Meeting industry demands

Jens K. Laursen and **Frands E. Jensen** of Haldor Topsøe A/S give an overview of the process principles of the WSA process for sulphur recovery, providing industry examples from a variety of applications.

The WSA process is a process for the conversion of sulphurous streams into sulphuric acid developed by Haldor Topsøe A/S, Denmark. Since its introduction in the 1980s, the WSA process has been recognised as an efficient process for recovering sulphur from various sources in the form of commercial quality sulphuric acid. The WSA process has found widespread application in the refineries, oil and coal based industries, the metallurgical industry, the steel industry (coking), the power industry, and the cellulose industry. More than 60 plants have now been licensed worldwide for treatment of process gases in a wide range of process industries.

Application

The WSA process is applied in all industries where removal of sulphur is an issue. Typical applications include:

Refinery and petrochemicals

- H_2S-containing gases from amine units
- Sour water stripper gases
- Regeneration of spent sulphuric acid from alkylation
- Treatment of stack gases from boilers fired by heavy residues and petroleum coke

Metallurgical industry

- Off-gases from metal sulphide roasters (Mo, Zn, Pb, Cu, and other)

Coal based industry

- H_2S, NH_3 and HCN containing gases in coking plants
- H_2S, NH_3 and HCN containing gases from coal gasification
- H_2S containing gases in crude benzene processing units

Cellulose industry

- H_2S and CS_2 containing gases in viscose fibre plants

Power industry

- Flue gases from combustion of high-sulphur fuels. Both sulphur oxides and NOx are removed.

Salient features

Compared to other sulphur treatment processes, the WSA process offers a wider range of features:

- More than 99% recovery of the total sulphur content, always in compliance with environmental legislation
- Product is clean, concentrated sulphuric acid of commercial quality, also in turndown situations
- Heat of reaction is recovered as superheated or saturated steam
- Gases containing hydrocarbons – also very high CO_2 content – are accepted
- Optional DeNOx for gases with high content of NH_3 and HCN
- No consumption of chemicals (except for optional DeNOx)
- Very low consumption of cooling water
- No consumption of process water
- No liquid or solid waste effluents
- Wide turndown range
- Simple layout, simple operation, overall attractive economy

