WSA TECHNOLOGY TURNS YOUR OFF-GAS INTO MONEY

Amrul Atiqi
Haldor Topsøe A/S
Email: aasa@topsoe.dk

Summary

When oil and gas is being processed the generated H_2S needs to be removed and converted, due to environmental legislation. Traditionally, acid gas is converted in a Claus plant forming elemental sulfur; however this is an inefficient approach both out of an economic and operational context.

Today the most optimal solution for treating acid gases from Acid Gas Removal Units (AGRUs) is with the innovative WSA (Wet gas sulfuric acid) technology that converts acid gases into sulfuric acid.

The WSA technology is a superior solution for treatment and conversion of acid gases, and this paper will describe both the potential economic benefits and the unique process principles of the technology.

Key words: *H_2S, SO_2, WSA , Claus, emission, refineries, gas processing, sulfur, off-gas, steam, sulfuric acid, environmental, flue gas, acid gas, desulfurisation, sour gas, SOx, NOx.*

1. Introduction

The reason why the WSA process today is the most optimal technology for converting acid gases is due to the following facts:

- A Topsøe WSA plant has lower investment costs than a plant producing elemental sulfur with the same emission requirements.

- A Topsøe WSA plant can meet the most stringent environmental regulations, even without tail gas treatment. Neither chemicals nor other additives are consumed in the process, and there will not be any solid or liquid effluents requiring additional treatment.

- A Topsøe WSA plant is much simpler than a plant producing elemental sulfur. This simplicity of the process also makes it easy to operate and thereby contributes to a higher availability and less unintended shutdowns.

- When producing sulfuric acid, a lot more energy is released than when producing elemental sulfur. The steam production is as much as 4 times higher when producing sulfuric acid as compared to producing sulfur. Why not utilise this energy yourself rather than "exporting" it with the sulfur?

- A Topsøe WSA plant requires neither tail gas treatment nor sulfur degassing. Pelletising is not relevant. There is no risk of sulfur dust being spread over the local community. Sulfuric acid just requires a simple carbon steel tank.

- In a Topsøe WSA plant, the first process step is a complete combustion of the feed gas with excess air. Therefore, ammonia and hydrocarbons in the feed gas will not cause problems and a higher feed-flexibility is possible.

The WSA and SNO™ processes are efficient for recovering sulfur from various sulfur containing processes and flue gases originating in the refinery in the form of commercial grade sulfuric acid. Today, more than 130 plants have been licensed worldwide for treatment of process gases in a wide range of process industries and oil refineries.

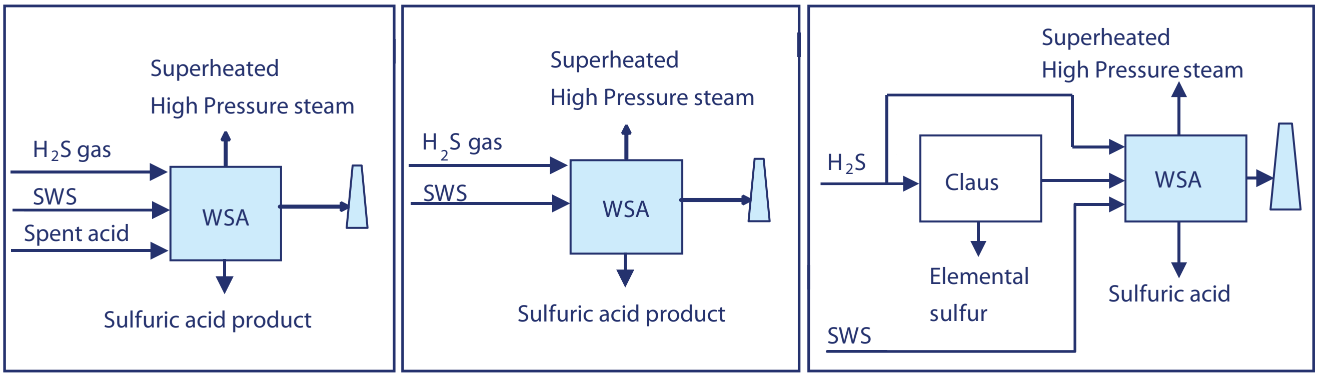
This paper shows various configurations of WSA and SNOX™ handling the following streams in the refinery: H_2S gas, Sour Water Stripper off-gas (SWS gas), Claus plant tail gas, Spent alkylation acid, Flue gas from combustion of sulfurous fuels.

