BAUXITE RESIDUE DESULPHURISATION SYSTEM (BRDS) AT EURALLUMINA

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Abstract

In order to comply with the regulations governing emission limits (SOx and particulate) the following possible solutions were analysed: to burn low sulphur fuel oil in the boilers and kilns and install new ESPs, or to build a desulphurisation plant, continuing to burn the cheaper high sulphur fuel oil. Eurallumina adopted the second choice based on project economics.

The BRDS technology selected by Eurallumina was developed and applied by Sumitomo Chemical Co. Ltd at its Niihama (Japan) refinery. Based on this technology, Hamon Research-Cottrell Italia S.p.A. was selected as turn-key contractor to design and build two desulphurisation units, one each in the boiler and calcination areas.

The BRDS process is a SOx/particulate scrubbing process based on contact between red mud and the flue gas to be treated. The neutralization reaction takes place in a multi-tray absorber using sodalite (DSP) as the reactive agent. SO_2 gas reacts with sodium contained in the sodalite and is absorbed as sodium bisulphite and sodium sulphite. Sodium sulphite reacts to become sodium sulphate through oxidation.

Main elements of the desox unit are: the *gas-gas heater* where raw flue gas is cooled and clean flue gas is heated; the *quencher* to saturate and dedust the raw flue gas; the *absorption tower* for the desulphurisation process; the *demister* to remove red mud particles; and the *red mud recycle tank* where fresh and treated red mud are handled.

The two units have been in operation at Eurallumina from the beginning of the year 2000, showing low plant operating cost, easy plant operation and high stability for varying loads. The results in terms of SO_2 and particulate emissions at the stack are significantly better than the design limits.

1. Introduction

The Eurallumina plant in Portoscuso, Sardinia, Italy, is fitted with three boilers of 170 ton/h steam capacity each and three alumina calcination kilns (2 rotaries up to 1050 tpd and 1 stationary, up to 1600 tpd capacity). Boilers and kilns burn high sulphur fuel oil with a maximum of sulphur content of 3.5 %.

In order to comply with the regulations governing the emission limits, Eurallumina was requested to reduce the particulate and SO_2 concentration in the flue gas from the boilers and calciners, starting from January 2000. At that time the flue gas emissions were much higher than the new requested limits. The untreated flue gas conditions are presented in Table 1.

Table 1 — Flue gas emissions at Desox inlet

	Boilers wet base 7.3% O_2	Calciners wet base 4.1% O_2
Max Flow [Nm^3/h]	360,000	280,000
Temperature [°C]	160	198
H_2O [%] vol	8.3	40
O_2 [%] vol	7.3	4.1
CO_2 [%] vol	9.3	6.7
N_2 [%] vol	75.0	49.1
SO_2 [mg/Nm^3]	6,100 3% O_2 on dry base	2,150 3% O_2 on wet base
Particulate [mg/Nm^3]	145 3% O_2 on dry base	85 3% O_2 on wet base

Italian enviromental law identifies some industrial areas in the country as “High Enviromental Risk Areas” and for these areas fixes emission levels which are more restrictive than the standard limits. Portoscuso industrial area, where the Eurallumina plant is located, is one of those areas. Italian and Eurallumina emission standards are reported in Table 2.

Table 2 — Italian and Eurallumina emissions limits concentration

	Italian standards	Eurallumina standards
Calciners [mg/Nm^3] 3% O_2 on wet base		
SO_2	500	375
Particulate	50	40
Boilers [mg/Nm^3] 3% O_2 on dry base		
SO_2	1,700	1,275
Particulate	50	50

By comparison between Tables 1 and 2 it is obvious that not only did the SO_2 emission exceed the allowed levels, but it was also necessary to reduce the dust emission level. Eurallumina had the two following options:

1) the first one was to move from High Sulphur Fuel Oil (HSFO) to a Low Sulphur Fuel Oil (LSFO) to reduce SO_2 emission levels, installing in the meantime new electrostatic precipitators to control the dust emissions.
2) the second was to set up a desulphurisation plant, which would allow burning of HSFO to continue, while reducing both SO_2 and dust emissions.

Eurallumina adopted the second choice based on economics but also considering the benefits in terms of red mud neutralization, i.e. 50 % of the mud produced in the Eurallumina refinery would be neutralized in the desox plant to desulphurate the flue gas. In this way the portion of mud dedicated to this process has the two associated

KEY WORDS: desox, particulate, red mud, flue gas

environmental benefits of neutralising its residual caustic content and cutting the sulphur/dust emission at the stack.

