The Topsøe SNOX™ Technology for Cleaning of Flue Gas from Combustion of Petroleum Coke and High Sulphur Petroleum Residues

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Summary

The Topsøe SNOX™ process is a regenerative, catalytic flue gas cleaning process, which removes up to 98% of sulphur dioxide (SO_2) and sulphur trioxide (SO_3), up to 96% of nitrogen oxides (NOx) and essentially all particulates from flue gases. The sulphur compounds are recovered as commercial-grade concentrated sulphuric acid (H_2SO_4), while NOx is reduced to nitrogen (N_2). The process does not consume water or absorption materials or other materials, except for ammonia (NH_3) for the catalytic NOx reduction, and it does not generate any secondary sources of pollution, such as waste water, slurries or solids. The cost of operation decreases with increasing sulphur content in the flue gas, even before taking credit for sales of the produced sulphuric acid.

Today (mid 2006), the SNOX process is used in large scale at a coal fired and a petcoke fired power plant. One further SNOX plant is being constructed at a refinery where heavy residual oil is being burned. The process under the name WSA (Wet gas Sulphuric Acid) – often without NOx removal – is used at a smaller scale in various applications in more than 50 plants. The SNOX process is in particular suited for treatment of flue gases with high contents of SO_2 and SO_3 from combustion of petroleum coke, orimulsion and asphaltenic residues with more than 3% sulphur.

This paper describes design and operating experience from the 1,000,000 Nm^3/h SNOX plant at the petcoke fueled power plant at the Gela refinery in Sicily, Italy, and compares SNOX equipped PC (powdered coal) boilers with alternative processes used for combustion of petcoke and flue gas cleaning in power stations. The SNOX plant in Gela has operated with more than 98% availability and practically unchanged performance, since it was commissioned in September 1999.

Left:
1,000,000 Nm^3/h SNOX plant at the power plant of the Agip Petroli SpA refinery in Gela, Italy

Right:
300 MW coal fired power plant equipped with SNOX at NEFO (Nordjyllands-værket), Denmark

Introduction

The SNOX process is a catalytic flue gas cleaning process which removes 95 – 99% of SO_2 and SO_3 and 90 – 96% of the NOx in flue gases. The sulphur is recovered as 94 – 96% concentrated sulphuric acid of high purity. NOx is catalytically reduced by ammonia to nitrogen and water. Essentially all dust and particulates are removed from the flue gas. The heat produced in the process and by cooling of the flue gas to 100°C is recovered as steam and preheating of combustion air, thus increasing boiler thermal efficiency and gross power production.

The process generates no secondary sources of pollution, such as waste water, slurries or solids. It consumes no water or materials, except for ammonia for the catalytic NOx reduction.

The principal SNOX process steps are (see fig 1):

- Dust removal in ESP (or bag filter)
- Heating of the flue gas to about 400°C
- Catalytic reduction of NOx by NH_3 added to the gas upstream of the DeNOx-reactor
- Catalytic oxidation of SO_2 to SO_3 in the subsequent oxidation reactor
- Cooling of the gas to about 260°C
- Further cooling of the gas to about 100°C in the "WSA Condenser", a falling film condenser and concentrator with vertical glass tubes, whereby the SO_3 and H_2SO_4 vapour is condensed and separated as concentrated sulphuric acid from the bottom chamber of the condenser.

The process is in particular suited for boilers burning high sulphur refinery residues, such as petroleum coke (petcoke), orimulsion, heavy oils and tars and sour gases. In theory, there is no upper limit to the content of SO_2 and SO_3 in the flue gas, but more than about 1% SO_2 in the flue gas would require a modification of the lay-out shown in Fig. 1.

The process makes it possible to burn petroleum coke in PC boilers without blending it with coal or co-firing more fuel oil than is necessary for efficient combustion of the petcoke. Essentially all SO_3 and particulate matter are removed from the flue gas without corrosion problems. Furthermore, the increased air preheat temperature and the freedom to choose the optimal air/fuel ratio for the combustion without regard to SO_3 and NOx formation improve burnout of the petcoke.

An added attraction is that, even before credit for sales of the produced sulphuric acid, the operating cost of SNOX units slightly decreases with increasing SOx content in the flue gas due to the recovery of the heat of formation of H_2SO_4 from SO_2.

The process is especially suited for treatment of flue gas from boilers burning up to 100% petcoke in down-shot (arch) fired PC boilers. The high combustion temperatures and excess oxygen required for obtaining sufficient burn-out of petcoke, and the high content of vanadium in the fly ash give high flue gas contents of NOx and SO_3. In other flue gas desulphurisation plants these compounds would give rise to problems, but in the SNOX process they are effectively removed without corrosion or other problems. The higher combustion air preheat temperature with SNOX also improves burn-out of the petcoke.

