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Topsoe wet gas sulphuric acid (WSA) technology—an attractive alternative for reduction of sulphur emissions from furnaces and converters

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Haldor Topsoe A/S has developed its WSA technology to meet the demand in the market for a simple and reliable process that converts sulphurous emissions from off-gasses into high-grade sulphuric acid. With more than 50 references in 25 countries, the WSA technology has proven its ability to generate acid at 98% concentration, efficiently and economically.

The wet gas sulphuric acid (WSA) technology treats the furnace off-gas directly from upstream gas cleaning plants. No further drying is required, since the humidity present in the off-gas is used to hydrate the SO_3 generated in the converter and produce sulphuric acid.

The heat generated during the oxidation, hydration and condensation processes is principally reused in the process to preheat the off-gas to the required temperature level, and also to generate high pressure superheated steam for process use. This advantage of steam production, coupled with lower water and power consumption requirements, is particularly important in the African production environment.

Having fewer process components than conventional acid plants, the WSA technology is a simple and compact operation, which makes it easier to retrofit into an existing smelter plant. Further, the WSA technology simultaneously offers the possibility to treat multiple gas streams arising within the production facility due to superior flexibility in terms of SO_2 concentration and turndown ratio.

Introduction

The Topsoe WSA technology was developed and commercialized during the early 1980s. The original intention was to make a cost-effective technology available to the industry for removal of sulphur compounds from modest gas flows having only a low content of sulphur. Such lean gases are produced in a variety of industries and were to a large extent vented to the atmosphere. Due to new and expected future environmental legislations and regulations, there was in that period an emerging demand for technologies capable of treating this type of gas without prohibitively high investment and operating costs.

History has proven, however, that the range of applications for the WSA technology is much wider than originally anticipated. Today, more than 55 units have been contracted for gas flows ranging from 2600 Nm^3/h to 1000000 Nm^3/h, and with daily sulphuric acid production ranging from 11 MTPD to 1200 MTPD. The WSA technology has found application in a variety of industries, viz:

- In the oil refining industry for treatment of amine regenerator and sour water stripper off-gases and for regeneration of spent alkylation acid
- In the non-ferrous metallurgical industry for treatment of SO_2 containing off-gases from a variety of process units
- In the petrochemical industry for treatment of acid gases from synthesis gas preparation units after heavy oil and coal gasifiers
- In the coke and coke chemical industry for treatment of acid gas streams from coke gas purification units and sulphurous gaseous and liquid streams from e.g. BTX rectification
- In the viscose fibre industry for treatment of hydrogen sulphide and carbon disulphide containing off-gases.

Fundamental principles of the WSA process

The fundamental principles of the WSA process are shown in block diagram, Figure 1, and described below.

The block diagram applies both to the case when the sulphurous feed is received as a combustible compound, as e.g. elemental molten sulphur or hydrogen sulphide gas, or as an SO_2 gas, e.g. from a metallurgical smelter. The name wet gas sulphuric acid was given to the Topsoe acid technology in order to emphasize that the concentrated acid is produced by condensation from a wet process gas. In consequence of this, the need for drying of the process feed gas prior to further processing (or for drying of combustion air when producing sulphuric acid from elemental sulphur) is eliminated.

The process layout of the front end and the heat management system depends on whether the sulphurous feed is received in a form that needs incineration in order to oxidize the sulphur compound to sulphur dioxide, or the sulphur content already is on sulphur dioxide form.

