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Recovery of SO_2 from low strength off-gases

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After the milling and flotation of the platinum bearing ore, the flotation concentrate is electrically smelted in 6-in-line electric arc furnaces and the resulting furnace matte treated in Peirce Smith converters to remove the iron. The iron-free (less than 1% Fe) converter matte is granulated and sent to the base metals and precious metals refineries for further processing.

During the smelting and converting processes two distinct gas-strength gas streams are produced:

- The Peirce Smith converter off-gas contains 4%–9% SO_2 which is treated in a conventional sulphuric acid plant to produce 94% H_2SO_4.
- The electric furnace off-gas contains 0.9% SO_2 which was (until September 2002) vented through a 91- metre high stack to atmosphere.

In October 2002 Impala Platinum commissioned a SULFACID® plant at its smelter in Rustenburg, which recovers the SO_2 from the electric furnace off-gasses into a weak sulphuric acid solution. The SULFACID® technology utilizes wet activated carbon to oxidize the SO_2 to SO_3. The SO_3 reacts with the water on the catalyst and is washed off the catalyst bed as a sulphuric acid solution with up to 13 wt. H_2SO_4. The plant operates at 60ºC and at atmospheric pressure.

The SULFACID® technology is widely used in the pigment industry. This is, however, the first application of the technology on electric furnace off-gas.

Keywords: SO_2, sulphuric acid, electric furnace, off-gas, SULFACID®

Motivation for the project

Impala continuously strives to minimize its impact on the environment, thereby achieving world-class environmental performance and also ensuring conformance to present and future emission limits set by environmental authorities.

Some of the sulphur in the smelter feed concentrate is converted to SO_2 during smelting in the electric furnaces, whereas the bulk is released as SO_2 during the converting step and captured as sulphuric acid (H_2SO_4) in the Acid plant. The SO_2 formed during electric smelting was, until September 2002, vented to atmosphere through a 91-m high concrete stack.

Prior to the installation of the SULFACID® plant, Impala's smelter emitted 34 tons of SO_2 per day to atmosphere from its off-gas stacks, 4.5 tons SO_2 per day were emitted from the acid plant stack and 1.5 tons SO_2 per day from the dryer stacks. The rest (28 tons) were emitted from the 91-metre furnace off-gas stack. Thus the bulk of SO_2 pollution to atmosphere originated from the electric furnaces.

Technology approaches

The removal of SO_2 from metallurgical off-gases can be divided into two distinct gas strength applications, i.e.

1. Stronger than 3% v/v SO_2
2. Weaker than 2% v/v SO_2

Stronger than 3% v/v SO_2

This gas strength can be handled in a normal dry contact sulphuric acid plant using vanadium pentoxide as a catalyst.

At Impala's smelter the Peirce Smith converter off-gas contains 4–9% SO_2 and is treated in a conventional sulphuric acid plant to produce saleable sulphuric acid (94% H_2SO_4).

Weaker than 2% v/v SO_2

Traditionally this is a much more difficult gas strength to handle and quite a few processes have been developed over the years to cope with this gas. A broad spectrum of process suppliers and technology approaches is available and the different technologies can be divided into a few main approaches, i.e.

- Scrubbing of the off-gas with an alkaline solution to produce an environmentally friendly and stable waste product, which can be discharged onto a tailings dam or permanent landfill site
- Physical absorption of the SO_2 into a chemical solution to produce high quality chemically pure process chemicals. The SO_2 can also be steam stripped from the chemical solution to produce a high strength SO_2 gas for further treatment in a standard sulphuric acid plant or for production of bottled pure SO_2. The absorption is achieved in a scrubbing plant
- Catalytic reaction of SO_2 with O_2 to produce SO_3 which is absorbed in water to produce sulphuric acid of less than 90% strength.

Impala process selection

Impala's electric furnace off-gas contains only 0.6%–0.9% SO_2.

An in-depth study was done to determine which one of the above-mentioned processes would best suit Impala's requirements. The final recommendation from the study (for reasons of CAPEX, OPEX, operability, complexity, ease of product discharge and ease of expansion) was the Donau Carbon SULFACID® process, which produces a 10% to 15% H_2SO_4 solution.

The SULFACID® process is a well-established process in the treatment of SO_2 containing off-gases in the pigment industry. At present Donau Carbon technology has 20 installations in the world of which 17 are in Europe, 1 in North America and 2 in South Africa. The first plant was installed in Germany in 1972.

Also of importance in the choice was the opportunity to decouple the furnace and converter off-gas handling systems.

Process description

The SULFACID® process is a catalytic process to convert the sulphur dioxide in flue gases to weak sulphuric acid by means of a wet activated carbon catalytic process.

