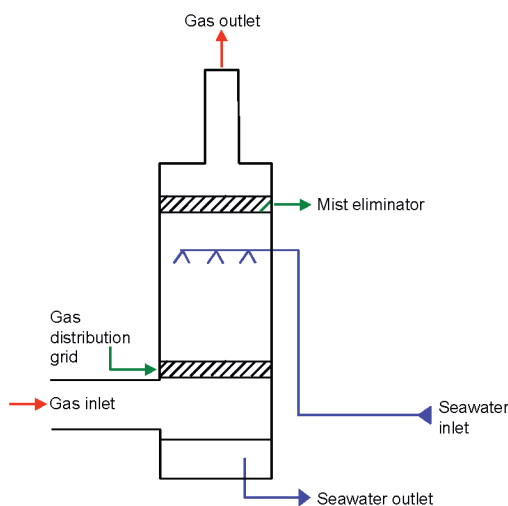


Figure 1. Flow diagram of the seawater scrubber operating at the Karmøy potline.

After leaving the dry scrubber, the gas follows two separate streams. Two centrifugal fans are arranged in parallel between the dry and wet systems. The SO₂ removal system comprises two concrete scrubbers, as seen in Figure 2, internally lined with an epoxy lining. The scrubbers are built together with a common separating wall. On top of each section are FRP stacks exhausting the cleaned gas approximately 30 m above ground level.

Inside the scrubber seawater and gas are arranged as a counter-current process. Seawater is supplied by means of medium-pressure full-cone nozzles spraying seawater from above. The gas passes a gas distribution grid after entering through the gas inlet duct in the lower section of the scrubber. The absorption takes place in the scrubbing section between the gas inlet duct and the nozzle bank. Through thorough design of gas inlet duct and gas distribution grid, an even gas flow is achieved. This ensures good contact between gas and seawater as well as even load on the mist

eliminator. Clogging of the mist eliminator has not been observed in these systems. The slightly acidic seawater leaves the scrubber over a common rectangular overflow weir. The overflow weir is designed to ensure a stable and controlled discharge flow.

Scrubbing efficiencies above 90 % is easily achieved at moderate gas velocities, pressure drops and water flows.

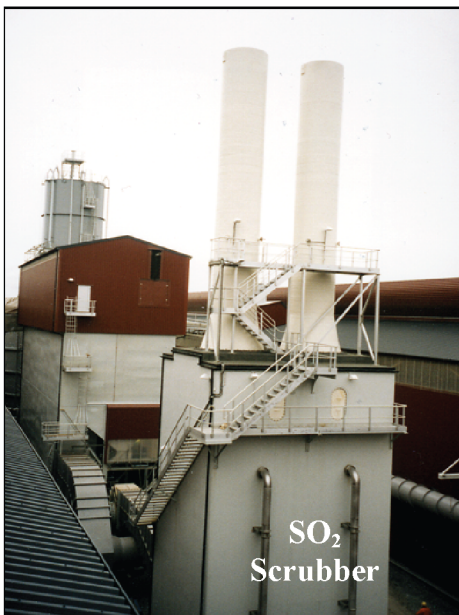
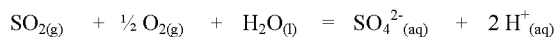


Figure 2. Photo of the dry HF recovery (at the back) and the wet SO₂ seawater scrubber at the Karmøy smelter.

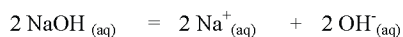
Sodium Scrubbers

For inland smelters SO₂ scrubbers must use an alkali as the neutralising agent. Sodium carbonate and soda lye (NaOH) as absorbing and neutralising agents are used for high performance and low maintenance of the scrubbers. The NaOH solution has proven to have a very high absorption capacity, and the reaction is considered to take place stoichiometrically according to:

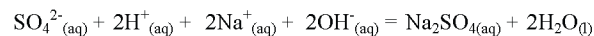
SO₂ absorption:



NaOH dissociation:



Neutralisation:



Overall reaction:



A flow diagram of the scrubbing system is shown in Figure 3.

