THE PROCESS PRINCIPLES

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The wet gas sulfuric acid (WSA) process is a proprietary development by Haldor Topsøe A/S. Since its introduction in the 1980s, it has been recognised as an efficient process for recovering sulfur from various process gases in the form of commercial quality sulfuric acid. The WSA process has found widespread application in the metallurgical, steel (coking plants), power and cellulose industries, but the majority of applications are within the refinery and petrochemical industry. More than 60 plants have now been licensed worldwide for treatment of process gases in a wide range of process industries and oil refineries.

This article describes the process principles for various applications illustrated with concrete examples from oil refinery applications.

Application

The WSA process is applied in all industries where removal of sulfur is an issue. Within the refinery and petrochemical industries typical applications include:

- Processing of acid gases from amine regeneration units in hydrodesulfurisation (HDS).
- Treatment of tail gases from Claus units.
- Regeneration of spent sulfuric acid from alkylation.

- Treatment of stack gases from utility boilers fired by heavy residues and petroleum coke.
- Treatment of hydrogen sulfide from coal gasifiers (synthesis gas based industries).

Salient features

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

- More than 99% recovery of the total sulfur content, always in compliance with environmental legislation.
- Product is clean, concentrated sulfuric acid of commercial quality, also in turndown situations.
- Heat of reaction is recovered as superheated or saturated steam.
- Gases containing hydrocarbons and with even 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.

Table 1. Reaction schemes for WSA/SNOX™ process	
Combustion	$H_2S + {}^3/_2O_2 \rightarrow H_2O + SO_2$ + 518 kJ/mole
Oxidation	$SO_2 + ½O_2 \rightarrow SO_3$ + 99 kJ/mole
Hydration	$SO_3 + H_2O \rightarrow H_2SO_4$(gas) + 101 kJ/mole
Condensation	H_2SO_4(gas) + $0.17H_2O$(gas)$\rightarrow$ H_2SO_4(liq.) + 69 kJ/mole
DENOX	$NO + NH_3 + ¼O_2 \rightarrow N_2 + {}^3/_2H_2O$ + 410 kJ/mole

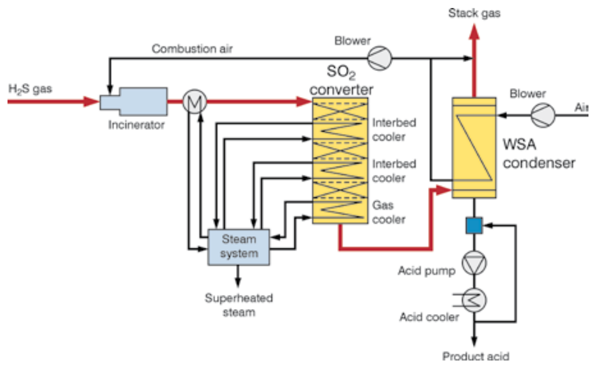

Figure 1. Process flow diagram for WSA plant treating H_2S gas.

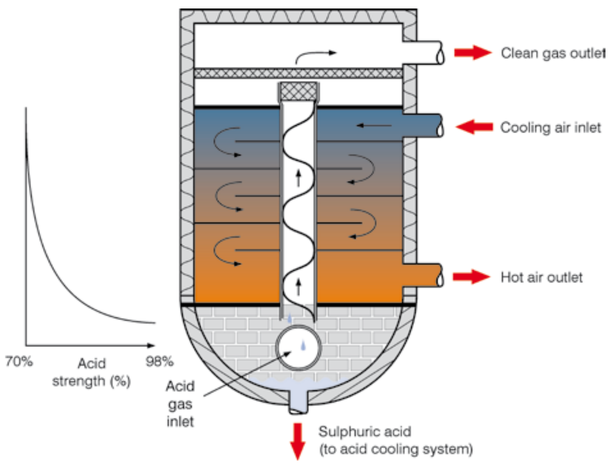

Figure 2. Principle sketch of WSA condenser.

- No consumption of process water.
- No liquid or solid waste effluents.
- Wide turndown range.
- Simple layout, simple operation, overall attractive economy.

Process principle

Contrary to conventional sulfuric acid processes, the WSA process treats the process gas with all of its water content. This means that no cooling/condensation prior to the SO_2 conversion stage is 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.

