

SO₂ Emissions Reduction – A New Challenge for Aluminium Smelters

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ABSTRACT

Metals producers worldwide are under increasing pressure to reduce emissions from their operations. Sulfur dioxide (SO₂) emissions are becoming more widely regulated with tighter emissions limits. Until recently, SO₂ capture and treatment technologies have not been regularly implemented in aluminum smelting, where sulfur from the bauxite ore and anodes can evolve as sulfur dioxide gas in the smelting process. Now the requirement for SO₂ emissions reduction has become a strong initiative in the aluminum smelting industry.

Other metals industries, including copper, nickel, and lead producers, have been capturing and treating sulfur dioxide gases from their processes for some time. Though the smelting processes for aluminum differ from the other industries, lessons learned and technologies used in those industries can be applied in aluminum smelting to meet future SO₂ emissions targets.

This paper discusses:

- SO₂ emissions reduction technologies used in other industries
- Technologies relevant for aluminum smelting
- Benchmarking of relevant technologies with capital and operating cost comparisons
- Typical gas conditions for other smelting processes, compared and contrasted to aluminum applications
- Byproducts, waste products, etc. associated with SO₂ emissions reduction
- Key concerns with systems design for SO₂ capture and treatment

INTRODUCTION

The process of primary aluminum production begins with the conversion of bauxite to alumina. The bauxite is first crushed, ground, and mixed with a caustic soda solution to produce a solution of sodium aluminate and bauxite residue. The residue is allowed to settle, while the aluminate slurry is sent to a digester which operates at high pressure to produce a sodium aluminate solution. The slurry is then transferred to flash tanks to reduce temperature and pressure before being transferred to settling tanks where the sodium aluminate solution is filtered of impurities.

Alumina crystals are then precipitated from the solution using fine alumina hydrate crystals as seeds. The alumina is then calcined in a rotary or fluid-bed kiln to produce pure alumina.

Aluminum is produced from alumina (Al_2O_3) in a reduction pot using the Hall-Heroult smelting process. The alumina is dissolved in a bath of molten cryolite (Na_3AlF_6) contained in the reduction pot. An electrical current is passed through the mixture from a carbon anode made from a mixture of coke and pitch, to the cathode formed by the carbon lining of the reduction pot. The alumina is reduced as the carbon anode is oxidized, producing CO_2 and aluminum. The denser aluminum settles to the bottom of the bath and is siphoned off into tapping crucibles.

The anodes are consumed as the alumina is reduced, therefore the anodes must periodically be replaced. The Söderberg and prebake technologies are the two main anode technologies presently in use. The Söderberg technology is a continuous anode production process where pitch is added to the top of the anode and, using the lost heat from the reduction pot, the pitch is baked. The prebake technology requires the use of anodes that are pre-baked in gas-fired ovens.

Air emissions generated from the bauxite operations consist primarily of dust emissions generated by the dryers, as well as secondary sources including material transfer points and conveyors. Baghouses and ESPs are generally used to provide particulate removal.

Control of emissions generated from the lime kilns and calciners at the alumina plant is typically accomplished through the use of baghouses and ESPs.

The primary air emissions generated during the smelting process occur at the potlines, and consist of particulate as well as gaseous and particulate fluorides. The particulate emissions are primarily controlled using fabric filters or ESPs, while dry scrubbing technology, using alumina as an adsorbent, is used to control fluoride emissions. Achievable emission levels of 0.2-0.4 kg/t for hydrogen fluoride, 0.4-0.4 kg/t for total fluorides and 0.3-0.6 kg/t for particulates have been reported.

Historically, sulfur dioxide (SO_2) emission limits have not been imposed on aluminum smelters, however increasingly stringent air emission standards are resulting in renewed interest in SO_2 emission reduction.

SO_2 emissions in the aluminum smelting industry are primarily a product of the sulfur contained in the anodes. Due to the use of heavier crude oils, sulfur content in the coke used to produce anodes is increasing. Some suppliers have been blending coke in order to meet the sulfur specification required, however the long term trend is for higher sulfur levels in the supply coke. Desulphurization of the supply coke can be considered, however, this can lead to undesirable coke quality.