Sulphurous feed on sulphur dioxide form

Sulphur dioxide containing gases generated in the

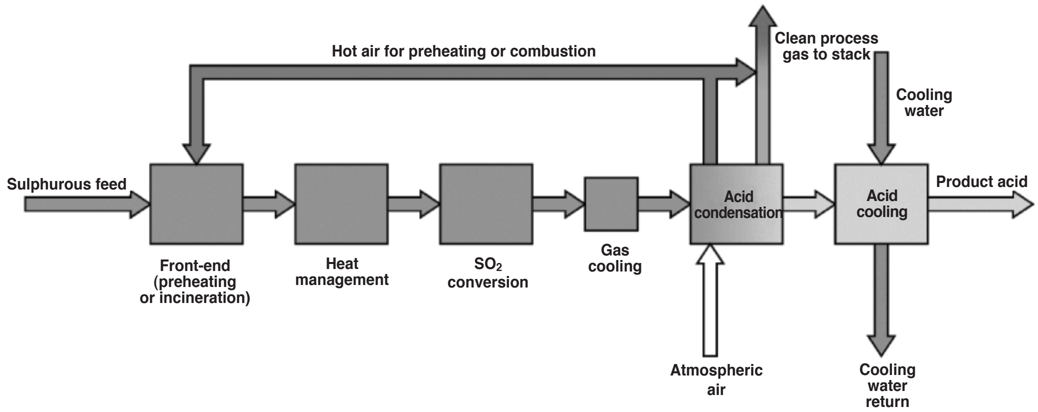

Figure 1. Principles of the WSA process

metallurgical industry vary greatly, both in gas flow and sulphur dioxide concentration, all depending on the processes upstream of the SO_2 fixation plant. If the SO_2 fixation unit is based on a catalytic SO_2 oxidation process, the gas must in any event be pretreated in order to remove particulate matters and catalyst poison, such as arsenic, down to levels acceptable to the SO_2 oxidation catalyst. Such gas pre-treatment systems typically consist of quench cooler, scrubbing unit, cooling tower and wet electrostatic precipitator. The feed gas to the WSA plant will in this case therefore usually be saturated, i.e. typically at the temperature of 30–35ºC and with a water content of approximately 6–7%.

The air, which has been used for cooling in the WSA condenser, will be available at a temperature of typically 210–220ºC and in sufficient quantities to preheating the process feed gas to approximately 150ºC. Further preheat of the process gas to the operating temperature of the SO_2 conversion catalyst of approximately 410ºC takes place in the heat management system, using the heat generated in the SO_2 conversion reactor.

Downstream of the heat management system, the process consists of the following process units:

- SO_2 conversion
- Acid condensation
- Acid cooling.

SO_2 conversion

The catalytic SO_2 conversion process in a WSA plant is similar to the SO_2 conversion in a conventional acid plant based on absorption, except that the catalytic reaction takes place in a wet gas. Wet SO_2 oxidation catalysis has been practised for decades, and most of the Topsoe SO_2 oxidation catalysts of the VK-series have in fact higher activity when operating in a wet gas.

The design of the SO_2 converter depends on the SO_2 concentration in the process gas and on the required degree of SO_2, conversion, i.e. degree of SO_2 removal, and features one, two or three catalyst beds. In case of a multi bed concept, interbed cooling is required.

Process gas cooling and acid condensation

The process gas will leave the last catalyst bed with a temperature typically between 400–450ºC and will typically contain SO_3 plus water vapour. Before the process gas enters the WSA condenser, the temperature must be reduced to a level acceptable to the construction materials of the condenser, which is maximum 290ºC. As will be described below, the process gas cooling can be performed in several ways, and contributes substantially to the excellent heat efficiency of the WSA technology. It is, however, equally essential that the process gas temperature is kept well above the sulphuric acid dew point, thus ensuring that no condensation of acid takes place outside the WSA condenser.

The patented WSA condenser, as schematically shown on Figure 2, is a vertical shell and tube falling film condenser/concentrator with tubes made of acid and shock resistant boron-silicate glass. While the process gas flows upwards inside the tubes, which are cooled on the shell side by ambient air, the sulphuric acid condenses on the tube walls. When flowing downwards and meeting the hot rising process gas, the acid will concentrate to typically 98% wt.

The WSA condenser generates hot air at a temperature of approximately 220ºC, which may be used either for process gas preheating or as combustion air, as described above, thus recovering the heat of sulphuric acid condensation.

The clean process gas leaves the condenser at approximately 100ºC and can usually be sent directly to stack without further treatment, it being a distinct feature of the WSA technology that the clean gas contains only a very low amount of acid mist.