Fig 1: **WSA process for H_2S gas**

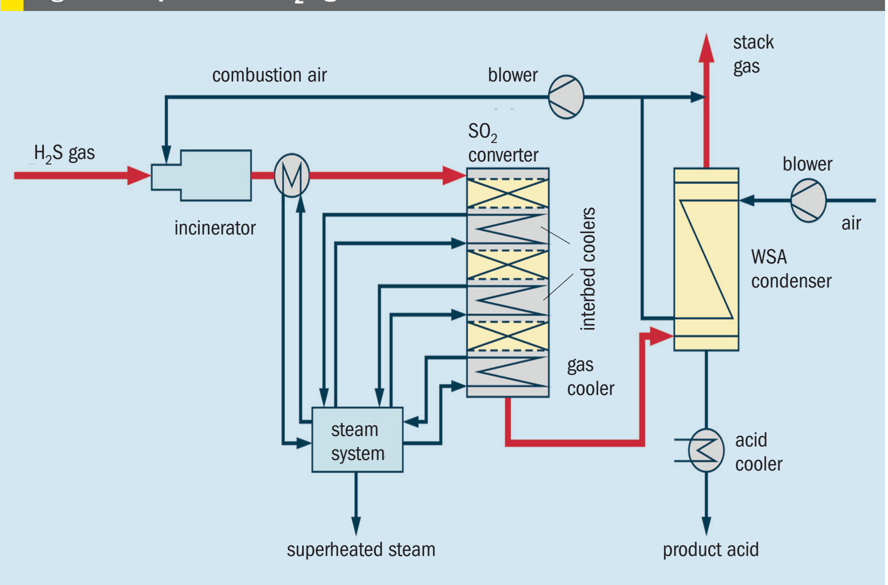


Fig 2: **WSA Condenser**

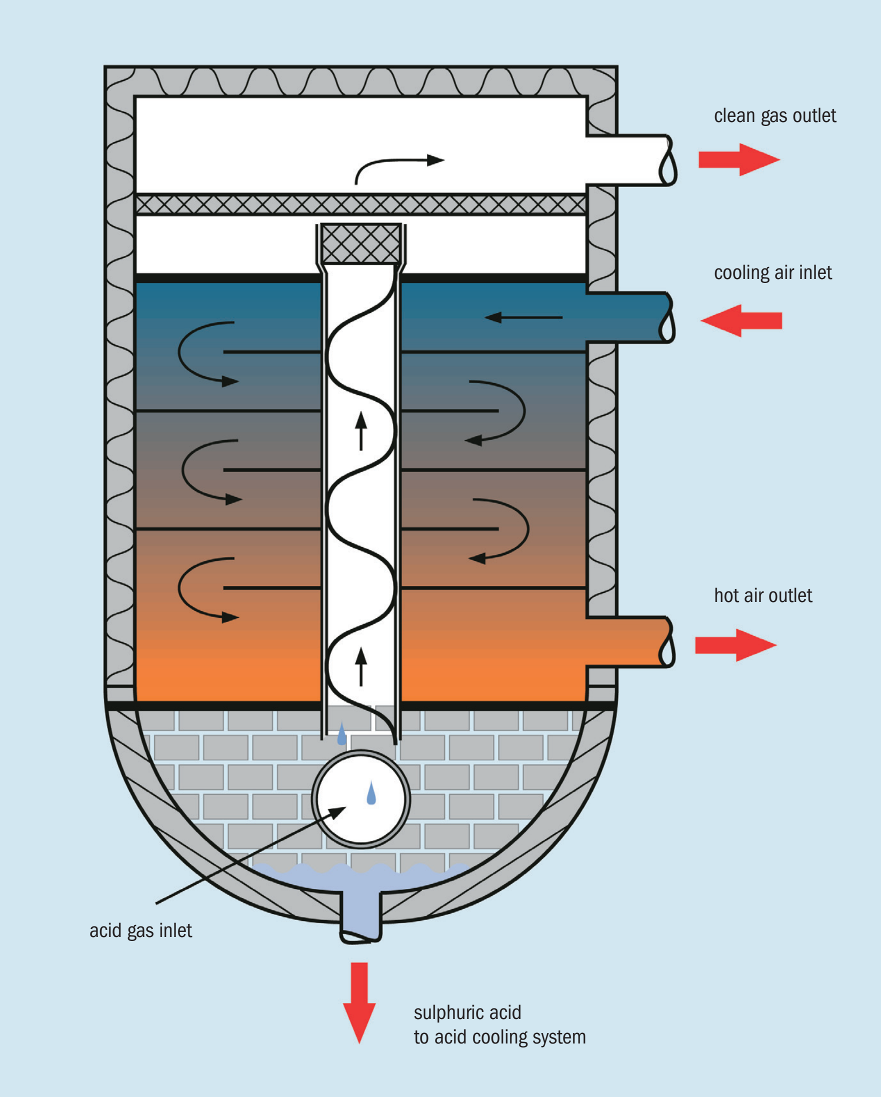
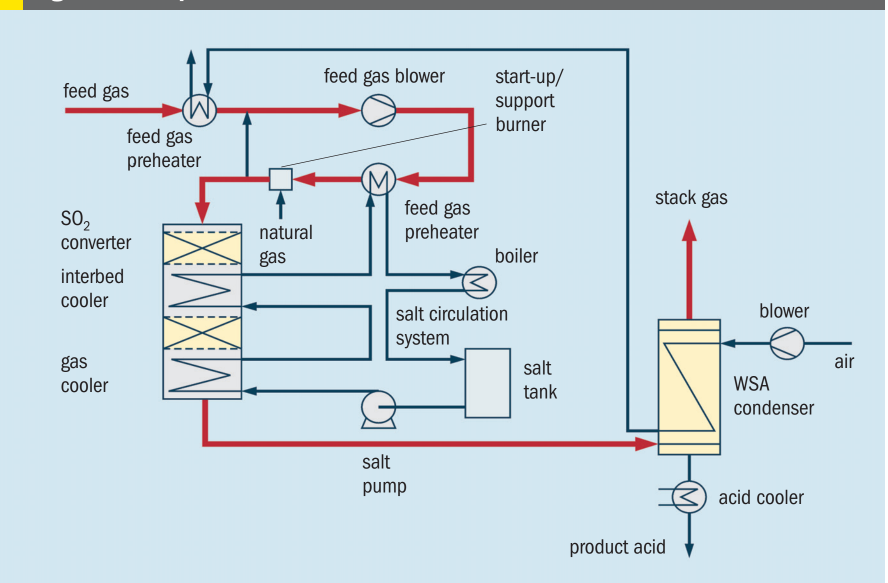