The technology adopted is called BRDS (Bauxite Residue Desulphurisation System) and was developed by Sumitomo Chemical Co. Ltd and applied in its Niihama (Japan) plant. The technology is based on the capacity of Bayer process red mud to react with the SO_2 present in the flue gas to form sodium sulphite and sulphate.

Eurallumina commissioned Hamon Research-Cottrell Italia S.p.A. to undertake detailed engineering for the BRDS process, introducing some different approaches in particular to critical areas such as material selection and chimney tray and demister design. Two desox units have been installed at Eurallumina, one to control SO_2 emissions from the boilers, and another dedicated to SO_2 emissions from the calcination kilns.

2. Sumitomo BRDS process

The BRDS process is a SO_2/particulate removal process based on the contact between the red mud and the flue gas to be treated. Reaction takes place in a multistage absorber. The number of stages and the operating conditions determine the SO_2 level in the treated gas stream. The efficiency of SO_2 removal can be as high as 96%.

Sumitomo Chemical Co.,Ltd first operated their Niihama BRDS plant in 1977 (104,000 Nm^3/h flue gas capacity). After a few years of uninterrupted operation it was apparent that this type of process, involving reasonable maintenance cost, can be considered reliable and efficient. The process flow scheme of the Sumitomo plant in Niihama is shown in Figure 1 and the main specific consumptions per cubic meter of fuel oil, are presented in Table 3.

Table 3 —Main specific consumptions per cubic meter of fuel oil at Niihama plant

		Niihama
Bauxite residue slurry	m^3	1.8
Electricity	kWh	126
Industrial water	T	1.8
NaOH (as 100%)	kg	2.4

Results from the Niihama plant over more than twenty years of operation have been excellent and the features of the unit are:

- High SO_2 removal efficiency
- Easy plant operation
- Long continuous operation
- High stability even with changing loads
- No scaling problems

3. Eurallumina Desox Unit description

3.1 *Sodalite is the reaction agent*

The principle of the desulphurisation process is the use of bauxite residue, or process mud, as a SO_2 absorbent. The mud contains caustic soda combined, in the complex molecule of the so-called desilication product, as sodium-silico-aluminate (sodalite), which in the presence of sulphur compounds breaks down, with the sodium linking up with the sulphur. The portion of sodalite which reacts is about 70% of the total sodalite contained in the mud.

Gaseous SO_2 reacts with sodalite and is absorbed as sodium bisulphite and sodium sulphite. The major absorption reactions occurring in the contact between mud and flue gas are:

$$2\ Na_2O{\cdot}2Al_2O_3{\cdot}3SiO_2{\cdot}3H_2O + 4SO_2 + 2H_2O \rightarrow 4NaHSO_3 + 2Al_2O_3{\cdot}3SiO_2{\cdot}3H_2O \quad (1)$$

$$2\ Na_2O{\cdot}2Al_2O_3{\cdot}3SiO_2{\cdot}3H_2O + 4NaHSO_3 \rightarrow 4Na_2SO_3 + 2H_2O + 2Al_2O_3{\cdot}3SiO_2{\cdot}3H_2O \quad (2)$$

The resulting sodium sulphite is converted into sodium sulphate by oxidation:

$$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4 \quad (3)$$

3.2 *A very simple flue gas treatment*

The treatment stages are described below and a basic flow diagram of the process is presented in Figure 2.

- the *flue gas* passes through the following sections:
  - temperature conditioning and heat recovery (the Gas-Gas-Heater)
  - saturation stage (the quencher)
  - absorption stage (the counter-current multi-tray tower)
  - mist and entrainment separator (the demister)
  - final heating-up stage (the Gas-Gas-Heater)
- the *reagent mud slurry* is operated as follows:
  - the mud feed into the tower is via a recirculating tank with associated pumps and piping
  - the quality of the recirculating mud, and its reaction ability are controlled by make-up of fresh mud to the system and blow-down of exhausted mud