Figure 4 shows the combined dry scrubber and the wet SO₂ removal scrubber at the Hydro Aluminium smelter in Årdal.

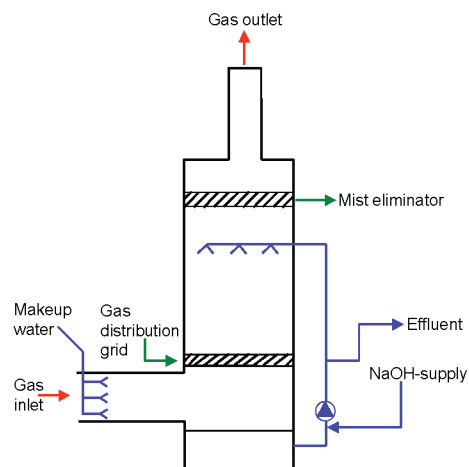


Figure 3. Flow diagram of the sodium scrubber.



Figure 4. Photo of the dry HF recovery and wet SO₂ removal scrubber at the Årdal smelter.

Gas Handling

The gases from the pots are led through the dry and wet scrubber with centrifugal fans operating in parallel and located between the dry and the wet scrubber. Make up water is injected in the SO₂ scrubber inlet duct to quench the gas. A wooden gas distribution grid just after the gas inlet ensures an even gas distribution and efficient gas – liquid contact. After passing the mist eliminator the gas is released to the atmosphere through the stack integrated in the scrubber top section. Experiences have shown that no flushing of the mist eliminator is necessary.

Circulating liquid

The absorbing liquor is sprayed counter-currently to the gas through full cone nozzles. Nozzle type and pressure are chosen to achieve a good atomisation. Spraying of the total cross-section of the scrubber ensures an efficient gas – liquid contact. A constant flow of scrubber liquid is circulating in the system. Liquid leaves the system through the effluent bleed off and by evaporation. To compensate for this, fresh water is added to the system in the inlet

duct. All circulating liquid is collected in the sump of the scrubber and is pumped back to the nozzle banks by the circulation pump. The scrubber has a relatively large sump with sloping bottom towards the drain in one corner. The inlet pipe to the circulation pump is located above the scrubber bottom to ensure undisturbed flow inlet to the pump.

The circulating absorption liquid must have a constant pH of 7.0 ± 0.1 . A pH sensor is automatically regulating the NaOH addition. Correct acidity of the liquid is required in order to achieve sufficient SO_2 absorption and prevent excess NaOH consumption. The density of the circulating liquid is kept constant by a density regulator, which is used for automatic regulation of the effluent bleed off.

The salt concentrations in the circulating liquid determine its density. Upon absorption of HF and SO_2 , the salts NaF and Na_2SO_4 are formed. Increased quantities of HF and SO_2 in the incoming gas increase the salt formation involving a higher NaOH consumption. Increased salt formation leads automatically to an increased effluent flow, due to the constant density regulation of the circulating liquid.

Minimum effluent flow and set point for the density regulator are chosen to avoid precipitation of salts. If the gas composition deviates from normal levels, precipitation of salts may occur. Should the concentration of the NaF-salt in the circulating liquid get too high or the temperature of the liquid get too low, there is a potential risk of precipitation of the double salt NaF Na_2SO_4 . All of these factors should be incorporated into the design ensuring a high operational flexibility of the scrubber.

Sodium supply and effluent flow

Sodium may be supplied as soda ash (Na_2CO_3) or soda lye (NaOH). Soda ash would require to be dissolved in tanks. All tanks should be insulated to reduce heat loss and a 40°C liquid temperature is achieved by heating with hot water. The temperature of the NaOH system is kept constant with self-regulating heat tracing. The effluent from the scrubber is pumped to the effluent storage tanks or to ponds. In warmer climates the evaporation of the water from the ponds ensures a dry disposal of the salt cake.