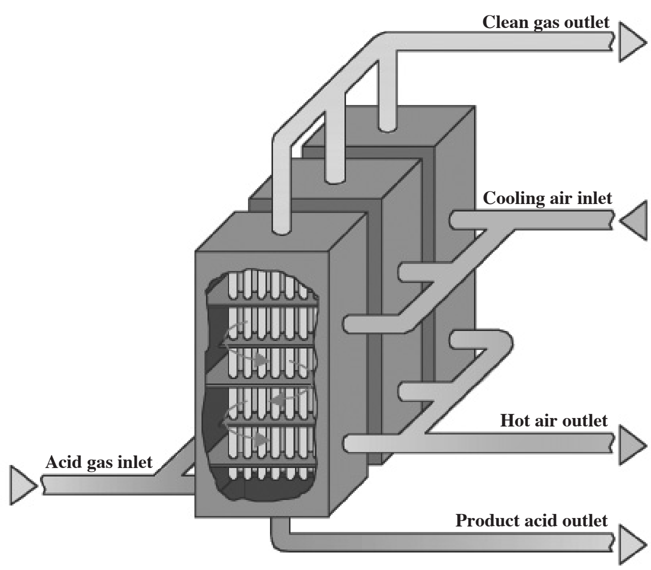

Figure 2. Principle design of the WSA condenser

Sulphuric acid cooling

The sulphuric acid leaves the condenser at the condensation temperature, typically in the order of 250–260ºC. By recirculation of cold acid, the hot acid is cooled immediately to a temperature acceptable to the fluorpolymer lined acid piping and to the plate type acid cooler with plates in Hastelloy. Figure 3 shows a cooling and recirculation system in a WSA plant producing 895 MTPD acid.

Development of the WSA technology

Process layout of an early WSA plant

One of the very first WSA plants constructed for the metallurgical industry was contracted in 1989 with the Belgium company, N.V. Sadaci S.A., and was startedup in 1990. The plant, which is still in operation, was designed to treat 35000 Nm³/h off-gas from a molybdenum sulphide roaster with an average content of SO_2 in the order of 2% vol.

The process layout of that early WSA plant is schematically shown in Figure 4.

It will be seen that hot air generated in the WSA condenser is used for the first preheat of the wet process gas as described above. This principle is also used in today's layout. The process gas temperature is further increased by approximately 90ºC by recycling a considerable amount of gas from downstream the second feed gas preheater. The second feed gas preheater is a gas/gas feed/effluent heat exchanger across the SO_2 conversion system.

With an SO_2 content in the process gas of only 2% vol., the system does not generate sufficient heat to operate autothermally, and a further increase in temperature, by means of support fuel, is therefore required before the process gas enters the SO_2 conversion system.

The SO_2 conversion system consists of two reactors in series. In between the two reactors, the temperature is decreased by adding approximately 8500 Nm³/h of quench gas taken from upstream of the second feed gas preheater. After being cooled in the feed/effluent heat exchanger (second feed gas preheater), the gas from the second SO_2

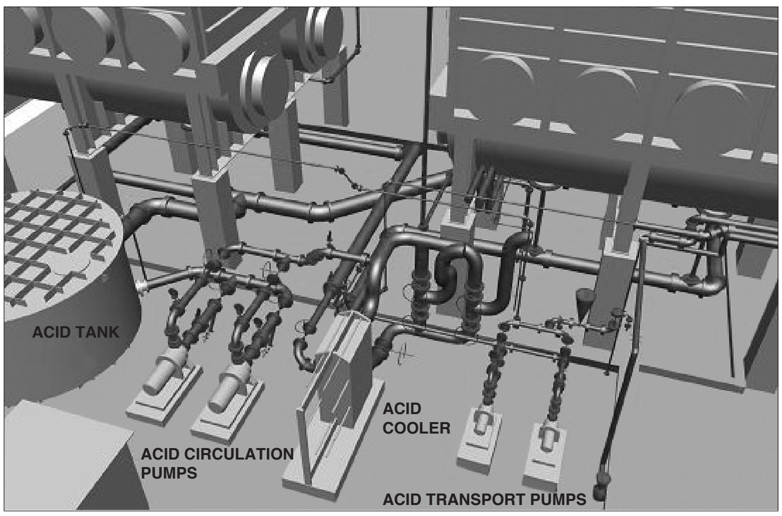

Figure 3. Acid cooling and recirculation system for a WSA plant producing 895 MTPD, 98% wt. acid at OAO Kazzinc, Kazakhstan