2. WSA - Tailored to every need

The WSA plant is engineered based on very individual refinery requirements to maximise energy recovery and to eliminate any waste production. Over the past 30 years we have continuously improved the design so that the current generation of WSA is the best available technology on the market for treatment of sulfur containing streams.

In this section, three possible refinery configurations using WSA technology are presented. It should be mentioned that the most suitable solution for the refinery needs to be evaluated on a case-to-case basis.

The first configuration shows the handling of regeneration of spent sulfuric acid from an alkylation unit,



(a) (b) (c)

***Figure 1.** WSA plant treating all acid gases and regenerating spent acid (a); WSA plant treating all acid gases (b); Integrated WSA with Claus (c)*

H_2S and SWS gases in one WSA plant. A block diagram of this configuration is shown in Figure 1a. The second configuration shown in Figure 1b is the same as the first, except no spent acid is being regenerated.

In this layout all sulfur removed from the oil fractions ends up as commercial-grade sulfuric acid. Moreover, in addition to the produced sulfuric acid there will be a large amount of superheated high pressure steam available for export. If this configuration is applied, the refinery can be designed completely without Claus plants, hence no handling of elemental sulfur is needed.

It is also possible to combine the WSA process with a Claus unit. A schematic of this configuration is shown in Figure 1c. A simple Claus plant handles most of the H_2S gas, and the Claus plant tail gas is treated together with SWS gas in a WSA plant, producing sulfuric acid. This layout makes it possible to design the Claus plant much simpler and cheaper as the tail gas treatment will be performed in the WSA unit and no NH_3 and hydrocarbons will cause problems in the more sensitive Claus plant. In addition to the above, co-generation of sulfuric acid and elemental sulfur will also add some flexibility to the product pool.

3. The WSA process principles

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

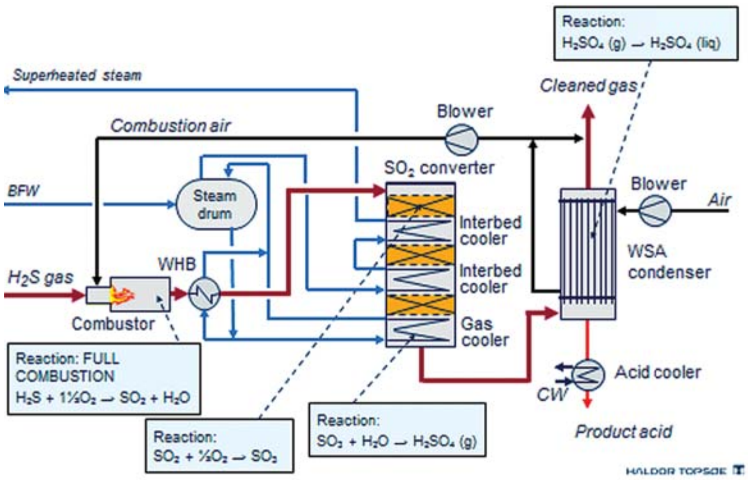


***Figure 2.** Flow diagram of a WSA plant treating H_2S gas*

effluent, no loss of acid, no use of cooling water for this part, and no loss of heat.

Because of the initial combustion process, the WSA has the ability to accept any stream from a refinery including streams containing NH_3 (sour water stripper gas).

A typical WSA plant treating a H_2S gas is shown in Figure 2. The process comprises the following major steps:

- The first step involves the combustion of the H_2S gas containing stream, typically at around 1,000°C. This thermally oxidises the H_2S to produce SO_2.