The first full scale SNOX plant treating 1,000,000 Nm^3/h flue gas from a 300 MW coal fired power plant at NEFO (Nordjyllandsværket) in Denmark was started up in 1991. In USA, SNOX was demonstrated in smaller scale (35 MW) at a coal-fired power plant in Niles, Ohio, in 1991 – 96 under the DOE Clean Coal II program. As of today (early 2006), 55 SNOX and WSA plants (smaller SNOX plants without the DeNOx step) treating a wide range of sulphur containing off gases have been contracted worldwide by Topsøe.

The largest SNOX plant treats up to 1,200,000 Nm^3/h flue gas from four petcoke-fired boilers at the Agip Petroli SpA refinery in Gela, Sicily, Italy. The SNOX plant was supplied on turnkey basis by Snamprogetti SpA and went into operation in September 1999. Topsøe supplied process engineering, catalysts, proprietary equipment and site supervision. The 4th boiler was connected to the SNOX plant in 2005, and the maximum load increased from 1,000,000 to 1,200,000 Nm^3/h without any changes in the plant.

Experience with the SNOX Plant in Gela

The Gela plant layout is shown in figure 1 (original three boilers in operation). The SNOX plant, as seen to the right of the dotted line, treats the flue gas from three existing utility boilers

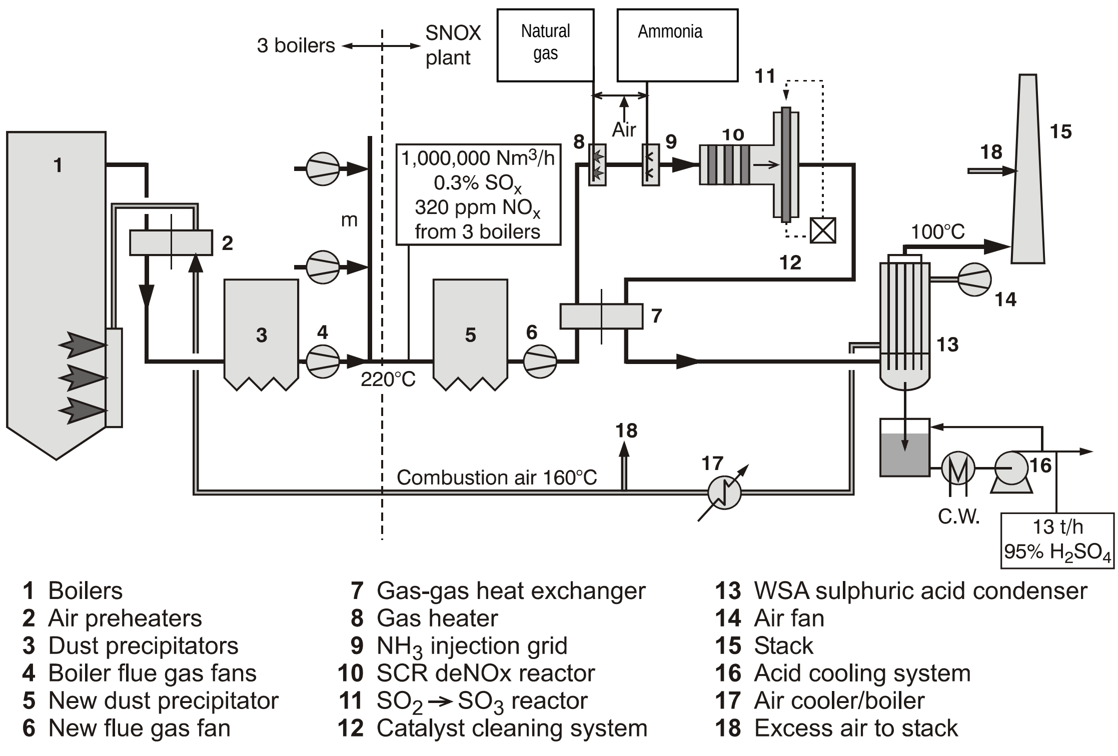

Fig 1: The SNOX plant at the Gela refinery, Italy, treating flue gas from three utility boilers.

of the down-shut PC type, shown to the left of the dotted line. The boilers (1) are fueled with 1900 t/d of high-sulphur petroleum coke and minor amounts of fuel oil and refinery sour gases. Each boiler emits up to 370,000 Nm^3/h flue gas and is equipped with an electrostatic precipitator (3) and a flue gas fan (4). The flue gas from the boilers is collected in the manifold (m) and passed to the new additional ESP (5).