Limestone Scrubbers

Limestone scrubbers are based on limestone, CaCO_3 , as neutralising agent. SO_2 is absorbed in the scrubber liquor in the same way as for sodium and seawater scrubbers, but upon neutralisation, gypsum is formed by forced oxidation in an oxidation tank normally located in the scrubber sump. For power stations the limestone gypsum Flue Gas Desulphurisation process is the dominating process. The system requires a complex limestone pre-treatment and gypsum drying system. For the aluminium industry with relatively low SO_2 concentrations, it is hence normally not feasible to introduce such a scrubbing system due to the high installation cost and the operational complexity.

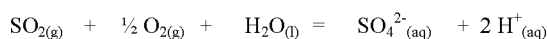
Double Alkali Scrubbers

This technology is more complex than seawater and sodium scrubbing. Sodium alkali is used in the scrubber to absorb SO_2 . The principle of the SO_2 removal is the same as for the sodium scrubber. The main difference is that the alkali is recovered. Some

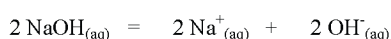
of the recycled sodium liquor is continuously bled off and mixed with lime in a regeneration tank. The soluble salts of SO_2 are precipitated as a mixture of gypsum and calcium sulphite hemihydrate. Active sodium alkali is regenerated and routed back to the scrubber to absorb more SO_2 . The precipitated calcium salts are settled in a thickener and then dewatered in a vacuum filter. The sludge with approximately 50% solids content is disposed of or further dewatered prior to disposal. This technology is an interesting option if seawater or sodium scrubbing from various reasons is inapplicable. The investment and operating costs are higher because more complex equipment is required⁽¹⁾.

The reactions of the system are as follows:

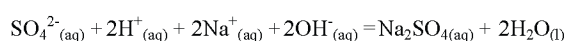
SO_2 absorption:



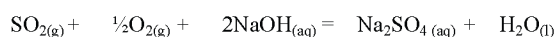
NaOH dissociation:



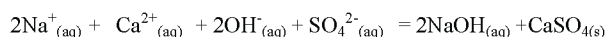
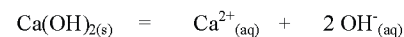
Neutralisation:



Total:



Alkali regeneration:



Overall reaction:



Dry SO_2 Scrubbing Technology

Dry systems for collection of SO_2 and other acidic gases are becoming increasingly popular in a variety of industrial processes. ABB and others have tested a variety of sorbents. Until now, no completely dry systems, based on regeneration of the sorbent have reached commercial status within the aluminium industry. Non-regenerative sorbents are, however, widely used. Soda ash and slaked lime are the most commonly used. A distinction should be made between the complete dry system frequently used to capture highly reactive gases like HF, HCl, and SO_3 , and the semi-dry system frequently preferred for SO_2 removal due to better utilisation of added alkali and higher SO_2 removal efficiency.

Interesting studies have shown that alumina may be used to remove SO_2 . It is well established and recognised that SO_2 adsorbs on alumina. Laboratory experiments have shown that adsorbed SO_2 will desorb in the presence of HF, as HF replaces adsorbed SO_2 on the surface of the alumina.

In a two step process whereby HF is removed or reduced to insignificant concentrations in the first step, the SO_2 may be adsorbed in the second step.

The Abart process in Figure 5 is therefore ideal for such a combined process. The SO_2 is adsorbed in the filter stage. The SO_2 -rich alumina is thereafter taken through a stripper where SO_2

is desorbed into a SO₂ concentrated gas. The regenerated alumina is then used in the reactor for HF removal and recovery.

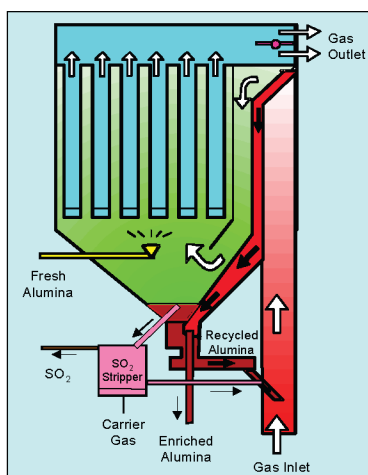


Figure 5. Dry SO₂ removal with the Abart filter.