- The converted SO_2 stream exits the combustor and is then cooled to roughly 400°C through a waste heat boiler.

- Upon exiting the waste heat boiler, the SO_2 stream enters the SO_2 converter which converts the SO_2 to SO_3. The gas passes through three stages of catalyst to achieve maximum conversion. The process of converting SO_2 to SO_3 is exothermic and the heat recovered is used to superheat the process steam.

- After the last stage of the SO_2 converter, the process gas is cooled to 290°C, and the hydration of SO_3 takes place to produce sulfuric acid in vapour phase.

- The gas containing sulfuric acid vapour is then passing to the WSA condenser where it is cooled using atmospheric air and a sulfuric acid liquid of 98% concentration is produced. The acid is subsequently cooled to 40°C and pumped to storage tanks.

- The heated atmospheric air that exits the condenser is then routed to the incinerator to improve the overall energy efficiency. The cleaned process gas exits the condenser and is emitted through the stack.

4. What makes the WSA technology superior

The WSA process converts the H_2S into sulfuric acid whereas the conventional Claus process produces elemental sulfur, and when selecting which route to go, a number of parameters must be considered, many of which are not subject to discussion in this paper. However, there are some inherent advantages in the WSA concept when compared with the Claus technology, where the major ones are:

4.1. Higher energy efficiency

Going from H_2S to H_2SO_4 instead of stopping at elemental S is much more favourable because of thermodynamics. This means that due to the number of exothermic reactions occurring in the WSA process, about four times the amount of steam, of higher quality, is produced when compared to the Claus process.

When converting hydrogen sulfide to elemental sulfur, the sulfur goes from oxidation state -2 to oxidation state 0. This is an exothermal process, yielding approx. 222kJ/mole of hydrogen sulfide processed (equal to 95,500Btu per lbmole).

When converting hydrogen sulfide to sulfuric acid, the sulfur goes in two steps from oxidation state -2 first to oxidation state +4 and finally to oxidation state +6. The reactions involved are also exothermal, but with an almost four times higher enthalpy jump, in total yielding approx. 804kJ/mole of hydrogen sulfide processed (equal to 346,000Btu/lbmole).

This difference in reaction enthalpies between Claus and WSA, illustrated in Figure 3, means that a WSA plant exports much more energy than a Claus plant. The export of energy from a WSA plant is in the form of superheated high-pressure steam.

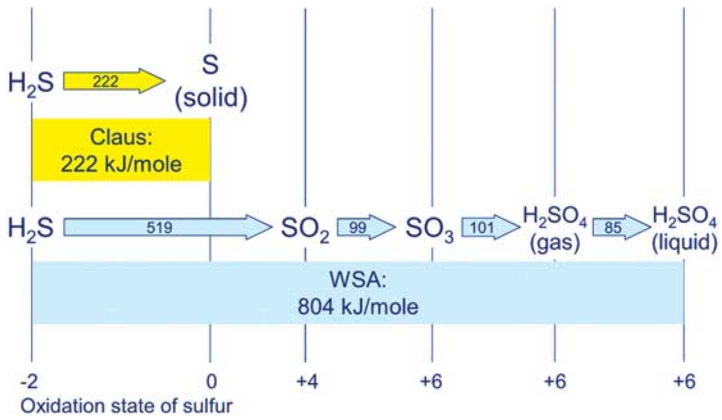


Figure 3. *Enthalpies of sulfur conversion*

4.2. Feed flexibility

In the feed streams to a Claus plant most other compounds than hydrogen sulfides are potential troublemakers. Other combustibles than hydrogen sulfide make it more difficult to hit the desired ratio of usually 2.0 between hydrogen sulfide and sulfur dioxide after the partial combustion. Additionally, ammonia may form polluting NOx, and hydrocarbons may form COS and CS_2 that makes it difficult to achieve the desired high sulfur recovery rate or carbon that blocks the Claus catalyst as the content of hydrocarbons fluctuating over the time, making the process more complicated to operate.