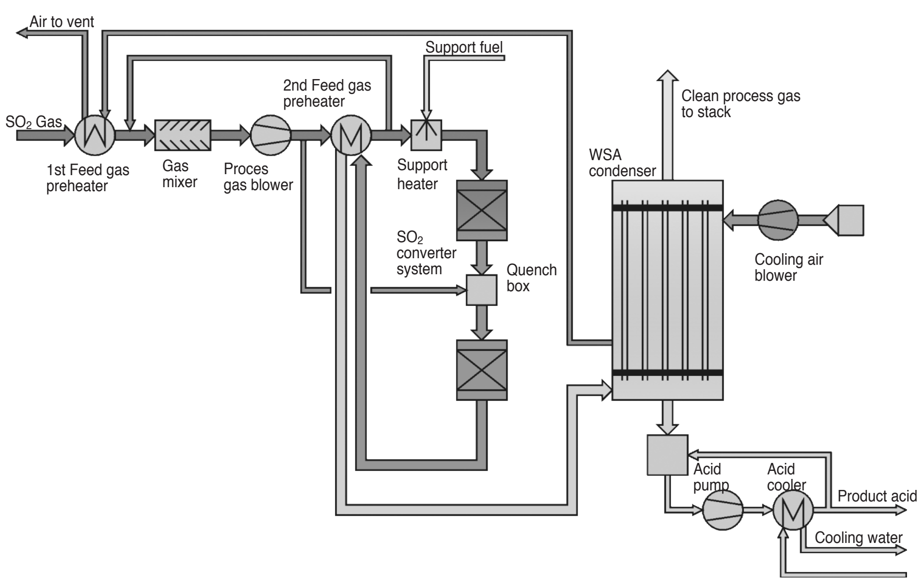

Figure 4. Process layout of an early WSA plant treating 35000 Nm³/h, 2% vol. SO_2 gas at N.V. Sadaci S.A., Belgium

reactor is sent to the WSA condenser, and the acid is condensed and cooled by recirculation of cold acid as described above.

Although the Sadaci WSA plant has been in operation successfully for 15 years, the principles of feed effluent heat exchange and quench gas cooling evidently have a number of disadvantages for design of plants with considerably larger gas flow and a higher SO_2 content in the process gas. To cope with this demand, the process layout has been further developed as described below.

State-of-the-art process layout

Figure 5 shows schematically the process layout of a WSA plant of the most recent design for treatment of SO_2 gases in the metallurgical industry.

Whereas the principle of using hot air generated in the WSA condenser for the first preheat of the process feed gas up to a temperature of approximately 150ºC is maintained, the feed/effluent heat exchange and the quench cooling principles have been abandoned.

Instead all heat management is performed by means of a system of circulating molten salt. The salt consists of a water-free mixture of potassium and sodium nitrate and nitrite, which has a melting point of 150–160ºC. In brief, the salt melt circulates between the heat exchangers in the plant. Thus, the melt cools the process gas leaving the first catalyst bed to the optimum temperature at the inlet to the second catalyst bed, and further cools the process gas leaving the second catalyst bed to the temperature of 280–290ºC, before the gas enters the WSA condenser. By circulation of the melt, the recovered heat is displaced to the process feed gas by means of the second feed gas preheater. Surplus heat will be removed in the salt cooler/boiler, and excess energy therefore exported as steam.

With this system, it is extremely easy to control the process gas temperatures, and optimum operating conditions in the SO_2 converter can therefore be sustained at all times.

The heat exchangers in the SO_2 converter, which is shown as a two bed converter, but also could contain three catalyst beds if requirements of SO_2 conversion so dictates, are fully integrated into the converter shell, thereby reducing the amount of ductwork to a minimum.