Fig 3: **SNOX™ process**



Process principles

WSA is short for Wet gas Sulphuric Acid, meaning that contrary to conventional sulphuric acid processes, the WSA process treats the process gas with all of its water content. This means that cooling and condensation prior to the SO_2 conversion stage are not required. Consequently, there will be no liquid waste effluent, no loss of acid, no use of cooling water for this part, and no loss of heat. This feature also reduces pressure drop and thereby electric power consumption.

The process principles can be illustrated by three different cases: One case treating hydrogen sulphide (Fig. 1), one case treating sulphur dioxide (Fig. 3) and one case treating flue gas from combustion of high-sulphur residual oil (Fig. 4). Basically, the same process steps apply for all feed gases:

- Combustion (except in the case of SO_2 gases)
- Heating or cooling of the gas to the reactor temperature
- Conversion of SO_2 to SO_3
- Hydration of the SO_3 to gaseous H_2SO_4
- Condensation of H_2SO_4 in the WSA condenser

Case 1 – H_2S gases (Fig. 1)

The WSA process is an effective and in some cases superior alternative to the Claus process. The process can be applied for gases with high H_2S content as in amine regenerator off-gas, and for gases with a lower H_2S content as in off-gas from Rectisol units in coal gasification. The latter type of gas typically has a high content of CO_2 and often a substantial content of hydrocarbons; this is also accepted by the WSA process.

In the case of H_2S, e.g. from an amine regeneration unit, the gas is incinerated to SO_2 in a burner followed by a waste heat boiler. Unless the feed gas contains other combustibles, support fuel is necessary if the feed gas contains less than, say, 25% H_2S. The incinerated gas typically contains 5-6% SO_2 and all the water from the combustion of the H_2S and other combustibles. The gas leaving the waste heat boiler has a temperature of approximately 400°C.

The gas then enters the SO_2 reactor which contains two or three catalytic beds, depending on the actual process conditions and the desired degree of conversion. As the reaction in the reactor is exothermal, the gas is cooled between the beds in order to optimise the SO_2/SO_3 equilibrium. After the last conversion stage, the gas is cooled and most of the SO_3 reacts with the water vapour and forms gas phase sulphuric acid (Table 1). The process gas then goes to the WSA condenser where final hydration and condensation of acid takes place.

The WSA condenser (Fig. 2) is a vertical shell-and-tube type falling film condenser and concentrator with tubes made of boron silicate glass resistant to thermal shock and acid. The process gas flows inside the tubes, which are cooled on the outside by ambient air in cross-current flow pattern. Sulphuric acid condenses in the tubes and flows downwards while being concentrated in counter-current contact with the hot process gas. The sulphuric acid is collected in the acid resistant brick-lined bottom part and is cooled to 30-40°C in a water-cooled plate type heat exchanger and then pumped to storage.

The cleaned process gas leaves the WSA condenser at approximately 100°C and can be sent directly to the stack. It is a notable feature of the WSA condenser that the gas contains only a very small amount of acid mist, typically less than statutory requirements.

The cooling air leaves the WSA condenser at approximately 200-250°C. Part of the hot air is used as combustion air in the H_2S burner, and the remaining part can be mixed into the stack for increased buoyancy or it can be used for boiler feed water preheating.