Higher sulfur levels in the anodes results in increased SO_2 emissions at the smelter. Due to the increased focus on SO_2 emission reduction, tighter SO_2 limits will require SO_2 scrubbing to achieve emission targets in the future.

Several smelters in Norway have recently had SO_2 emission limits imposed, ranging from 1.4-2.5 kg /ton Al. These smelters have installed seawater flue gas desulphurization (FGD) downstream of the fabric filters and dry scrubbing system. In seawater FGD, the SO_2 is absorbed and oxidized to SO_3 using seawater in a scrubbing vessel. The filtered solution is then discharged back to the sea. Reported removal efficiencies ranged from 97.7-99.9%. This is the simplest and most economical method of SO_2

removal for aluminum smelters located near the sea. Plants without ready access to sea water, however, will need to consider an alternative technology.

SO₂ EMISSION REDUCTION TECHNOLOGIES

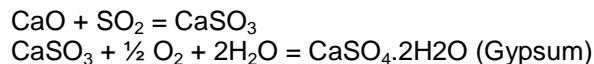
Capture and treatment of sulfur dioxide gases outside of the aluminum industry, in industries such as copper, nickel, and lead production, is now prevalent and found in a large majority of the smelters operating around the world. Several different technologies currently exist for removal of SO₂ from gas streams. Among the most common are lime scrubbing, sodium scrubbing, dual-alkali scrubbing, regenerative scrubbing, acid plants, and sulfur recovery. Due to differences in site conditions, available resources, and waste stream requirements, SO₂ removal solutions are very site and process specific.

Key design considerations to consider when selecting a scrubbing technology include:

- Inlet SO₂ concentration and variation
- Efficiency and outlet concentration requirements
- Scrubbing liquor pH
- Liquid-to-gas ratio
- Prevention of scaling and plugging
- Liquid and gas distribution and contact
- By-product handling and disposal
- Remoteness of site

LIME SCRUBBING

Lime scrubbers are relatively low cost scrubbing systems that utilize CaO to remove SO₂ from the gas stream. Dry lime spray into the gas stream with a downstream baghouse system can be utilized for gas streams with less than 0.5% SO₂, while a lime slurry system using a spray tower can treat gas streams with up to 1% SO₂. The collection efficiency of lime scrubbers is generally between 90-95%. The primary effluent is CaSO₄ (gypsum). The relevant reactions are as follows.



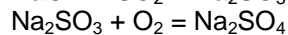
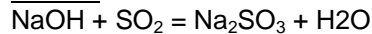
Lime scrubbing has several disadvantages compared with other SO₂ removal technologies. Running the lime scrubber at too high a pH will cause soft scaling (calcium sulfite) on the scrubber walls, pumps, and piping. A lime scrubber operating at too low a pH will result in a hard scaling (calcium sulfate) on the scrubber walls, pumps, and piping. This results in reduced equipment availability and difficulty maintaining high SO₂ removal efficiency. Magnesium enhanced lime helps to increase SO₂ removal and reduces the scaling potential. Higher liquid to gas ratios in lime scrubbers results in higher control efficiencies and a decrease in the formation of scale. However, these both add significant cost to the system. In addition, lime scrubbers have difficulty meeting target efficiencies at high inlet SO₂ concentrations of greater than 1% or when there are large fluctuations in inlet SO₂ concentration.

SODIUM SCRUBBING

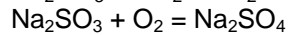
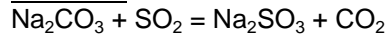
A sodium based scrubber using caustic or soda ash can achieve efficiencies of 99%. Sodium based scrubbers are generally much smaller than lime scrubbers due to the reactivity of the reagent and the ability to use tower internals for greater gas to liquid contact. In addition the potential for scaling is reduced to almost zero since the sodium based scrubber operates in an acidic mode. The power consumption is also lower due to lower pump recirculation rates compared to lime scrubbers and a low pressure drop. However, sodium scrubbing requires treatment of the Na₂SO₃ effluent. The effluent is generally oxidized to Na₂SO₄ and can be sent to landfill. Caustic and soda ash supply costs are also higher than lime, so once through sodium scrubbing will have higher reagent consumption costs.