The WSA process is sensitive neither to hydrocarbons nor to nitrogen containing compounds such as NH_3 in the feed gas, and it is also able to accommodate significant changes in feed gas flow and composition. This is mainly due to the fact that in the WSA process there is complete combustion of the feed gases as initial step, whereas the Claus process has a somewhat more complex combustion which controls the H_2S to SO_2 ratio to the optimum 2:1. It should be noted that if significant amounts of nitrogen containing compounds are present in the feed gas, a Selective Catalytic Reduction (SCR) reactor has to be installed in order to reduce NOx formed in combustion.

4.3. Meeting the environmental regulations

Treatment of the gas exiting the Claus plant is always required, since the Claus plant itself rarely achieves more than 98% sulfur recovery. Even in the rare cases where 98% sulfur recovery is sufficient to fulfil emission regulations, it is required to incinerate the tail gas, because emission of hydrogen sulfide is not allowed.

In a WSA plant, all sulfur compounds must be oxidised to sulfur dioxide, so the feed streams are combusted with sufficient air to oxidise also any ammonia, hydrocarbon and other combustibles. Even the simplest process lay-out of a WSA plant allows more than 99% removal of the sulfur compounds, and an advanced WSA plant can be designed for up to 99.99% sulfur removal. This is higher than any environmental standard requires today.

4.4. End-product

Sulfuric acid can in many aspects be a beneficial product when compared to elemental sulfur, but this should be evaluated on a case-to-case basis taking local conditions into consideration. However, one basic fact is that approximately 90% of all the elemental sulfur produced worldwide will be further processed into sulfuric acid. One could therefore argue that going from H_2S to sulfuric acid in one step compared to a multi-step approach where elemental sulfur is produced as an intermediate is more efficient in many aspects. Moreover, sulfuric acid also has a broader market segment with users such as the fertiliser industry, steel industry, water treatment, polymer industry, oil refining, and chemical industry, etc. In addition, sulfur can also liberate H_2S which makes product handling troublesome.

4.5. Cost

A WSA plant will typically have lower investment cost when compared with a Claus plant equipped with downstream tail gas treatment unit (TGTU). This is mainly due to the simple WSA design consisting of relatively few pieces of equipment. When considering operating costs, the WSA technology also has some important benefits. The large amount of high pressure steam produced in the WSA process, see section above, will have a positive impact on the operating income. Finally, the relatively simple design and operation of a WSA plant results in lower O&M cost compared to the more complex Claus plant.

Table 1. *Economical comparison between Claus and WSA*

Basics	**Unit**	
Feed stream/acid gas	Nm^3/h	2,700
Content of H_2S	Vol-%	30
Total sulfur amount	tons/day	28
Sulfuric acid amount equivalent	tons/day	85
Sulfur recovery	%	99.5

Consumption figures	USD/ton	**Claus + TGTU**		**WSA**	
		Cons. tons/hour	USD/year	Cons. tons/hour	USD/year
Fuel gas	130	0.23	257,152	-	-
Oxygen	47	0.56	226,363	-	-
HP steam	17	1.33	194,455	-	-
Boiler feed water	0.34	3.70	10,819	11.2	32,750
Cooling water	0.03	-	-	30.8	7,947
Electric power	USD 0.08/kWh	400kWh	275,213	205.0	141,047
Total consumption cost	**USD**		**964,002**		**181,744**

Production figures	USD/ton	**Claus + TGTU**		**WSA**	
		Prod. tons/hour	USD/year	Prod. tons/hour	USD/year
Sulfuric acid	32			3.56	978,939
Sulfur	80	1.16	799,980		
HP steam	17			9.5	1,388,965
LP steam	12	2.7	278,653		
Total production value	**USD**		**1,078,633**		**2,367,904**
Net production income	**USD**		**114,631**		**2,186,160**

Financial figures	**Claus + TGTU**	**WSA**
Investment (USD)	10,000,000	10,000,000
Net present value (USD)	-7,000,000	18,500,000
Comparative advantage of WSA over 20 years		**USD 25,500,000**

**Plant life time 20 years, inflation 4% p.a., discount rate 7% p.a.*

If more than 99.6% conversion of the sulfur is required, WSA-DC, which is a double condensation version of the WSA technology, can be applied. In this way the SO_2 conversion can reach a level of 99.99%, which is much higher than required by any legislation today. Alternatively, a tail gas treatment can be applied, where the tail gas is scrubbed with hydrogen peroxide. Neither of the two methods produces any by-products.