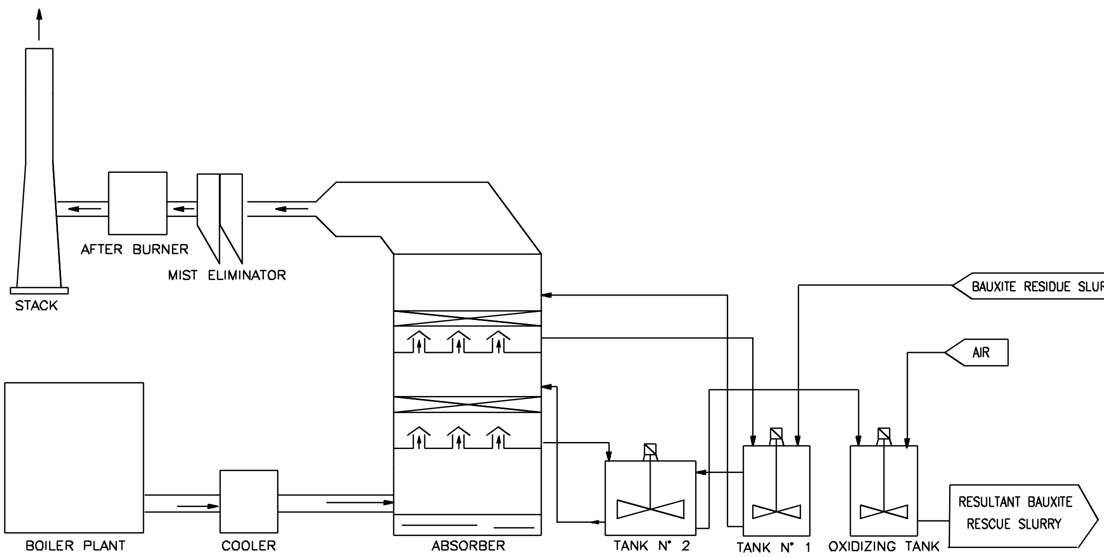

Figure 1 — Sumitomo plant at Niihama

- the *key control parameter* for the chemical reactions is the pH of the recirculating mud. The make-up of fresh mud is determined by the pH value, and the blow-down, by consequence, is given by the balance at the recirculating tank.

3.3 *Gas stream conditioning*

The raw flue gas coming from the boiler/calciner section is cooled by a regenerative type Gas-Gas-Heater which heats up the treated gas from the absorber. A flue gas fan pressurises the gas as a function of the pressure drop of the whole system. Then the cooled gas is fed into the quencher where it is saturated and further cooled by means of recirculation water. The quenching area consists of a cylindrical duct of 8.5 m length and 4.0 m diameter. Saturation water is supplied by four injection rings, each equipped with eight–ten nozzles.

Flue gas saturation temperature in the boiler area is about 54°C, whilst in the calciner area the equilibrium is up to 80°C, because of the higher water content of the gas. Make-up sea water is supplied to the quenching section in order to compensate for evaporation and blow-down water loss. A certain proportion of the make up is as a consequence of the blow-down necessary to prevent the recirculation water from accumulating dust and salts. SO_3 gas is easily absorbed by sea water and produces sulphuric acid; so the pH of the recirculation solution is strictly acidic.

3.4 *The Absorber stages*

A pictorial representation of the absorber is shown in Figure 3. The saturated and cooled gas from the quenching section is conveyed to the bottom part of the absorber. Uniform distribution of the flow is obtained by means of a gas distributor. A vertical flow demister is installed to remove droplets and mist from the flue gas.

A chimney tray divides the bottom from the top of the absorber. The gas contacts the recirculating mud slurry in the absorbing upper section. The absorber is in fact a slurry/gas contactor where the gas intimately contacts the slurry and the SO_2 can react with the sodalite. Slurry concentration is approximately 20 to 22 % wt. solids.

Red mud consumption is a function of the pH in the recycled slurry: the set point value for the boiler treatment unit is 5.0 to 5.5, whilst in the calciner unit it is 7.0 to 7.5.

The mud slurry, fed by recycle pumps, is spread out through a distribution system installed at the top of the absorber. The slurry flows down through the trays and is finally collected on the chimney tray. Between the distribution pipe and the chimney tray, the slurry and the gas come in contact with each other on the perforated plates and SO_2 gas is absorbed. The reacted slurry, collected in the chimney tray returns to the slurry recirculation tank by gravity. A part of the reacted slurry is removed from the slurry recycle tank and transferred by a slurry return pump to the residue pond.

The treated gas passes through a double-stage horizontal flow mist eliminator, where the entrainment is separated. The absorber, the hood and the demisters are intermittently washed by sea water injection.

Afterwards, the gas is heated up by the Gas-Gas-Heater to prevent condensation in the stack and to assist gas diffusion into the atmosphere.

4. Description of the equipment

4.1 *Gas-Gas-Heater (GGH)*

The heating surface of GGH in the boiler section is 1550 m^2, whilst in the calciner section it is 1650 m^2. Required ΔT is approximately 30°C and 35°C respectively.