The resulting water-clear acid has a concentration of about 10 to 15 wt.% H_2SO_4.

The process requires the following conditions:

- The raw gas preferably be saturated with water when it enters the reactor
- The gas temperature must be between 30–80°C
- The gas contain not less than 10 vol.% O_2
- The dust content of the gas must be less than 30 mg/m³.

The sulphuric acid formed on the catalyst surface is intermittently washed out from the catalyst particles by spraying with potable water onto the catalyst bed.

The water-saturated clean off-gas is discharged via a stack to atmosphere.

The reaction of SO_2 to H_2SO_4 on the catalyst surface takes place according to the following reaction steps:

$$SO_2 + nH_2O \Leftrightarrow 2H^+ + SO_3^{2-} + (n-1)H_2O \quad [1]$$

$$SO_3^{2-} + \tfrac{1}{2}O_2 \Leftrightarrow SO_4^{2-}(\text{exothermic}) \quad [2]$$

$$2H^+ + SO_4^{2-} \Leftrightarrow H_2SO_4(\text{exothermic}) \quad [3]$$

$$SO_2 + \tfrac{1}{2}O_2 + nH_2O \Leftrightarrow H_2SO_4 + (n-1)H_2O \quad [4]$$

and can be described in detail as follows:

- O_2 and SO_2 are adsorbed by the aqueous acidifying envelope of the catalyst grain as a function of temperature and partial pressure
- Diffusion transports both components to the active centres in the catalyst pores
- SO_2 reacts with oxygen to form sulphuric acid according to Equation [4], which is the sum of Equations [1], [2] and [3]
- The resulting sulphuric acid diffuses from the pores into the aqueous envelope of the catalyst grain
- The sulphuric acid is washed off with potable water, being diluted in the process.

As shown by the reaction formula, the reaction consumes 1 part of oxygen for every 2 parts of sulphur dioxide. Hence, it would be ideal for the process if the components were present in this ratio in the liquid phase.

However, the solubility of SO_2 and O_2 in water or dilute sulphuric acid always causes oxygen to be present at an under stoichiometric ratio and thus makes it one of the limiting factors determining the conversion rate.

Other major parameters influencing the SO_2 removal efficiency are the washout cycle, the wash water rate, the reaction temperature and the specific catalyst surface area. In the washout cycle, the following three phases are distinguished:

- The water-spraying phase with the lowest SO_2 conversion rate
- The dripping phase and
- The main phase with the highest SO_2 conversion rate, which is at the same time the longest phase of the washout cycle.

To make up for the lower SO_2 conversion rate during the water-spraying phase, the catalyst bed is—with respect to the spraying operation—divided into different zones, which are successively subjected to water spraying.

While the catalyst of one zone is being sprayed with water, the other zones are either still in the dripping phase or already in the main phase of high SO_2 conversion. A constant mean SO_2 removal efficiency is, therefore, obtained over the entire wash cycle with a minimum SO_2 removal efficiency being ensured at all times.

The main difference in SULFACID® plant installations between the pigment industry and electric furnace smelting, is the off-gas strength. The SULFACID® plant's exothermical process reactions risk igniting the carbon catalyst if the gas strength exceeds 0.5% v/v SO_2. Gas strength from the pigment industry is less than 0.5% v/v SO_2 and can be treated directly in a SULFACID® plant. The electric furnace off-gas at Impala's smelter, however, contains 0.6%–0.9% SO_2 and has to be diluted with atmospheric air before treatment in the SULFACID® plant.

Plant description

The furnace off-gases contain flue dust, which is removed in electrostatic precipitators. The off-gas exiting the precipitators normally contains between 40 mg/Nm³ and 60 mg/Nm³ dust and passes through a quench-scrubber before entering the reactors. The quench-scrubber cools the electric furnace off-gas down from ± 200°C and acts as a final dust removal stage.

The contact section of the plant consists of eight 12.7 m long x 4.5 m diameter cylindrical reactors filled with activated carbon. The eight reactors are grouped in two phases with four reactors per phase. Each reactor has 7 pairs of spray nozzles, which spray potable water over the catalyst to wash off the formed sulphuric acid.

Two induced draft fans (one running and one stand-by) move the gas through the quench-scrubber and reactors and vent the cleaned gas through a 77-metre high fiber-glass stack to atmosphere.

The modular design of the plant eases future expansion of the plant in terms of either volume throughput or recovery. The design also enables reactors to be bypassed and maintained without shutting down the complete plant.

The weak sulphuric acid is disposed either to the adjacent Omnia Phosphates plant or to Mineral Processes' milling circuit. Omnia utilize the acid for fertilizer production, whereas the acid pumped to the milling circuit is neutralized and buffered in the milling water circuit.