If sufficient steam is available in the system, e.g. in case sulphuric acid is produced by burning molten elemental sulphur, the molten salt recirculation system can with certain advantages be replaced by a steam cooling system, allowing production and export of high pressure steam with a pressure of approximately 60 bar and superheated to a temperature in the order of 450ºC, suitable for generation of electric power.

Conservation of resources

Conservation of resources is inherent in the process design of a WSA plant, both with respect to electric power, thermal energy and cooling water.

Electric power

With the need for drying of the process gas prior to further processing being eliminated and with heat exchangers incorporated in the SO_2 converter shell, it is obvious that the total number of itemized equipment is very low, and the amount of ductwork is therefore also reduced to a minimum. This, together with the low pressure drop over the WSA condenser, as compared to the pressure drop over conventional absorbers, results in a total pressure drop on the process gas side for a plant, as shown in Figure 5, as low as approximately 100 mbar, and on the cooling air side, as low as 40 mbar.

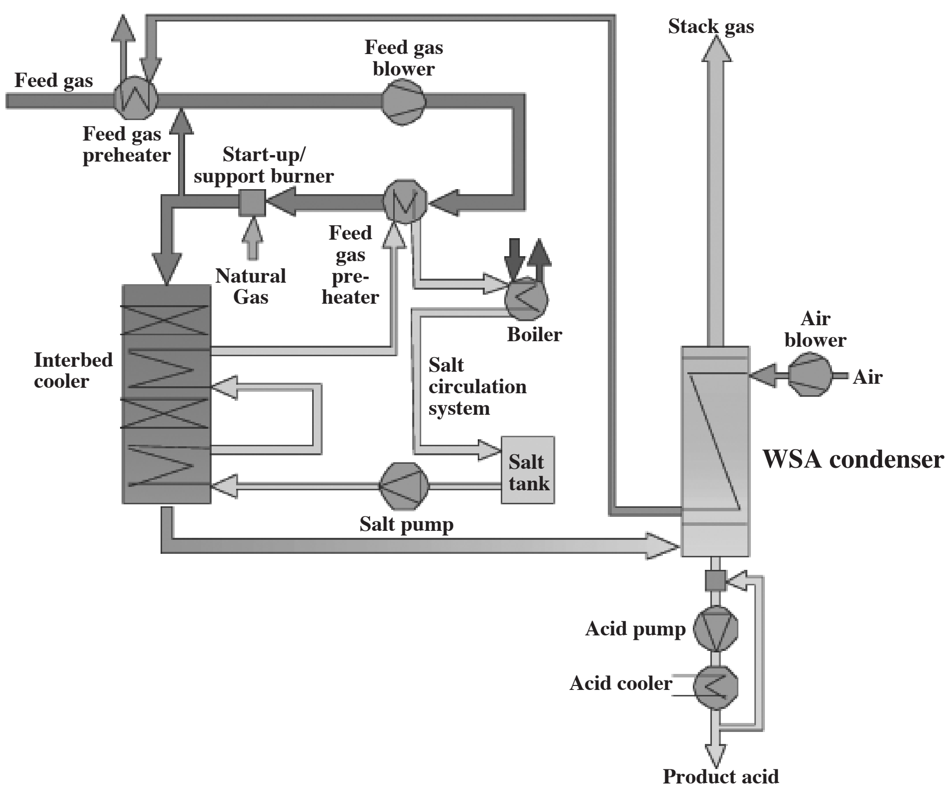

Figure 5. State-of-the-art process layout of WSA plants in the metallurgical industry

This translates into a power consumption of only 45–50 kWh/MT produced acid, when processing a gas received at battery limit at 0 barg with 6% SO_2.

Thermal energy

The chemical reactions involved in production of sulphuric acid from sulphur dioxide are highly exothermal.