The relevant reactions are as follows:

Caustic



Soda Ash

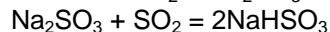
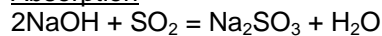


DUAL ALKALI SCRUBBING

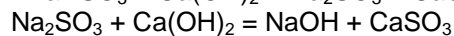
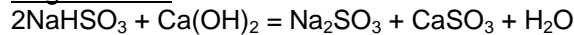
The NaOH used in a sodium based scrubber can also be regenerated by treating it with lime in a second step. The sodium-lime treatment process is called a dual-alkali system and uses lime to regenerate the sodium hydroxide scrubbing solution and precipitate gypsum in separate agitated regeneration tanks. Sodium-lime dual alkali scrubbers typically use NaOH or Na₂CO₃ in a tray or packed tower to treat gas streams with up to 3% SO₂ and achieve up to 99% collection efficiency. The resulting sodium sulphite Na₂SO₃ generated is further treated with lime to produce CaSO₄ (gypsum) and regenerate the NaOH scrubbing solution. Dual alkali scrubbers have been used for gas streams with up to 15% SO₂, but these are exceptions and generally not recommended.

Dual alkali scrubbers provide the performance of sodium scrubber with the reagent consumption costs of a lime scrubber. However, a dual alkali system requires more equipment than either lime or sodium scrubbing alone and initial capital costs are also higher. The process effluent from Dual Alkali scrubbing is sulfite calcium sulfite/sulfate products. The relevant reactions are as follows:

Absorption



Regeneration



CANSOLV SYSTEM

The Cansolv SO₂ Scrubber System is an amine-based regenerative SO₂ scrubbing process. The technology uses an aqueous amine solution to achieve high efficiency selective absorption of SO₂ from a variety of gas streams. The gas containing SO₂ flows upward through an absorption tower while the amine flows down the tower (counter-current flow). The absorption tower can be a packed bed or spray type, arranged to maximize contact between the amine and the gas. The amine containing the SO₂ discharges from the bottom of the tower through a heat exchanger and into the top of the regeneration tower. In the regeneration tower steam is introduced to the amine-SO₂ mixture and the SO₂ is released from the amine. The SO₂ exits through the top of the tower with water vapor. The SO₂-rich water vapor passes through a condenser that removes the water from the stream down to the saturation point of the SO₂ gas. The condensed water is fed back into the top of the tower while saturated SO₂ exits as the final product. The Cansolv plant can accommodate gas streams with up to 40mg/Nm³ of particulate loading. This allows for treatment of gas streams after ESP, venturi scrubbers, or baghouse based gas cleaning systems. The collection efficiency of the Cansolv plant is generally greater than 98% for gas streams with 0.5% to 5% SO₂.

The primary product is water-saturated SO₂ gas which can be sold or processed further. Due primarily to the use of steam, Cansolv is a more energy intensive process than lime, sodium, or dual alkali scrubbing.

WETGAS SULPHURIC ACID (WSA) PROCESS

The WSA process is a catalytic process which recovers SO_2 as concentrated sulfuric acid without the addition of chemicals or absorbents. The acid plant uses a special catalyst to convert the SO_2 to SO_3 which then reacts with water in the gas to form gaseous Sulfuric acid. The acid is condensed in an air-cooled WSA condenser.

The WSA process is autothermal for SO_2 concentrations from 3-5% SO_2 ; however for gases below 3%, additional process heat input is required which is commonly supplied by a gas fired heater. For concentrations above 6% SO_2 , the WSA process will require air dilution to control the temperature in the catalyst bed, making for a larger acid plant. The collection efficiency of the WSA plant is generally greater than 98%. The primary product is (98%) sulfuric acid.