Operation

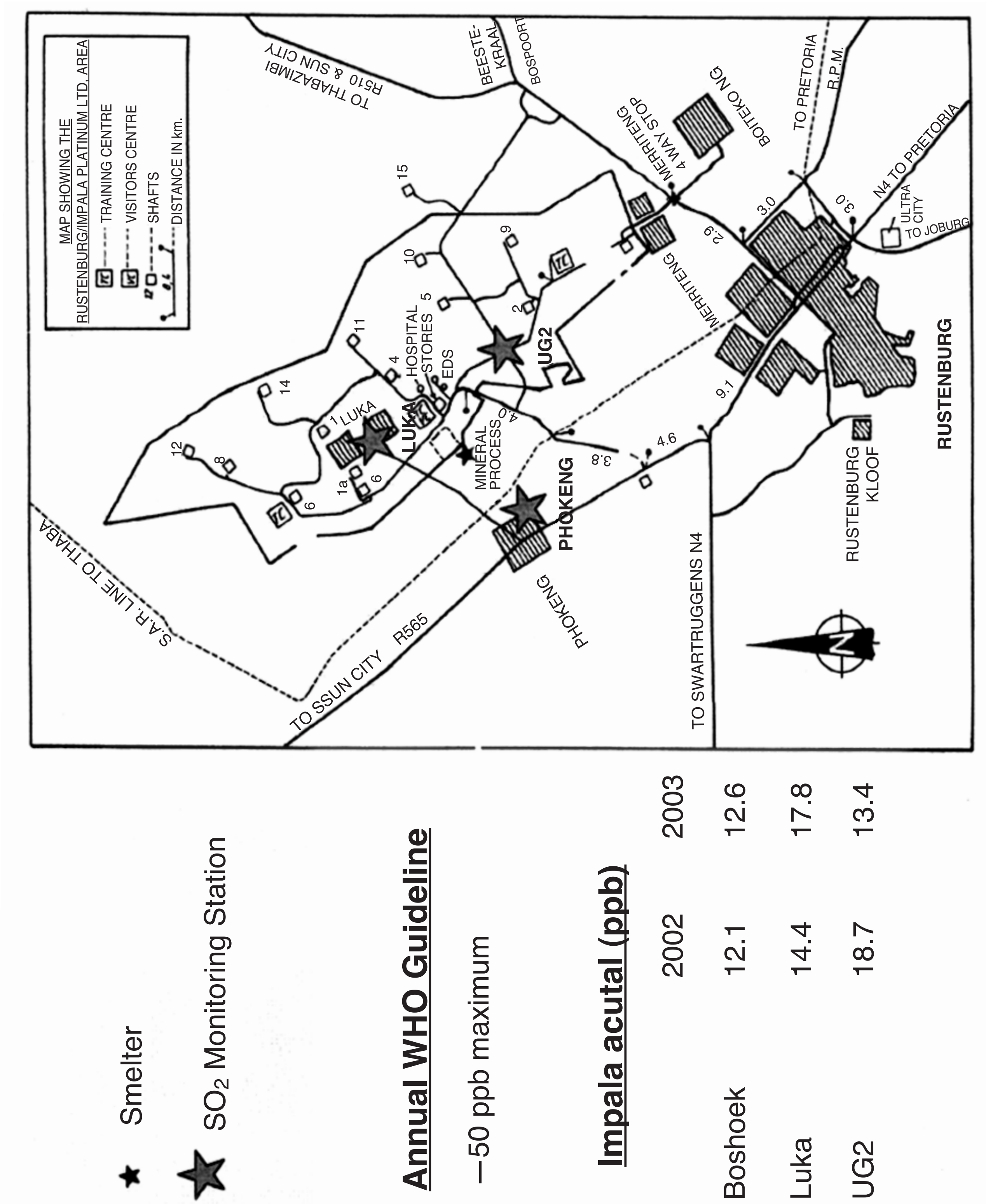
The plant was commissioned during the second half of October 2002 and forms part of the waste gas handling section of Impala's smelter. The plant requires very little operator interaction and is, therefore, operated from the sulphuric acid plant control room. No increase in operating personnel was required.

The plant was designed to achieve 83% SO_2 recovery, but is constantly achieving in excess of 85% recovery.

Conclusion

The installation of the Donau Carbon SULFACID® technology at Impala's smelter for the removal of SO_2 from off-gases with a low SO_2 content has proven successful and has enabled Impala's smelter to reduce SO_2 emission levels in line with World Health Organization ambient air quality guidelines (see Appendix 1).

Appendix 1



	2002	2003
Boshoek	12.1	12.6
Luka	14.4	17.8
UG2	18.7	13.4