For the past 20 years, Fives (namely Solios Environnement and previously Procedair) has specialised in the supply of turnkey plants for gases desulphurisation. This article looks at the technologies dedicated to SO_2 treatment in the context of the aluminium industry.

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Desulphurisation techniques

At the end of the past century, the company was covering various industrial markets such as diesel motors production, paper fabrication, sulphuric acid production or waste incineration[1]. However, since the early 2000s, Fives has been dedicating its know-how in terms of desulphurisation, to the treatment of electrolysis pot gases and anode-baking furnaces for primary aluminium smelters.

As part of the construction of large-scale smelters, Fives supplies two main kinds of pollution-control plants: Gas Treatment Centres (GTCs), which treat polluting emissions from huge gas flows (up to 9,500,000 Am^3/h) from electrolysis pots and Fume Treatment Centres (FTCs), which treat smaller flows coming from anode baking furnaces (up to 180,000 Am^3/h). These emissions mainly include hydrogen fluoride (HF), polycyclic aromatic hydrocarbons (PAHs), tars and dust. However, in most configurations, GTCs and FTCs do not include a specific desulphurisation unit and only allow a moderate sulphur dioxide (SO_2) reduction.

Due to increasingly stringent national and international standards on air pollution control, Fives also supplies various technologies dedicated to maintain SO_2 levels at stack far below the most restrictive regulations.

Seawater scrubbing

The most widespread technology consists of implementing a seawater wet-scrubber downstream gas treatment plant to absorb gaseous SO_2. Indeed, gaseous SO_2 is not easily soluble in water and only the use of basic solutions allows its capture.

As seawater is slightly basic (pH comprised between 8.1 and 8.2), it can be used wherever it is easily available, such as in coastline regions. Gaseous SO_2 will be dissolved with hydrogen carbonate ions to create sulphurous acid (H_2SO_3), as per the following reactions:

$$HCO_3^- + H_2SO_3\ (SO_2 + H_2O) \Leftarrow\Rightarrow HSO_3^- + H_2CO_3\ (CO_2 + H_2O)$$

$$HCO_3^- + HSO_3^- \Leftarrow\Rightarrow SO_3^{2-} + H_2CO_3\ (CO_2 + H_2O)$$

Wet-scrubbers efficiency is often measured by comparing seawater pH before and after SO_2 treatment. At Qatalum, Fives' wet-scrubbers have been designed for a pH decrease from 8.2 to 3.5.

The seawater scrubbing process includes three major steps: Gas cooling (when necessary), SO_2 removal and elimination of remaining droplets.

Depending on smelters' operational conditions, gases can reach temperatures up to 190°C at the electrolysis pots outlet, and even more at the anode-baking furnace outlet. They are therefore cooled first upstream at the GTC or FTC to reach optimum temperature to capture pollutants. However, at the GTC/FTC outlet, gases may still be excessively hot for the scrubber. Gases are therefore cooled a second time at the bottom of the wet-scrubber to reach temperatures around 80-100°C. This prevents sprayed seawater from evaporating into gases.

Then, gases make their way through column sections filled with packing. A packing column is composed of numerous pieces of complex shapes offering a high contact area. Seawater is sprayed above this column, in counter flow from the gas, and SO_2 is therefore removed in the wet-scrubber at this step, following the chemical reactions detailed earlier.

However, these reactions generate a remainder of polluting bisulphite (HSO_3^-) and sulphite (SO_3^{2-}) ions in seawater residual droplets. To avoid their dispersion in ambient air and their fallout in the vicinity of the stack, these droplets are eliminated at the outlet of the packing column with a demister. It consists of separating droplets from gases with variations of flow direction, which are generated by demister baffles. These baffles result in such separation, which is called "primary collection". Once droplets have been stopped, they are accumulated in dead areas sheltered from the gases flow, until they form a seawater film heavy enough to oppose re-entrainment by gases. A "secondary collection" is therefore performed to collect the charged seawater. Later on, sulphite and bisulphate ions are transformed into sulphate ions outside of the scrubber by an oxidation reaction, which is generally facilitated by aeration through air or, in some cases, with a dedicated oxygen injection tank. The resulting amount of sulphate ions added to seawater after oxidation does not influence the quality of residual seawater, as sulphate concentration in fresh seawater is naturally very high (>2.5 g/l). Before re-injection in its natural environment, residual seawater is also neutralised by mixing it with fresh seawater, in order to preserve ecosystems.

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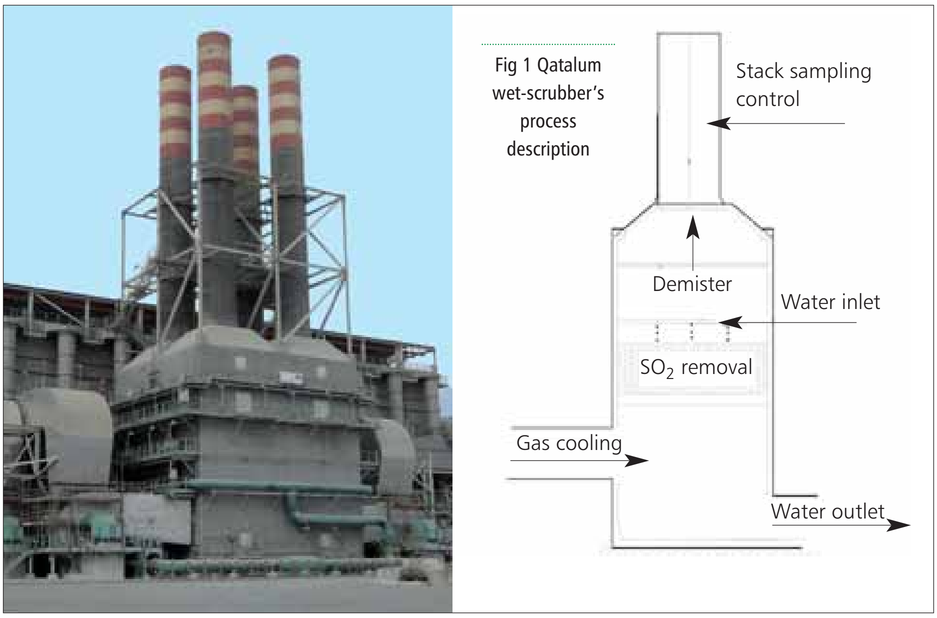