The reactions in the WSA process are the following:

SO_2 oxidation:

$SO_2 + {}^1/_2O_2 \rightarrow SO_3$ + 99 kJ/mole (242000 kcal/MT acid)

SO_3 hydration:

$SO_3 + H_2O \rightarrow H_2SO_4$ (gas) + 101 kJ/mole (247000 kcal/MT acid)

H_2SO_4 condensation:

H_2SO_4 gas $\rightarrow$ H_2SO_4 liquid + 90 kJ/mole (219000 kcal/MT acid)

Whereas it is state of the art in all known sulphuric acid technologies to recover the heat of SO_2 oxidation, only very few technologies are capable of recovering the heat of SO_3 hydration and the heat of sulphuric acid condensation. For instance, in sulphuric acid technologies based on absorption, the heat from these two sources, which is essentially equal to the heat of absorption of SO_3 in the absorbers, is lost to the cooling water.

In the WSA technology, both the heat of SO_3 hydration, and the heat of sulphuric acid condensation are recovered to a very high degree.

As described above, the process gas leaving the last catalyst bed in the SO_2 converter is cooled to a temperature of approximately 290ºC in the final gas cooler, which is integrated in the converter. At this temperature, a large part of the SO_3 will be hydrated to H_2SO_4 on gas form. The corresponding amount of the heat of hydration will therefore be recovered in the molten salt heat displacement system and available for process feed gas preheating in the second process feed gas preheater and/or for production of steam.

The remaining hydration of SO_3 together with condensation of the sulphuric acid will take place in the WSA condenser in which the process gas is cooled to 100ºC. The corresponding amounts of heat will be removed by means of ambient air, resulting in generation of a hot air stream with a temperature of approximately 210–220ºC. This hot air is, as described above, available for process gas preheating in the first process gas preheater, and the latent heat is therefore utilized down to a temperature of 125–135ºC.

In consequence, the WSA technology is extremely efficient for thermal energy conservation. This is illustrated by the fact that a WSA plant is capable of operating autothermally, i.e. without use of support fuel for process gas preheating, when processing feed gas with an SO_2 content as low as 3%, whereas other sulphuric acid technologies, not capable of recovering the heat of hydration and condensation, will need an SO_2 concentration of 6–7% in order to operate autothermally.

Cooling water

Cooling water is used only for cooling of the produced sulphuric acid from the temperature of condensation, typically 250–260ºC, down to the storage temperature of typically 30-35ºC. Therefore the cooling requirement is only 80000–90000 kcal/MT produced acid, corresponding to a cooling water flow of 8–9 m^3/MT produced acid at a temperature increase of the cooling water of 10ºC.

Environmental considerations

When one is designing and operating a sulphuric acid plant, environmental considerations essentially concentrate on emissions to the atmosphere of SO_2 and acid mist.

SO_2 emission

Most national environmental legislations related to SO_2 emissions, including the American Code of Federal Regulations, Protection of Environment make distinction between emissions from dedicated sulphuric acid production units, e.g. based on elemental sulphur or roasting of pyrite and other sulphuric acid production units, constructed for the purpose of controlling SO_2 emissions from fatal SO_2 sources. Most SO_2 fixation plants in the metallurgical industry will fall in the second category with less strict requirements for SO_2 removal efficiency than plants falling in the first category.

All newer WSA plants in the metallurgical industry feature two catalyst beds in the SO_2 converter, as shown in Figure 5, and a charge of conventional SO_2 oxidation catalyst of the Topsoe VK-series with an operation temperature of approximately 410ºC.

With this design, it is, depending on the SO_2 concentration in the process gas, possible to achieve an SO_2 conversion of between 98-99%, which conversion has proved sufficient in most cases.

However, when the Chilean company Molibdenos y Metales S.A., Santiago at the beginning of 2005 decided to construct a new WSA plant at their molybdenum sulphide roasting facility in Santiago de Chile, the environmental authorities required that the SO_2 conversion was increased as the roasting facility is situated in a densely populated area close to the city of Santiago de Chile. Therefore, the new plant, which will be the fourth in operation at the Molymet group and which is scheduled to start up in 2007, will be equipped with an SO_2 converter featuring three catalyst beds with conventional catalyst in the two upper beds, and a low temperature, alkali promoted catalyst in the last bed. With this configuration, an SO_2 conversion of 99.6% is achieved.