The process principle can be illustrated by a case of treating hydrogen sulfide, such as acid gas from a HDS amine regenerator (Figure 1). Basically, the same process steps apply for other feed gases, i.e. heating/cooling of the gas to the reactor temperature, conversion of SO_2 to SO_3, hydration of the SO_3 to H_2SO_4 and condensation to liquid H_2SO_4 in the WSA condenser.

The gas is incinerated to SO_2 in a burner followed by a waste heat boiler. If the feed gas does not contain combustibles, support fuel will be necessary if it contains less than approximately 25% H_2S. The incinerated gas will typically contain 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 will have a temperature of approximately 400 ˚C.

The gas then enters the SO_2 reactor, which will contain one, 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_3/SO_2 equilibrium. After the last conversion stage, the gas is cooled and the SO_3 will react with the water vapour and form gas phase sulfuric acid (Table 1). The process gas then goes to the WSA condenser, where final hydration and condensation of acid takes place (Figure 2).

The WSA condenser is a vertical shell and tube type falling film condenser/concentrator with tubes made of shock and acid resistant boron silicate glass. The process gas flows inside the tubes, which are cooled on the outside by ambient air in crosscurrent flow pattern. Sulfuric acid condenses in the tubes and flows downwards while being concentrated in countercurrent contact with the hot process gas. The sulfuric acid is collected in the acid resistant bricklined bottom part and is cooled to 30 - 40 ˚C in a watercooled 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 stack. It is a notable feature of the WSA condenser that the gas will contain only a small amount of acid mist, typically less than statutory requirements.

The cooling air will leave 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, nitrogen oxides (NOx) will be formed. In order to comply with statutory requirements and to avoid discoloration of the stack emission, it may be necessary to remove the

NOx. This can conveniently be done by introducing a selective catalytic reduction (SCR) process stage upstream of 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 water and nitrogen (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 of 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 >400 ˚C, or it can be conditioned to other properties. The required steam pressure is determined by the content of sulfur and water in the process gas so that all surface temperatures are well above the acid dewpoint.

The construction materials of the WSA plant is generally carbon steel, except where design temperature necessitates heat resistant steel (stainless or ½Mo 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 fluor 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.

Catalysts

The SO_2 conversion catalysts applied in the WSA process are the Topsøe VK series catalysts. The catalyst is based on vanadium pentoxide and sodium/potassium pyrosulfates on a diatomaceous earth silica carrier material; special versions for low temperature activity are available. The Topsøe 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.

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

Refinery and petrochemicals applications

Typical applications in the refinery and petrochemical industry are discussed below.

Alkylation

The WSA process is the ideal choice for regeneration of spent sulfuric acid. The spent sulfuric acid is thermally decomposed in a burner assisted by auxiliary fuel. The gas is cooled to approximately 400 - 450 ˚C in a waste heat boiler, and after dust removal in an electrostatic precipitator or another type of high temperature filter the gas goes to the SO_2 converter and condensation, essentially like the scheme in Figure 1.

No drying of the gas takes place. This means that there will be no loss of acid, no acidic waste material ('black acid'), and no heat is lost in process gas reheating. Compared with the conventional processes, this means that the operation economy is better with respect to heat recovery (steam production), cooling water consumption, and power consumption. The selective condensation in the WSA condenser ensures that the regenerated fresh acid will be 98% w/w even with the humid process gas. It

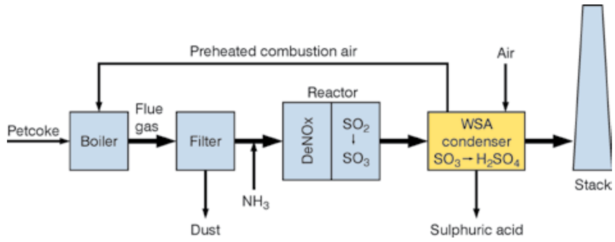

Figure 3. Process flow diagram for SNOX™ plant.

Table 2. Key parameters of WSA spent acid plants

	Plant A	Plant B
Spent acid		
H_2O (%wt)	4	4
H_2SO_4 (%wt)	91	92
Hydrocarbons (%wt)	5	4
Fuel	H_2S/refinery gas	H_2S/LPG
Typical performance		
Spent acid (tpd)	160	155
Acid production (tpd)	280	220
Acid concentration (%wt)	98	98
Steam production (tph)	14	10
Cooling water consumption (m^3/h)	110	83

will be possible to combine spent acid regeneration with disposal of hydrogen sulfide by using hydrogen sulfide as fuel. If all support fuel is substituted with hydrogen sulfide, the resulting fresh acid production will increase by approximately 50%.