Heating is carried out via rotating heating elements, according to the Ljungström principle. The heating elements consist of enamelled corrugated and undulated plates which are housed in baskets and arranged within a rotor, approximately 5 m diameter, which rotates at 1.5 rpm.

The two heater areas (the raw and the clean gas) operate at different pressures, as the pressurizing fan is located between the two sides. The clean-gas section works at a pressure higher than the raw-gas section, and maximum gas leakages expected to occur between the two sides of the heater are 1% of flow.

Minimum flue gas temperatures at the outlet of the desulphurisation plant are 80°C for the boiler unit and 110°C for the calciner unit.

4.2 *Flue gas fan*

The fans are designed for the maximum flue gas flow rates in both areas. The flow-rate regulation system consists of two dampers placed on the double fan suction.

Material selection for the equipment was very critical, because of the highly corrosive conditions and presence of dust in the gas. Moreover, the high gas humidity (> 40% vol) and the high content of alumina dust contained in the flue gas coming from calciners represent an even more critical factor for the fan blades.

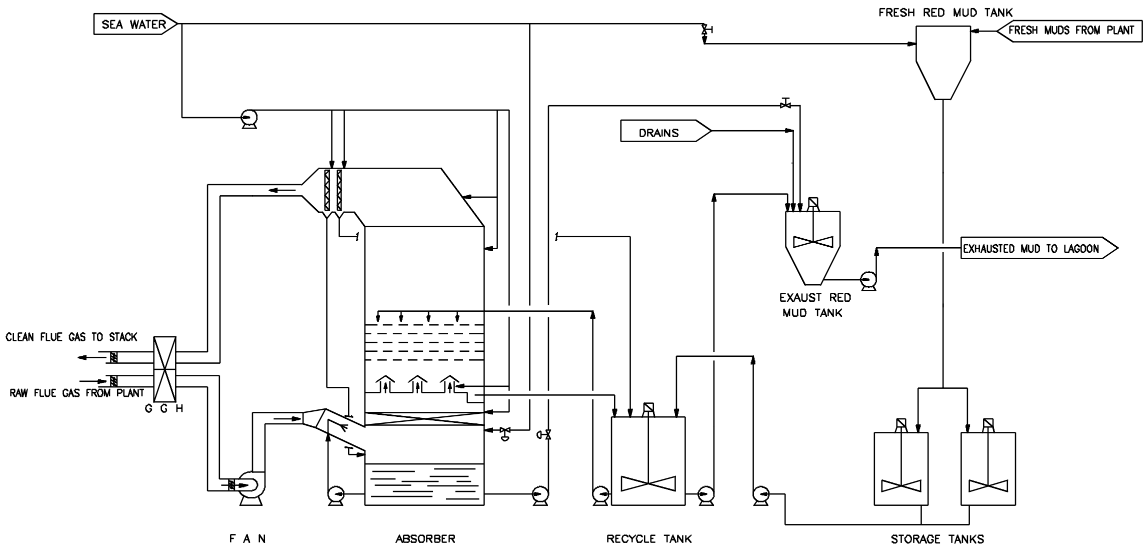

Figure 2 — Process flow diagram for the Eurallumina bauxite residue desulphurisation system

The impeller material selected for this application is an austenitic/ferritic stainless steel; internal casing has a high Ni-Cr-Mo alloy wallpapering.

4.3 *Quencher*

The quenching section represents the most critical area because of its corrosive and abrasive environment. Moreover, the flue gas enters at high temperature and it must be quenched to saturation. So, the major process parameters for material selection are:

- high flue gas temperature at the inlet quenching section
- high content of SO_x in gas and then high sulphuric acid presence in the recirculation solution
- dust content in liquid due to the particulate removal in the quencher
- presence of chlorides (above 20,000 ppm) because of sea water used as make-up

Solid content expected in normal operating condition is less than 1% in recycle liquid, so pipes and nozzles must be resistant to erosion. Solid and dust deposits in the quenching section represent a real problem, especially in the calciner section, because of the presence of alumina dust. The material selected for the quencher is high Ni-Cr-Mo alloy (Hastelloy type). The recirculation pipe is made of FRP (Fiber Reinforced Polymer) whilst the recycle pumping station is made of a high alloy impeller with a rubber-lined casing.