Acid mist

The design and operating conditions of the WSA condenser ensure a very low content of acid mist in the clean process gas leaving the WSA condenser, and usually a mist content of less than 10 vol. ppm is achieved. In spite of this, a few clients have decided to install a mist filter at the clean process gas outlet duct, often dictated by local environmental authorities' requirements.

Two main options based on different operating principles (the so-called candle filters and wet electrostatic precipitators respectively) are available for mist filtration.

Case study

OAO Kazzinc, Kazakhstan

OAO Kazzinc is a fully integrated zinc producer with considerable copper, lead and precious metal credits. It employs some 22000 people in mining, ore dressing and metallurgy. OAO Kazzinc has chosen Topsoe's WSA technology to treat the off-gasses coming from the lead sinter plant and zinc roaster at their metallurgical complex in Ust-Kamengorsk. The complex consists of a 180000 TPY zinc refinery, a 140000 TPY lead smelter and a precious metals refinery.

In May 2002, OAO Kazzinc signed a contract with Topsoe for the supply of its WSA technology. OAO Kazzinc undertook the erection works by themselves and during summer 2004 the plant was put on stream, hence the total lead-time from order date to on-stream production was less than 24 months.

Figure 6 shows a computerized model of the WSA plant. The plant treats 125000 Nm^3/h of off-gas with an SO_2 content of 6.5% vol. and produces approximately 900 MTPD, 98% sulphuric acid. The footprint of that plant is only 61.5×25.0 metres = 1537 m^2.

Now, in what way has the WSA plant contributed to the business of OAO Kazzinc? Clearly, it has brought the plant at Ust-Kamengorsk in compliance with its stated objective, which is to reduce the emissions of SO_2 from its metallurgical operations to an insignificant level. This in itself constitutes a priceless value in terms of securing its ecological responsibility and provision of a clean environment to the densely populated surrounding areas. Experiences have shown that public focus on a severely irresponsible environmental policy of a particular smelter plant could, in fact, have a significant impact on its share prices, causing losses to the owner, which may be even bigger than the corresponding investment required for an off-gas treatment plant.

In addition to such economical considerations, the WSA plant itself generates valuable products from the reduction of SO_2 and this even with very low overall operating expenses.

The sulphuric acid produced at the Ust-Kamengorsk complex is sold to customers within the fertilizer, refinery or petrochemical industry. To secure off-take of the acid also during low demand periods in the sulphuric acid market, OAO Kazzinc has also constructed an acid neutralization plant producing saleable gypsum for use by the cement and construction material industries.

From the exothermal processes of the WSA technology, heat is generated and converted into valuable steam providing OAO Kazzinc with more than 7 tons/h steam at 15 barg. If OAO Kazzinc, in theory, had installed a small multi-stage condensing steam turbine, they would have been able to generate approx. 1.1 MWe. All steam, however, is sent into their common steam system and used for heating and tracing purposes, hence saving them from additional investment and operating expenses associated with such steam production.

The WSA technology differs from other conventional plants by its limited consumption requirements, resulting in reduced operating expenses, and for OAO Kazzinc, this means that less than 400 m^3/h of cooling water is needed to remove excess heat from the sulphuric acid. Finally, the total power requirement for their ID/FD fans is low due to the limited pressure drop, caused by the few and simple components of the WSA plant. Reference is made to Table I for a summary of consumption details and OPEX for a plant operated in South Africa, having a size and capacity similar to the OAO Kazzinc project.