A heated carrier gas controlled to desorb only SO₂ without desorbing the more strongly bound HF molecules achieves the selective stripping of SO₂ from the alumina. The SO₂-rich gas can be processed to valuable products or reacted with lime or limestone to commercial or disposable gypsum.

Preliminary investigations show that a SO₂ removal efficiency of >90% is achievable with this new system. The cost reduction is significant of such a system in comparison with the traditional and current technology of wet scrubbing systems⁽⁶⁾.

Selection of SO₂ Removal Process

Many complex interrelated factors affect the selection of a SO₂ removal process at a specific aluminium plant location. At least four main areas of concern must be evaluated:

1. Plant site considerations
2. Availability and price of alkali
3. End-product disposal options
4. Performance requirements.

Specific requirements dictated by the specific conditions inevitably must lead to different selection of SO₂ removal system from one smelter to another. There exists no "overall optimum system" applicable for all plant sites. For the primary aluminium industry sole wet SO₂ removal systems have been selected.

A wet system can be designed to very high SO₂ removal efficiencies, over 90% at favourable stoichiometry. The seawater scrubbing system is normally the most economical solution if seawater is available. The seawater scrubber offers high removal efficiencies and does not require advanced process control.

The dry scrubber currently under development by ABB utilising the benefits of the two-step Abart HF-recovery process is

promising. ABB ALSTOM POWER is installing a pilot plant to further test the industrial viability of such an SO₂ removal process.

Implication of adding SO₂ Scrubbing

Pressure from authorities to control the emission of SO₂ is increasing as the SO₂ emission exceeds earlier emission levels due to smelter capacity expansions, higher sulphur content in anodes, and increased knowledge on how SO₂ affects the environment and people.

Adding wet scrubbers downstream of existing dry scrubbers will reduce the emissions to the surroundings by more than 90%, but will not reduce the SO₂ exposure of potroom workers. A system that removes sulphur from the enriched alumina will, however, prevent the recycling of sulphur to the pots with increased release of SO₂ in to the potroom.

The complexity and costs of adding wet scrubbers downstream of existing dry scrubbers will depend on the arrangement and design of the dry scrubber. For multi-stack fluid-bed dry scrubber designs the gas streams from each stack need to be collected and fed through (booster-) fans and the scrubbing system (absorber).

For injection type of dry scrubber with centralised fans and common stack the complexity of adding a SO₂ removal system will be much reduced.

For inland smelters the liquid handling system would be much more extensive than for a once-through seawater system.

Costs

Capital investments needed to remove SO₂ from potgas will depend on the size and location of the smelter; the type and design of the SO₂ scrubbing system and its possible integration into the existing dry scrubber; and the extent of the liquid handling system.

The capital costs for a moderate sized inland smelter could be in the range of 50–80 USD per annual metric ton of metal produced. A smelter located at the sea using a seawater scrubber would require a capital investment only of the order of 50 % of the inland smelter investment. Operating and maintenance costs excluding costs for residue disposal may be about 2-5 USD per annual ton of metal.

Conclusion

Wet systems like seawater scrubbing, sodium scrubbing and double-alkali scrubbing are proven SO₂ removal technologies. They offer a broad range of established and emerging technologies, which are readily available if and when the industry has to meet stricter regulations of SO₂ emissions and if low-sulphur coke is no longer available. The economy of each technology is related to the specific conditions at each location and the most optimal solution must be based on a case-to-case study.

The seawater process is the simplest and most economical wet process if seawater is available. A new dry scrubber for removal of SO₂ utilising alumina as adsorbent has been tested in laboratory scale and pilot plant studies have been initiated.

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