Table 1 shows an economical comparison between Claus and WSA for a specific anonymous case. Of course, the unit prices and other particulars differ from one location to another, but it is clearly seen that the WSA comes out very favourably compared to the Claus plant. The investment in a Claus unit plus tail gas treatment is comparable to the investment in a WSA unit. Usually the WSA unit is a little cheaper, but for easy comparison the investments are assumed to be equal.

5. Case Story - WSA Technology for lean H_2S gas from a gas sweetening plant

JOB Pertamina - Medco Tomori Gas Sweetening site generates additional 5.5MW power using WSA technology for treating lean acid gases from AGRU.

Using the WSA technology, JOB Tomori manages to comply with the local environmental regulation while producing huge amounts of HP superheated steam and saleable sulfuric acid.

5.1. Background

The project is named Senoro Upstream Gas Project and is located in Central Sulawesi Province, Indonesia for upstream production of feed gas pipelined for Donggi-Senoro LNG production. Senoro Upstream Gas Production facility has a total production capacity of 310MMSCFD of gas and 8,500 barrels/day of condensate. It is jointly owned by MedcoEnergi, Pertamina and Tomori EP.

The WSA technology has been chosen to treat acid gases, originating from the gas sweetening process at the gas production facility. The H_2S in the gases coming from both acid gas removal unit (AGRU) and the LP fuel gas treatment are converted into sulfuric acid of commercial grade with the WSA process.

5.2. Challenges

- Meet local emission regulations;

- Low H_2S concentration of only 1.78 - 2.33vol-% and a gas flow of 2,200lbmole/h;

- High reliability and availability are needed for this kind of project.

5.3. Evaluation model

JOB TOMORI has created the evaluation model based on several criteria, namely:

- Availability/Reliability factor - it needs to be a proven technology with many references;

- Technical feasible solution for very lean H_2S gases without concentrating;

- Simplicity of the process will bring down the cost for maintenance and overall OPEX;

- Investment cost - concentrating of the acid gas would be too expensive;

- The energy recovery needs to be sufficient to justify a steam turbine;

- The market potential for sulfuric acid is more diverse compared to sulfur.

Based on the above criteria, JOB Tomori´s internal and a 3rd party evaluation done by Worley Parsons, Topsøe's WSA technology emerged as the optimal solution for their gas sweetening project.

5.4. Topsøe´s WSA solution

- A WSA plant that produces 45tons/day of sulfuric acid;

- Production of 780tons/day of steam (433°C, 28.5bar g) allowing production of 5.5MW power;

- Minimum SO_2 conversion of 97% has been guaranteed.

The WSA plant will, in this single catalytic bed layout, convert minimum 97% of the sulfur and produce 45tons/day of commercial grade sulfuric acid, which is sold on the local market. In addition, about 780tons/day of superheated steam will be produced and the steam will be routed to a turbine to produce power. In order to maximise steam production in the WSA plant, energy from the condensation of sulfuric acid is recovered in the form of hot air, most of which is supplied to the combustor. The rest of the hot air is used for preheating the incoming boiler feed water. This design makes the plant extremely energy efficient due to the fact that most of the heat is recovered back into the process.

6. SNOX - Efficient and cost-effective removal of SOx and NOx

As sweet crude oil reserves diminish, energy companies are forced to turn to heavy crude oil with high content of sulfur in order to satisfy the demand for petroleum.

At the same time, these companies have to strive for high energy efficiency and low emission levels.