When the feed gas contains appreciable amounts of ammonia, hydrogen cyanide or other nitrogen compounds, or if the incineration takes place at elevated temperatures, a certain amount of nitrogen oxides (NOx) will be formed. In order to comply with statutory requirements and to avoid discolouration of the stack emission, it may be necessary to remove the NOx. This can conveniently take place in an SCR process stage (Selective Catalytic Reduction) upstream the SO_2 reactor. Ammonia in stoichiometric amounts relative to the NOx content is injected into the process gas which passes over an SCR catalyst whereby the NOx is reduced to nitrogen and water vapour (Table 1).

The heat of reaction is recovered in the form of steam. Saturated steam at typically 50-60 barg is generated in the waste heat boiler and in the gas cooler downstream the SO_2 reactor. Saturated steam drawn from the steam drum is then used for cooling between the catalytic reactor stages and is exported as superheated steam, typically at more than 400°C, or it can be conditioned to the desired properties. The required steam pressure is determined by the content of SO_3 and water in the process gas in such a way that all surface temperatures are well above the acid dew point.

The construction materials of the WSA plant is generally carbon steel, except where design temperature necessitates heat resistant steel (stainless or ½ Mo alloy). The combustion chamber of the H_2S burner and the waste heat boiler inlet are protected by refractory lining. The parts of the WSA condenser in contact with condensing acid will be protected by a fluoro-polymer lining, and the bottom of the condenser is lined with acid resistant bricks. The acid cooler is typically made of Hastelloy C. The acid pump is lined and has magnetic coupling.

For example, in a large refinery expansion project, TNK-BP in Ryazan, Russia decided to use WSA for the sulphur recovery of the entire site, including SWS gas treatment. This decision was made based on eight years of successful operation of two other WSA plants on the site. Alkylation was part of the expansion and naturally it was decided to incorporate acid regeneration in the overall system; in this case the H_2S capacity was much more than needed as fuel for the spent acid regeneration. Two separate WSA plants were built, one for H_2S plus SWS gas, including SCR reactor,

Table 1: **Reactions in WSA and SNOX™ plants**

Combustion	$H_2S + {}^3/_2\, O_2 \rightarrow H_2O + SO_2$	+ 518 kJ/mole
Oxidation	$SO_2 + {}^1/_2\, O_2 \rightarrow SO_3$	+ 99 kJ/mole
Hydration	$SO_3 + H_2O \rightarrow H_2SO_4$ (gas)	+ 101 kJ/mole
Condensation	H_2SO_4 (gas) + 0.17 H_2O (gas) $\rightarrow H_2SO_4$ (liq)	+ 69 kJ/mole
DeNOx	$NO + NH_3 + {}^1/_4\, O_2 \rightarrow N_2 + {}^3/_2\, H_2O$	+ 410 kJ/mole