4.4 *Absorbing tower*

The absorbers can treat the maximum flue gas flow-rate for both of the areas. Diameter is 8.6 m for the boiler area and 7.6 m for the calciner area; height is approximately 22.0 m. The absorber shell is made of Ni-Cr-Mo alloy.

After passing through the quencher saturation section, the flue gas enters into the lower part of the absorber. The internals are:

- A washing nozzle system for the gas distributor and lower absorber wall. The nozzles are pressurised (2 bar) and operate continuously. The washing liquid is part of the recirculation water pumped into the quenching saturation lances. Washing pipes are made of FRP with PVDF (polyvinylidene fluoride) nozzles.
- A gas distributor, consisting of fixed and partially regulated sectors, made of Ni-Cr-Mo alloy.
- A horizontal demister — Chevron type, for liquid particles and mist removal from the gas. The horizontal demister is made of polyester/polypropylene (in the calciner/boiler areas respectively). Demister is provided with a washing nozzle system (discontinuous washing with sea water) which is made of FRP with PVDF nozzles.
- A chimney tray, separates the lower section of the tower (saturation) from the upper section (absorption). It has a conical shape to collect the mud after gas treatment and directs it to the recirculation tank. The eight chimneys fitted in the tray feed the raw gas into the absorption section

  Each chimney has a conical hat to prevent mud passage into the lower area. The chimney tray is resin-lined and is provided with a washing nozzle system which is made in high Ni-Cr-Mo alloy (discontinuous washing with sea water).
- Five perforated plates (each with a different number of holes and different diameter), on which the SO_2 containing flue gas comes into contact with red mud. Plate spacing is about 1.2 m. To prevent short circuiting, each plate is divided into several sectors by dams 50 mm high. The ΔP through the plates is 100 mm H_2O when the absorber is clean although scaling can increase this value to 200 mm H_2O. The perforated plate material is high Ni-Cr-Mo alloy.
- A red mud recycle and distribution system consisting of four main distribution groups which spread the slurry to multiple injection points (splashdown systems). The distribution system is made of FRP.
- A washing nozzle system for the absorber upper wall and hood (discontinuous washing with sea water) which is made of FRP with PVDF nozzles.