Fig 1 Qatalum wet-scrubber's process description

Fives has supplied 16 seawater scrubbers (**Fig 1**) (4 per GTC) for the Qatalum smelter (Qatar)[2]. Performance measurement tests have shown that Qatalum's performance criteria were met, as the SO_2 concentration at the outlet of each wet-scrubber was lower than 20 mg/Nm^3[3] (guaranteed value: 35 mg/Nm^3). For an average inlet concentration of 300 mg/Nm^3, it means that the smelter prevents the emission of 400 kg/h/GTC of sulphur dioxide into the atmosphere – i.e. more than 40 tons per day with this 4-GTC configuration.

However, relying on its long-standing experience, Fives is able to propose customised solutions in order to provide all kinds and sizes of SO_2 scrubbers – as seawater is not necessarily available for all projects. Other compounds such as limestone, lime, lime milk, ammonium bisulphate or activated carbon can be used as reagents.

Dry-scrubbing

Fives is a dry-scrubbing expert as it supplies multiple references of dry-scrubbing filters to capture HF via an injection of alumina. With a change of reagent (e.g. lime), these filters may be used to capture SO_2. Fives proposes four main varieties of filters, which allow a cost-efficient design for all projects, whatever their size. These filters include Sonair, Vibrair, TGT-RI and Ozeos, Fives' latest filtering technology which has been awarded with the Engineered Sustainability label[4]. All these technologies are renowned in the industry for their robustness, efficiency and easy maintenance.

Enhanced all dry-scrubbing

The Enhanced All Dry-Scrubbing (EAD) process was developed in the 1980s by Procedair, a former Fives entity, and has been widely implemented since then, especially on the North-American market. It has been used for different industrial applications, including boilers and kilns.

The EAD technology consists of adding a conditioning drum to the dry-scrubbing process, in order to moisturise the reagent before its injection into the filters' reactor. Conditions for SO_2 removal are therefore optimised to increase the surface area for chemical adsorption. It ensures a high efficiency (up to 97% of SO_2 removed) as well as many other advantages such as compactness and a lower pressure drop compared to other dry-scrubbing technologies.

One of Fives' main EAD references was the supply in 1999 and 2006 of two lime-based desulphurisation plants on the Virginia Tech campus (USA) for a total flow of 30,000 Nm^3/h[5]. The desulphurisation ratio for these plants reaches 92%, a performance which is crucial for the health of students in the vicinity of the two coal-fired boilers treated by Fives' plants.

More recently, in 2013, Fives supplied and installed two EAD Scrubbing System for the two bauxite calciner kilns (**main picture**). The customer's objective was to reduce SO_2 emissions at its ceramic proppant plant and the desulphurisation ratio reaches 90%[6].

Semi-wet scrubbing

Fives' semi-wet scrubbing process treats acid gases in a spray dryer, where the reagent (e.g. lime milk) is atomised into fine droplets in order to maximise the contact with SO_2. Then, gases are draught in a pulse jet fabric filter, which collects particles and dust. The desulphurisation is intimately linked to the injected reagent and the process temperature, which can be controlled by water consumption. These parameters are easy to manage, allowing a rapid response to variations of inlet pollutant levels. Such configuration is specifically recommended for unsteady acid gas concentrations processes. It has been selected by Fives in Spain for the desulphurisation of two diesel engines of 5 MW each, for a total flow of 66,000 Nm^3/h, with an overall efficiency of 91%.

Wet scrubbing

The seawater scrubbing process has been described earlier in this article, but the same technology can also be adapted with other reagents in case seawater is not available. Depending on the project parameters, the reagent may either be sprayed through pulverisation nozzles or injected on packing, where the contact surface between liquid and gas is optimised with the created pressure drop. The choice of technology relies mostly on the dust concentration in the gas flue, as the packing requires a special protection against fouling which may reduce the desulphurisation efficiency and increase energy consumption.

Fives has experienced both configurations in various plants. In France, Fives supplied a wet-scrubber where caustic soda is injected on packing to desulfurise the methionine production for the animal food industry (overall flow: 78,000 Nm^3/h). In the United States, pulverisation nozzles are used to spray sodium carbonate (Na_2CO_3) for the desulfurisation of an electrolysis potline (overall flow: 637,000 Nm^3/h).

Conclusion

Depending on the pollutants composition, efficiency target and operational parameters, SO_2 reduction can be achieved with many different options. All these processes have been successfully experienced by Fives in various industrial applications. Given the variety of SO_2 reduction technologies and the huge number of parameters to integrate when designing a desulphurisation plant (pollutants compounds, inlet concentration, temperatures, dust, geographic location, etc.), expertise, know-how and customised are among the main keys towards success. ■

References

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