The gas treated by the WSA must be free from particulate matter. The dust content must be reduced to below 1-2 mg/Nm³ to reduce dust accumulation on the catalyst. Therefore WSA may require an additional wet gas cleaning system upstream, depending on the application.

SULFUR RECOVERY

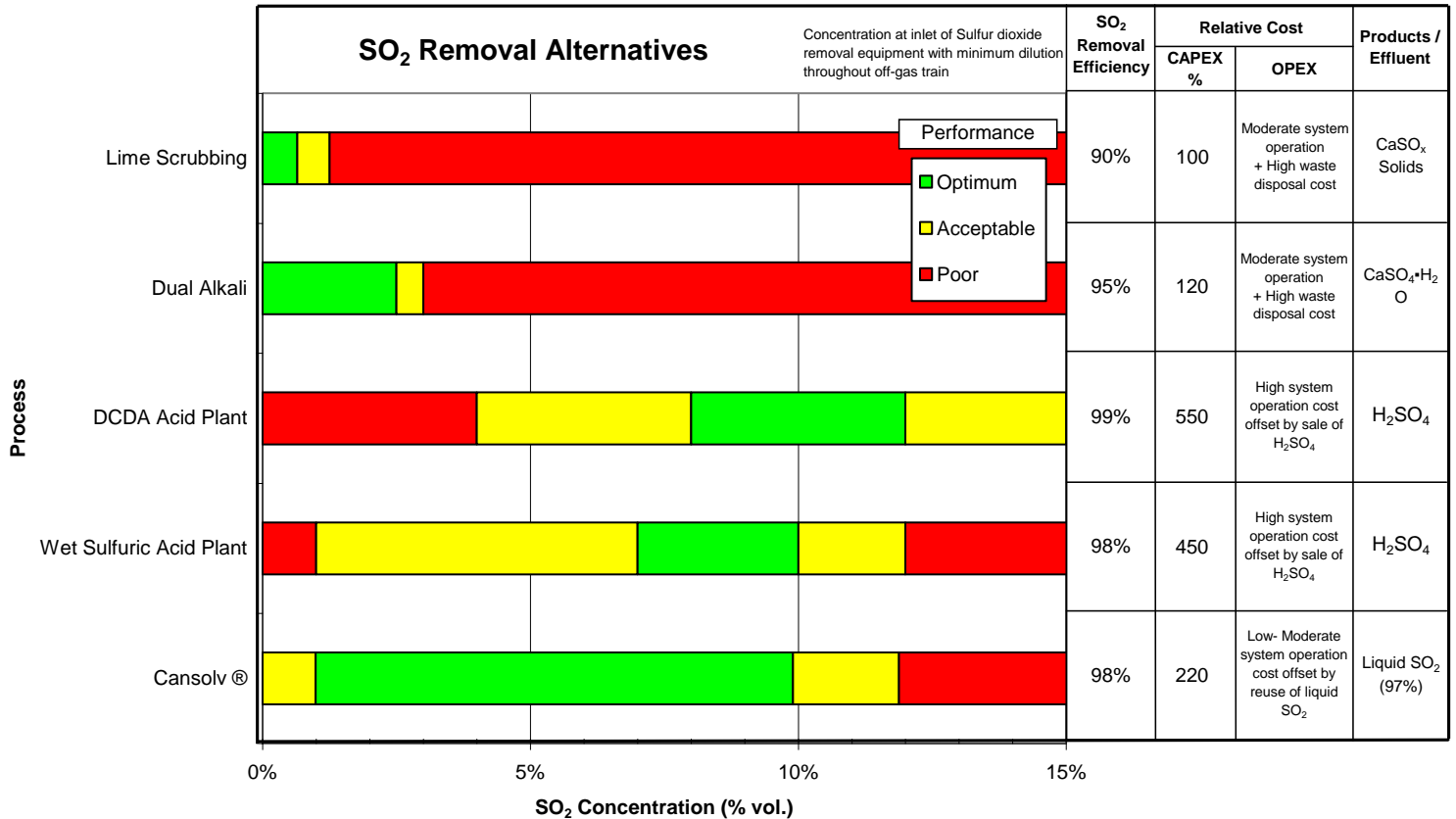
A regenerative scrubbing system using an amine solution produces a concentrated SO_2 stream that can be converted to elemental sulfur in a Sulfur Recovery Unit (SRU), or sulfuric acid if an acid plant is available. The system consists of a pre-scrubber to cool and condition the gas, an absorption tower for SO_2 removal, a regeneration plant evaporator system to release the absorbed SO_2 from the solvent, and a process unit for removing sodium sulfate.