Refineries using petcoke and/or heavy residue as a fuel for generation of steam and electrical power are finding that conventional methods of flue gas desulfurisation (FGD) using limestone wet scrubbing are becoming significantly more expensive and troublesome to operate as fuel sulfur content increases.

The SNOX™ process combines removal of NOx, SOx, Hg and particulates into a process that is not only less expensive to operate at high fuel sulfur levels, but also produces commercial-grade sulfuric acid as a revenue source while avoiding purchase of absorbents and eliminating waste treatment and disposal costs.

Recycling of hot combustion air back to the boilers ensures a high degree of fuel burn-out and high thermal efficiency, keeping energy costs at a minimum and reducing specific CO_2 emission.

Finally, the SNOX™ process demonstrates a higher level of sustainability than conventional processes because it consumes hardly any water and produces no waste requiring expensive handling, treatment and disposal.

SNOX™ plants (e.g. at OMV - Austria, Agip - Italy and Vattenfall - Denmark) have demonstrated consistently high availabilities and efficiencies over many years. All new SNOX™ plants, at for instance Petrobras (Brazil), are designed for the same proven availabilities and reliabilities.

7. Refinery configurations with Topsøe SNOX™ technology

When the flue gas from combustion of high-sulfur heavy residues shall be cleaned, a SNOX™ plant is the ideal solution, since it neither requires absorption materials nor produces waste materials.

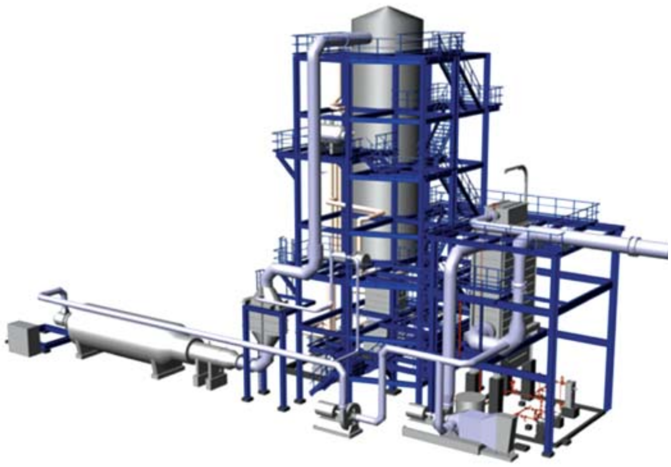


Figure 4. *3D computer model of a WSA plant treating H_2S gas*

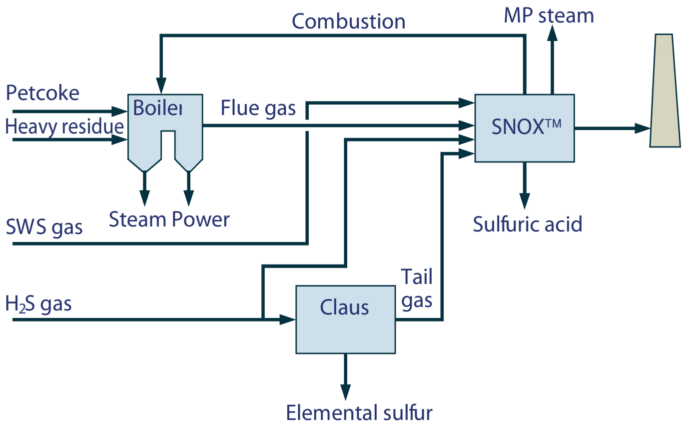


Figure 5. *SNOX™ plant treating H_2S, SWS, Claus tail and boiler flue gases*

Table 2. *Comparison of a SNOX™ plant equipped pulverised coal boiler with a CFB boiler with SCR DeNOx and tail-end FGD producing 300MW electricity from petcoke with 6% sulfur content and an LHV of 32MJ/kg*