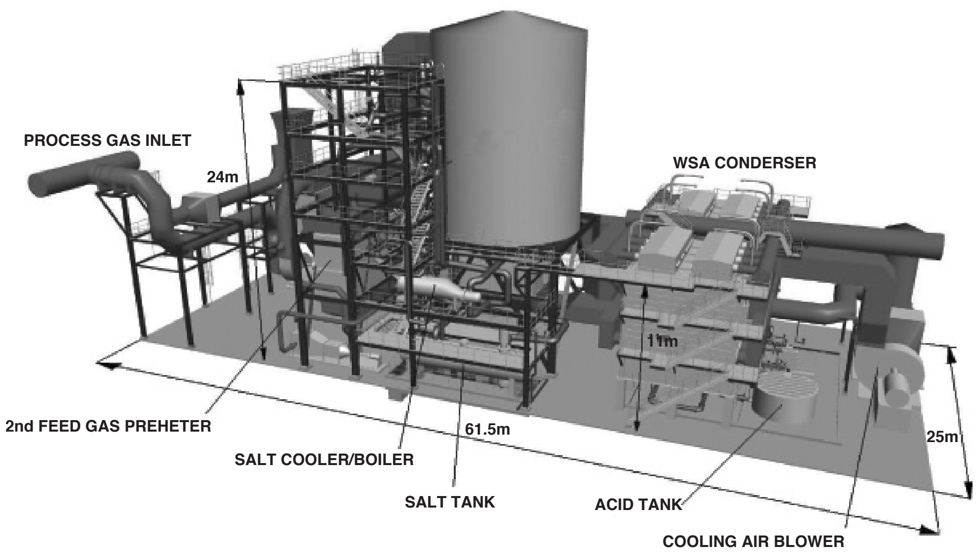

Figure 6. Model of the WSA plant at OAO Kazzinc, Kazakhstan

Table I
Summary of OPEX as applied for a project in RSA with a capacity similar to OAO Kazzinc

Consumption:	Specification	Annual operating cost/earning	Assumptions
Cooling water	398 m^3/h (25 -> 35ºC)	- R1.6m	R0.5 /m^3
Power	2130 kW	- R6.0m	R0.35/kWh
Fuel	N.A		N.A.
Production:			
Sulphuric acid	854 MTPD (98%)	+ R114.0m	R400/ton
Steam	7036 kg/h (15 barg)	+ R5.1m	R90/ton
Total operating income		+ R111.5 m	

Table II
Tapsoe clients using WSA technology

Client	Type of up-stream plant	Initial Content of SO_2	Process gas Nm^3/h	H_2SO_4 prod.MTPD	Start-up year
N.V. Sadaci S.A., Belgium	MoS_2 Roaster	0.6–2.8%	35.000	106	1990
Molibdenos y Metales S.A., Chile	MoS_2 Roaster	2.0–2.4%	40.000	104	1993
Metaleurop S.A., France	PbS Roaster	3.4%	110.000	380	1993
Molymex S.A. de C.V., Mexico	MoS_2 Roaster	2.0–4.5%	20.000	65	2001
Zhuzhou Smelter, China	PbS Roaster	2.2–4.6%	110.000	525	2001
ZAO Karabashmed, Russia	CuS Smelter	6.5%	170.000	1140	2003
OAO Kazzinc, Kazakhstan	PbS Sinter ZnS Roaster	6.5%	125.000	895	2004
Molibdenos y Metales S.A., Chile	MoS_2 Roaster	1.4–3.8%	60.000	170	2007

Table I is based on 8000 operating hours per year. Spare parts and staff expenses are not included.

In total, OAO Kazzinc has been furnished with a state-of-the-art sulphuric acid plant, which has not only released them from certain environmental burdens, but also has managed to do so within commercially attractive conditions.

Table II lists metallurgical plants that have profited from Topsoe's WSA technology.

Conclusion

The WSA technology has been constantly developed and improved during the past two decades, and the list of references now counts more than 55 plants in a variety of industries treating sulphurous feed stocks, ranging from concentrated hydrogen sulphide gas, over spent alkylation acid, to lean SO_2 gas in the metallurgical industry.

The technology features a very high degree of energy efficiency, meaning that gases containing as little as 3% vol. SO_2 allow autothermal operation. Moreover, the consumption of utilities, such as electric power and in particular cooling water, is extremely low.

The only product streams from a WSA plant are commercial quality, concentrated sulphuric acid, clean process gas and steam, and no solid or liquid effluents needing subsequent treatments are produced.

The WSA technology is also an attractive alternative for small-to medium-sized plants, producing sulphuric acid from elemental molten sulphur.