Fig 4: **WSA process for SO_2 gas**

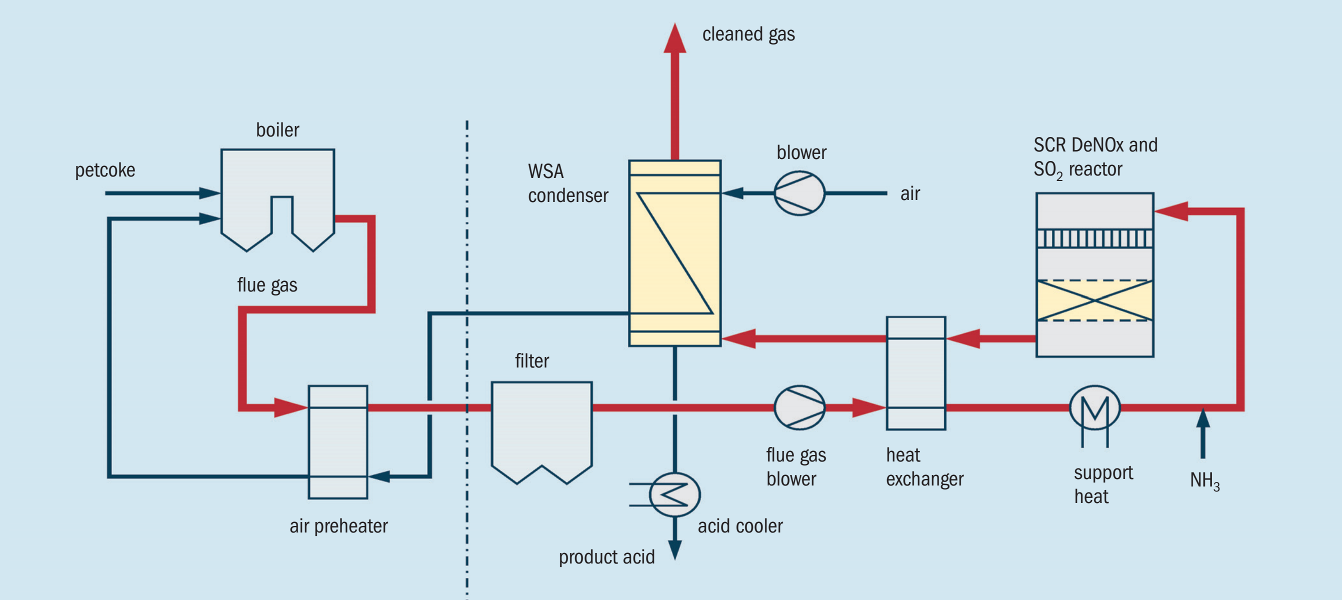


Table 2: **Key parameters of WSA plants for H_2S gas**

	Plant A	Plant B
Spent acid		
H_2O, wt-%	4	-
H_2SO_4, wt-%.	90	-
Hydrocarbons, wt-%	6	-
Acid gas		
H_2S, vol-%	91	91
SWS gas		
NH_3, vol-%	-	53
H_2S, vol-%	-	47
Typical performance		
Spent acid, t/d	100	-
Acid production, t/d	330	400
Acid concentration, wt-%	98	98
Steam production, t/h	25	45
Cooling water consumption, m^3/h	125	195

Table 3: **Key Parameters of WSA Plant for SO_2 Gas**

Flow of feed gas, Nm^3/h	60,000
SO_2 concentration, vol-%	1.40–3.75
Typical performance	
Acid production, t/d	170
Acid concentration, wt-%	98
Cooling water consumption, m^3/h	57

Table 4: **Key parameters of SNOX™ plants**

	Raffineria di Gela, Italy	OMV, Austria
Fuel	Petcoke, residue	residue
Sulphur in fuel, wt-%	5-7	4
Flue gas vol., Nm^3/h	1,200,000	820,000
SO_2 in flue gas, mg/Nm^3	10,000	7,000
Typical performance		
Acid production, t/d	440	220
Acid concentration, wt-%	94-95	94-95

and one for spent acid plus H_2S. The new WSA plants were started up in 2005 and 2006, respectively. Table 2 shows the key parameters of the two plants.

Case 2 – SO_2 gases (Fig. 3)

In the case of SO_2 gases, e.g. from a minerals roaster, the feed gas is received from a scrubbing unit upstream of the WSA plant at a temperature of around 40°C, saturated with water, free from particulates, and typically containing some SO_3. In order to avoid corrosion of downstream equipment, the temperature is increased by heating with hot air from the WSA condenser in a glass-tube gas/gas heat exchanger. In most cases a heat distribution system with molten salt is applied to recover the heat of reaction and deliver it to preheat the SO_2 gas to the operating temperature of the SO_2 converter. If the content of SO_2 is in the order of 3 vol-% or higher, there will be sufficient heat in the system to preheat the SO_2 gas. Otherwise support fuel must be applied. Excess heat is exported as steam.

The WSA process is of particular interest for low and medium SO_2 concentrations (1 – 8 vol-%, but depending on the actual application), such as off-gases from smelters of molybdenum, zinc and lead sulphide, and several types of off-gases from copper sulphide smelters. SO_2 gases with higher SO_2 content have to be diluted with air before they can be treated in the WSA process.

For example, the Chilean-based molybdenum group, Molymet, has been operating WSA plants at their molybdenum roasters in Belgium, Chile and Mexico since 1990, 1993 and 2001, respectively. It was therefore natural for Molymet to choose a WSA plant for their expansion project in Nos near Santiago, Chile. This means that they will now have two WSA plants at this site, where the requirements for efficient gas cleaning are high because of the location near Santiago. The new plant was started up successfully in the summer of 2007. Table 3 shows the key parameters of the plant.