Generating elemental sulfur generally requires the presence of H_2S in the gas stream. However, the Rameshni SO_2 Reduction Process (RSR) allows elemental sulfur to be produced when no H_2S is present in the gas stream. The RSR process involves reacting CH_4 with sulfur vapor to produce CS_2 , which then undergoes catalytic hydrolysis to H_2S . The H_2S is then reacted with SO_2 to form elemental sulfur.

SO_2 REMOVAL TECHNOLOGY COMPARISON

The following diagram compares the performance and cost of several SO_2 removal technologies based on inlet SO_2 concentration. Due to the low inlet SO_2 concentration gasses found in the primary aluminum smelting industry, lime, sodium or dual alkali scrubbing systems are typically the most appropriate for this application. As inlet SO_2 concentrations increase, lime and sodium based systems become less effective and alternative technologies must be considered. However, the scrubbing technology utilized is also very site specific since it is largely dependent on the site requirements for waste disposal.

Lime and sodium scrubbing are relatively simple to operate and are effective at low inlet SO_2 concentrations. Initial capital expenditure for a lime or sodium based system is also much lower than acid plants or amine based systems. However, the disadvantage of these systems is that waste disposal of the gypsum or sodium sulfate effluent is required.



The table above shows only a selection of the SO₂ removal technologies used in the metallurgical industry. Other technologies such as magnesium oxide, hydrogen peroxide, and ammonia scrubbing are available and may be considered in the selection of the most appropriate SO₂ removal technologies for a particular application or site.

The following table compares SO₂ removal technologies in place at several plants in various industries. The high volume, low SO₂ concentration gas generated in the aluminum smelting processes are similar to the secondary gas collection systems in place at many primary sulfide smelting applications. As shown, these applications typically employ lime, sodium, or dual alkali scrubbing technology.