Hydrogen sulfide (acid gas and SWS gas)

The WSA process is an effective and in many cases superior alternative to the Claus process. The process can be applied for gases with very high H_2S content as in amine regenerator offgas, and for gases with a lower H_2S content as in offgas 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 oil refineries, sour water stripper (SWS) gas containing hydrogen sulfide and ammonia often presents a problem. Typically, this type of gas is not readily accepted by the Claus process, and flaring is normally not an option due to environmental restrictions. The SWS gas can be accepted by the WSA process if a DeNOx stage is incorporated due to the formation of NOx during combustion. In certain cases it will not be necessary to use imported ammonia for the NOx reduction, but part of the SWS gas is used instead.

Utility boilers fired by heavy residual oil and petroleum coke

The WSA process is 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, thus the process is termed the SNOX™ process. The SNOX™ process is more advantageous for fuels with very high sulfur content, and

Table 3. 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 (tpd)	100	-
Acid production (tpd)	330	400
Acid concentration (%wt)	98	98
Steam production (tph)	25	45
Cooling water consumption (m^3/h)	125	195

Table 4. Key parameters of SNOX™ plants		
	Plant A	**Plant B**
Fuel	Petcoke, residue	Residue
Sulfur in fuel (%wt)	5 - 7	4
Flue gas vol. (Nm^3/h)	1.2 million	820 000
SO_2 in flue gas (mg/Nm^3)	10,000	7000
Typical performance		
Acid production (tpd)	440	220
Acid concentration (%wt)	94 - 95	94 - 95

its main application is therefore for high sulfur 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 sulfur residues, petroleum coke, H_2S gas, Claus tail gas, SWS gas and the like. This will bring the flue gas SO_2 content to 0.4 - 0.5% or higher, which is unacceptable to most other FGD processes. In contrast, the SNOX™ is advantageous at high content of sulfur. The heat of reaction is utilised and returned to the boiler, and a 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 Figure 3. Flue gas from the boiler is cleaned in an electrostatic precipitator and heated by feed/effluent heat exchange with the gas leaving the SO_2 converter in a regenerative or recuperative heat exchanger. After the heat exchange, NOX is reduced in the SCR reactor, and the gas is then introduced to the SO_2 converter. The converted gas is cooled in the feed/effluent heat exchanger, and final 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.

Case studies

Spent acid recovery

The WSA process is applied at refineries in North America, Asia, Europe and Russia for alkylation units supplied by both the major alkylation licensors. In case A, it was desired to increase the alkylation capacity of an existing alkylation unit and to convert from offsite to onsite regeneration for reasons of high transportation costs and to ensure secure supplies. At the same time the overall site sulfur capacity was expanded. As there was a local need for acid, it was decided to use H_2S as fuel, supplemented by refinery gas, thus avoiding expansion of Claus capacity and also generating profits from sale of acid. In case B, the WSA technology was selected for a grassroots alkylation unit; LPG and H_2S was selected as fuel. Table 2 shows the key parameters of the two plants.

H_2S gases

In a large refinery expansion it was decided to use WSA for the sulfur 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 it was naturally 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, and one for spent acid plus H_2S. Table 3 shows the key parameters of the two plants.

Flue gas treatment

Two large SNOX™ plants are installed at two European oil refineries. Refinery A is based on heavy crudes with high sulfur 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 sulfur flue gases.

Refinery B had an existing flue gas treatment plant installed on its boilers fuelled with visbreaker residue. The existing flue gas treatment plant proved inadequate to fulfil the environmental requirements, and operating costs had become unacceptable. Therefore, 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 also treats tail gases from the Claus units. Table 4 shows the key parameters of the two plants.

Conclusion

The WSA process is a simple and efficient sulfur recovery process that meets the demands of the modern process industry for environmental compliance, low energy usage and low overall operating costs.

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

In the oil refining industry, the WSA process is applied for HDS acid gases, spent alkylation acid, Claus tail gases, flue gases, and various combinations hereof. In all cases, the main criteria for selecting the WSA process have been low operating costs, the value of the sulfuric product, and the absence of any secondary effluents.