Case 3 – Flue gases from combustion of high-sulphur fuels (Fig. 4)

The WSA process principles are also applied for large process gas volumes as in power plants, and units are in operation for both coal fired power plants and for utility boilers (typical unit size is 1 million Nm^3/h). Usually, DeNOx is incorporated in such installations. This version of the process is termed SNOX™. The SNOX™ process is more advantageous for fuels with very high sulphur content, and its main application is therefore for combustion of high sulphur residues in refineries rather than for the average coal fired power plant.

When a utility boiler is equipped with a SNOX™ plant, it will be possible to fuel the boiler with very high sulphur residues, petroleum coke, H_2S gas, Claus tail gas, SWS gas and the like. This will bring the SO_2 content of the flue gas to 0.4-0.5% or higher, which is unacceptable to most other FGD processes. Additionally, the SNOX™ process readily accepts SO_3 which is troublesome to other FGD processes. The heat content of the flue gas and the heat of reaction are utilised and returned to the boiler, and substantial revenue is received from sale of the product acid. There are no secondary waste materials, and the only reagent used is ammonia for the DeNOx.

The SNOX™ process is illustrated in Fig. 4. Flue gas from the boiler is cleaned in an electrostatic precipitator and heated by the gas leaving the SO_2 converter in a regenerative or recuperative heat exchanger. After heat exchange, NOx is reduced in the SCR reactor, and the gas is then sent to the SO_2 converter. The converted gas is cooled in the feed/effluent heat exchanger, and further cooling and condensation takes place in the WSA condenser. The cleaned gas is sent directly to the stack, and the heated cooling air is returned to the boiler, thereby increasing its efficiency.

For example, two large SNOX™ plants are installed at two European oil refineries.

Raffineria di Gela, Italy, is based on heavy crude oil with high sulphur content and coking processes. As environmental regulations have become stricter, proper disposal of the heavy residues and the petroleum coke is a prerequisite for the operation. The refinery boilers are fuelled mostly with petroleum coke, and the SNOX™ process was selected as the only viable process able to deal with the high sulphur flue gases. The SNOX™ plant was started up in 1999.

The Schwechat refinery of OMV, Austria, had an existing flue gas treatment plant installed on its boilers fuelled with heavy residual oil. The existing flue gas treatment plant could not fulfil new environmental requirements, and operation costs could be improved very much by installation of a SNOX™ plant. Therefore, in 2005, it was decided to replace the existing flue gas treatment unit with a SNOX™ plant which was able to fulfil all statutory requirements in the foreseeable future. The SNOX™ plant will also treat tail gases from the Claus units of the refinery. Start-up is scheduled for October 2007.

Table 4 shows the key parameters of the two plants.

Catalysts

The SO_2 conversion catalysts applied in the WSA and SNOX™ processes are the Topsoe VK-series catalysts. The catalysts are based on vanadium pentoxide and sodium and potassium pyrosulphates on a diatomaceous earth silica carrier material and specially adapted for moist gases. The Topsoe VK-series of catalysts will cover all relevant process conditions and make it possible to select the best catalyst or combination of catalysts for a given performance specification. They are also widely used in conventional dry sulphuric acid plants.

The SCR DeNOx catalyst is one of the Topsøe DNX series catalysts, a corrugated monolithic catalyst based on titanium, tungsten and vanadium as active materials.

Conclusion

The WSA and SNOX™ processes are simple and efficient sulphur recovery processes which meet the demands of the industry for environmental compliance, low energy usage, and low overall operating costs.

Sulphur in any form is recovered as concentrated sulphuric acid of commercial quality. The WSA technology can be applied for a variety of process streams, ranging from flue gases to concentrated H_2S gases as well as for elemental sulphur and various sulphur containing liquid waste materials.

In oil refining, the WSA process is applied for HDS acid gases, spent alkylation acid, Claus tail gases, flue gases, and various combinations hereof. In the metallurgical and other process industries, the WSA process is recognised as a suitable process, in particular for treating of low to medium SO_2 gases. In all cases, the main criteria for selecting the WSA process are low operating costs, the value of the sulphuric acid product, and the absence of secondary effluents.