	Unit	SNOX™ with pulverized coal boiler	Limestone FGD + SCR with CFB boiler
Comparison SNOX™ versus limestone FGD + SCR			
Net electric output	MW	300	300
Net electric efficiency (on LHV basis)	%	39	38
Petcoke consumption	tons/hour	88.3	89.7
SOx removal efficiency	%	98	98
NOx content in stack gas	ppm	< 20	30
H_2SO_4 production	tons/hour	15.6	0
Total Ca/S ratio in SOx absorption		0	2.8
$CaCO_3$ consumption	tons/hour	0	47*
Waste production	tons/hour	0	75**
NH_3 consumption	tons/hour	0.25	0.1
Financial impact in USD/year at 8,000 full-load hours			
H_2SO_4 sold at USD 15/ton	USD/year	1,800,000	0
$CaCO_3$ supplied at USD 20/ton	USD/year	0	-7,500,000
NH_3 supplied at USD 300/ton	USD/year	-600	-240,000
Waste disposal cost at USD 20/ton	USD/year	0	-12,000,000
Cost of difference in fuel consumption at USD 40/ton petcoke	USD/year	0	-400,000
Total	**USD/year**	**1,200,000**	**-20,140,000**
Cost impact per MWh	USD	-0.50	8.40

** Use of $CaCO_3$ containing CFB waste for tail gas FGD in assumed.*
*** Mixture of $CaSO_4$, CaO, $CaCO_3$ and ash.*
Weight depends on H_2O content. Figure varies considerably with the location.

The product is sulfuric acid of 94 - 97wt.% concentration. A very special advantage of the SNOX™ technology is that it becomes more economical the more sulfur is contained in the feed streams, hence, it is also beneficial to treat H_2S and SWS gases in the SNOX™ plant. Figure 5 shows a configuration where H_2S gas is primarily handled in a Claus plant producing elemental sulfur, while the flue gas from combustion of heavy residues is cleaned in a SNOX™ plant together with SWS gas and Claus plant tail gas.

8. Competitive cost profile of SNOX™

Table 2 compares the economics of a pulverised coal boiler using the SNOX™ process and a CFB boiler using SCR and tail-end FGD with limestone-based scrubbing.

Table 2 also shows that the much lower operating costs of a pulverised coal boiler using the SNOX™ process results in a 8.90USD reduction per MWh, compared with CFB boiler power generation using SCR DeNOx and tail-end FGD with limestone scrubbing.

9. Conclusions

The WSA and SNOX™ processes are simple and efficient sulfur recovery processes which meet the demands of the 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 and SNOX™ technologies can be applied for a variety of process streams in various industries.

The WSA technology can meet the most stringent environmental regulations, even without tail gas treatment. One of the main advantages over a traditional Claus plant is that the steam production is as much as 4 times higher when producing sulfuric acid as compared to producing sulfur. Moreover, the WSA technology is a simple and reliable process that contributes to a higher availability and less shutdowns.

The SNOX™ process enables trouble-free burning of petcoke and heavy residue. Essentially, all SO_3 and heavy metal oxides are removed from the flue gas without corrosion problems.

The SNOX™ process is particularly suited for treatment of flue gas from combustion of up to 100% petcoke and heavy residue in pulverised coal boilers. The high combustion temperatures and 3 - 4% excess O_2 required for high burn-out of petcoke and the high content of vanadium in the fly ash result in a high flue gas content of NOx and SO_3, which can both be removed without corrosion or other problems in a SNOX™ plant. The higher air preheat temperature of the SNOX™ process also improves petcoke burn-out.

The main attraction of the SNOX™ process is that it requires much lower operating costs compared to traditional FGD technology and that it enables the combustion of cheap, high-sulfur petcoke and heavy residue for generation of steam and power without any significant water consumption or formation of waste products. Neither does it pose emission and operating problems other than those normally associated with burning coal and oil.

The SNOX™ process demonstrates high energy efficiency by recycling hot, preheated air to the boilers. In addition, the SNOX™ process can be used for handling of other sulfur waste streams such as H_2S, SWS gas and Claus tail gas.