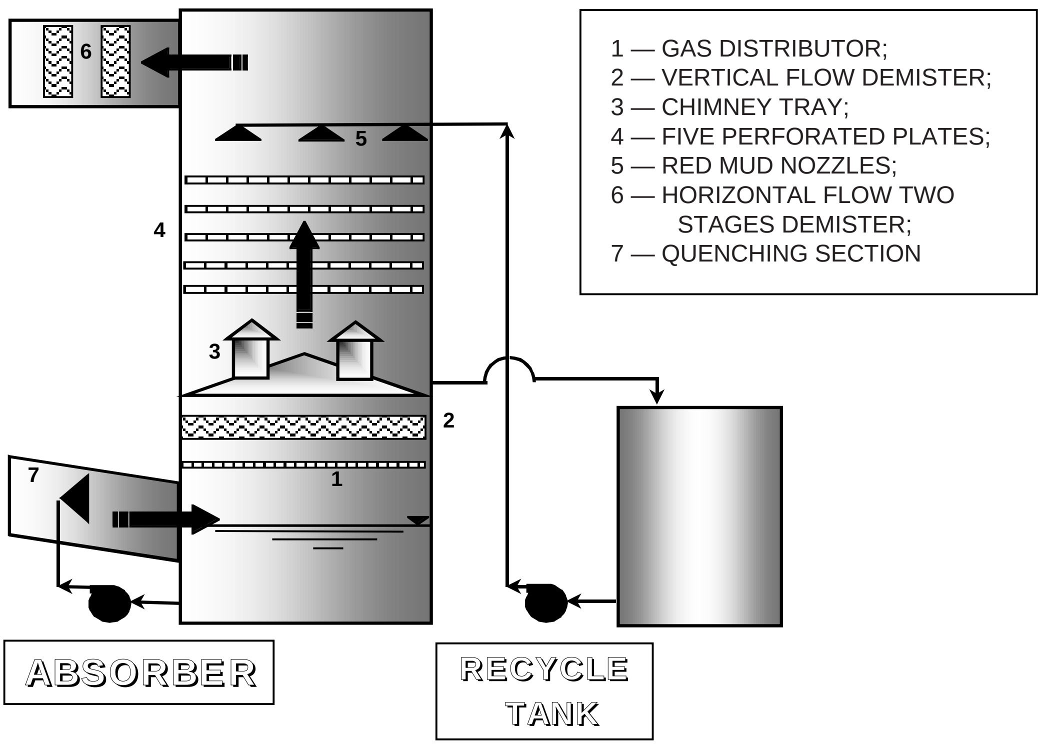

Figure 3 — The absorber

Table 4 — Yearly average emissions

	Units	Year			
		1999(1)	2000	2001	2002 First Quarter
Boiler Area(2)					
Plant performance: SO_2	mg/Nm^3	5,469.0	1,238.0	727.0	824.0
Particulates	mg/Nm^3	93.0	49.0	42.0	38.0
Eurallumina standard limits: SO_2	mg/Nm^3	1,275.0			
Particulates	mg/Nm^3	50.0			
Calciner Area(3)					
Plant performance: SO_2	mg/Nm^3	1,625.0	114.0	68.7	140.0
Particulates	mg/Nm^3	156.0	23.7	28.8	27.5
Eurallumina standard limits: SO_2	mg/Nm^3	375.0			
Particulates	mg/Nm^3	40.0			
Total Production (Alumina and Hydrate)	Ton/year	973,000	1,022,000	992,000	1,002,000(4)

1. Sumitomo plant under construction
2. Sumitomo plant started in March 2000
3. Sumitomo plant started in February 2000
4. Annual base

- A two-stage vertical demister, Chevron type, to remove red mud particles coming from the slurry spreading section. This equipment protects the Gas-Gas-Heater and keeps emissions at the stack free from mud particles. The demister is provided with a washing nozzle system (discontinuous washing with sea water) which is made of FRP with PVDF nozzles.

4.5 *Red mud and slurry handling*

Smooth red mud handling is essential in order to have a continuous and homogeneous reagent feeding to the absorber. The mud slurry made available from the mud filtration area contains about 30 % wt. solids. For safe handling in the absorber, the solid content of the mud slurry is reduced to 21-23 % by the various water entrances into the system.

All of the piping for mud recycle, originally in carbon steel, has been replaced with internal rubber lining because of erosion/corrosion problems caused by the very low pH values experienced during process upsets. For the same reason, the bottom of the recycle tank has been treated with FRP and the agitator has been rubber lined. Pumping stations have a stainless steel impeller and high alloy wall-papering on the casing.

5. Results

5.1 *Performance*

Plant performance to date is considered more than adequate. SO_2 and particulate monthly emissions values are always lower than Eurallumina limits, with the exception of only two months per year in which the planned maintenance is done. The yearly average emissions (without considering the long shutdown for maintenance) are shown in Table 4.

The specific consumptions per cubic meter of fuel oil in 2001, are presented in Table 5. The specific consumptions are satisfactory and the major differences between the Eurallumina and Niihama plants are the use of seawater instead of industrial water as make-up liquid and the absence of NaOH as a reagent.

Table 5 — Specific consumptions for the Eurallumina BRDS plant (2001)

	Units	Eurallumina
Bauxite residue	m^3/m^3 fuel oil	3.19
Electricity	kWh/m^3 fuel oil	92
Sea water	T/m^3 fuel oil	2.44

5.2 *Operating Factor*

The operating factor for both units has not yet reached the aim value (90%), however the yearly average emissions, even including the long shutdown for maintenance, are still lower than the internal standards. This means that a high efficiency is obtained in both units, which is able to compensate for the high emissions suffered during the shutdown and provide acceptable ‘average’ values on an annual basis. The operating factors for the two units are shown in Table 6.

Table 6 — Operating factors

	Units	Year			
		1999 (1)	2000	2001	2002 First Quarter
Boiler Area — Operating Factor (2)	%		74.1	81.1	86
Calciner Area — Operating Factor (3)	%		92.5	84.6	85.1
Total Production (Alumina and Hydrate)	Ton/year	973,000	1,022,000	992,000	1,002,000 (4)

1. Sumitomo plant under construction
2. Sumitomo plant started in March 2000
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6.0 Conclusions

The Eurallumina flue gas desulphurisation unit, based on the Sumitomo BRDS process, has proven capable of meeting SO_2 emission limits in a cost-effective manner. The Eurallumina system achieves this by means of a reagent which is a waste product (the "red mud") from the alumina refinery, providing the following significant advantages:

- Possibility of burning fuel oil with high sulphur content (cheaper)
- Avoidance of a costly raw material purchase for flue gas treatment purposes
- Use of a waste product for an environmental goal
- Low operating cost
- Possibility to operate at variable loads with the same good SOx and particulate removal efficiencies.