LOW STRENGTH SO₂ TREATMENT BENCHMARKING

Plant	Primary Smelting Equipment / Source	SO ₂ Treatment Technology	Inlet Flow Rate Nm ³ /hr	Inlet Temp °F/ °C	Inlet SO ₂ Concentration	Outlet SO ₂ Concentration	Collection Efficiency
Base Metals							
Molybdenum	MoS ₂ Roaster	WSA	35,000	-	6,000 ppm to 28,000 ppm	980	-
Molybdenum	MoS ₂ Roaster	WSA	40,000	-	20,000 ppm to 24,000 ppm	960	-
Molybdenum	MoS ₂ Roaster	WSA	20,000	-	20,000 ppm to 45,000 ppm	500 ppm	>97.5%
Zinc / Lead Smelter	PbS Sinter Plant	WSA	110,000	-	22,000 ppm to 46,000 ppm	-	-
Copper Smelter	CuS Smelter	WSA	170,000	-	65,000 ppm	-	-
Zinc / Lead Smelter	PbS Sinter Plant/ZnS Roaster	WSA	125,000	-	65,000 ppm	-	-
Molybdenum	MoS ₂ Roaster	WSA	60,000	-	14,000 ppm to 37,500 ppm	-	-
Copper Smelter	PS Converter Secondary Gas	H ₂ O ₂ Scrubber	50,000	-	1000 ppm	-	>95%
Copper Smelter	Converter Secondary Gas	DOWA	180,000	-	1,000-2,000 ppm	20 ppm	98.0%
Copper Smelter	Acid Plant Tail Gas	DOWA	-	-	2,000 - 3,000 ppm	10 ppm	>99.5%
Copper Smelter	Converter Secondary Gas	Caustic Scrubber	130,000	-	800 - 1500 ppm	5 to 50 ppm	>96.6%
Copper Smelter	Converter Secondary Gas and Acid Plant Tail Gas	3 Limestone Scrubbers	480,000	-	2,000 ppm	30-50 ppm	97.5%
Platinum	Furnace and Converter Gas	Sodium Lime Dual Alkali Scrubber	197,100	-	3,000 - 10,000 ppm	35 to 350 ppm	>98.7%
Copper Smelter	Copper FSF/FCF Secondary Gas	Caustic Scrubber	534,000	150F	175 ppm	40 ppm	77.1%
Copper Smelter	PS Converter Secondary Gas	Lime Scrubbers	198,000	57C	-	200 ppm	-
Copper Smelter	Isasmelt & RHF Secondary Gas	Lime Scrubber	107,000	45C	-	80 ppm	-
Zinc Smelter	Lead Smelter Ausmelt Gas	Cansolv	20,000	-	10,000 ppm to 110,100 ppm	150 ppm	>98.5%
Copper Smelter	Copper Smelter	Cansolv	42,000	-	900 ppm to 19,000 ppm	150 ppm	99.2%
Copper Smelter	Converter Secondary Gas	Lime Scrubber	500,000	-			
Copper Smelter		Mg(OH) ₂ Scrubber + Wet ESP	450,000	-			
Other Plants							
Oil Refinery	Fluid Coker Gas	Cansolv	375,000	-	2,000 ppm	25 ppm	98.8%
Rubber / Chemicals	SRU Tail Gas	Cansolv	18,000	-	10,000 ppm	30 ppm	99.7%
Zinc Smelter	Zinc Smelter Acid Plant Feed Gas	Cansolv	5,600	-	80,000 ppm	30 ppm	100.0%
Oil Refinery	Acid Plant Tail Gas	Cansolv	45,000	-	3,000 ppm	15 ppm	99.5%
Oil Refinery	FCCU Flue Gas	Cansolv	640,000	-	800 ppm	25 ppm	96.9%
Oil Refinery	SRU Tail Gas	Cansolv	32,000	-	1,280 ppm	200 ppm	84.4%
Catalysts Recovery	Catalyst Calciner Gas	Cansolv	48,000	-	9,600 ppm	150 ppm	98.4%
Oil Refinery	SRU Tail Gas	Caustic Scrubber	41,000 24,800	140F	19,100 ppm	45 ppm	99.8%

CONCLUSION

Increasing sulfur levels in the coke materials used to produce the anodes used in primary aluminum smelting operations are resulting in increased SO₂ emissions at the smelter. Due to the increased focus on SO₂ emission reduction, tighter SO₂ limits will require SO₂ capture to achieve emission targets in the future. Seawater FGD units have been demonstrated to effectively remove SO₂ from the smelter flue gasses at several plants in Norway. However smelters without access to seawater have to consider alternative technologies in order to meet future SO₂ limits.

Several SO₂ emission reduction technologies have been implemented and proven in other smelting applications that could be applied to the aluminum industry. Due to the relatively high volume, low SO₂ concentration gas, the most practical technologies for application in the primary aluminum smelting industry are lime, sodium and dual alkali scrubbing. These technologies are well proven in the primary sulfides smelting industry for treatment of secondary process gases that are similar to the composition to the flue gas generated in primary aluminum smelting. These technologies are also relatively simple to operate and require less capital expenditure than other available SO₂ reduction technologies. However, depending on site specific waste disposal requirements, the application of these technologies may be limited due to the required disposal of gypsum or sodium sulfate wastes.