The content of dust (mainly unburned petcoke) in the flue gas from the "old" ESPs is further reduced in the additional ESP to less than 1 mg/Nm^3, of which 70% is carbon. The rest is ash of metal oxides (mainly vanadium oxide), most of which accumulates in the catalyst panels of the SO_2-reactor as oxy-sulphates.

After passing through the three parallel flue gas fans (6), the flue gas is heated in the rotating gas-gas heat exchanger (7) to 385°C and further heated to 395 – 400°C in the heater (8) using natural gas or H_2S-gas from the refinery. Superheated steam at above 500°C, as used in the Danish SNOX plant for heating the flue gas, was not available at the Gela plant.

NOx Reduction

NH_3 (pre-mixed with hot air) is then injected and mixed with the flue gas through a grid of nozzles (9) placed in the flue gas duct upstream of the DeNOx reactor (10). In the DeNOx reactor the gas flows horizontally through blocks of monolithic DeNOx catalyst. Almost all of the NOx is present as NO, which is reduced by the SCR reaction:

$$NO + NH_3 + 0.25\ O_2 \rightarrow N_2 + 1.5\ H_2O + 410\ kJ/mol$$

The degree of NOx removal obtained depends on the NH_3/NOx ratio and on how well the NH_3 is distributed in the flue gas. With typically 320 ppm NOx in the flue gas and an NH_3/NOx ratio of 1.0, the flue gas exiting the DeNOx-reactor contains about 10 ppm NOx and 20 ppm NH_3. The slip of NH_3 is destroyed in the SO_2 reactor.

After 6 years of operation, no decrease in NOx conversion across the reactor is observed.

SO_2 Oxidation

In the subsequent SO_2 oxidation reactor (11), the gas passes in parallel through a number of catalyst panels loaded with sulphuric acid catalyst in the form of "daisy" shaped rings which give low pressure drop and high capacity for dust uptake. The DeNOx reactor and the SO_2 reactor are integrated in one single vessel.

In the SO_2 reactor, about 98% of the SO_2 is oxidized to SO_3:

$$SO_2 + 0.5\ O_2 \leftrightarrows SO_3 + 100\ kJ/mol$$

At the same time, the NH_3 slip from the DeNOx reactor is completely oxidized whereby the NOx concentration increases to about 15 ppm, which corresponds to an overall DeNOx degree of about 95% measured after the SO_2 reactor. Higher hydrocarbons in the flue gas, if any, are also oxidized completely.

After 6 years of operation at about 400°C, the SO_2 oxidation catalyst has deactivated by only about 10%. A catalyst life time of up to 10 years is expected.

Final Dust Removal

At operating conditions, the sulphuric acid catalyst is slightly sticky and acts as an effective dust filter removing practically all of the remaining dust content. The catalyst is sticky because of the liquid pyro-sulphate melt in the catalyst pores at operating conditions. The dust accumulates in the void between the catalyst particles so that the catalyst in the panels must be cleaned at intervals. The interval between screenings is inversely proportional to the dust content in the gas and is 10 – 15,000 full load hours with 1 mg/Nm^3 of ash being caught in the bed. The cleaning can be performed by circulating and screening the catalyst in two panels at a time in a closed system, without interrupting the operation of the SNOX plant.

Actually, less than 1 mg/Nm^3 dust in the gas enters the SO_2 reactor. About 70% of the dust is carbon (unburned petcoke), which is oxidized to CO_2 when it gets in contact with the hot catalyst.

Any trace of dust passing through the SO_2 reactor is removed by the condensing sulphuric acid in the WSA condenser and will end up in the product acid. The water clear appearance of the acid indicates that no dust passes through the SO_2 reactor.

The WSA Condenser

After the SO_2 reactor, the gas is cooled to below 300°C in the rotating heat exchanger (7). The heat exchanger is equipped with recycle of sealing gas, reducing the gas leakage to 2 – 2.5%. The leakage means that 98 – 98.5% SO_2-conversion obtained in the reactor decreases to 95.5 – 96% measured downstream of the heat exchanger.

During the cooling, most of the SO_3 reacts with H_2O in the flue gas, forming H_2SO_4 vapour:

$$SO_3 + H_2O \leftrightarrows H_2SO_4 \text{ (gas)} + 100 \text{ kJ/mol}$$

The gas temperature is well above the acid dew point when it enters the WSA-condenser (13), which is a falling film condenser in which the gas is further cooled to about 100°C in air cooled glass tubes before the gas is passed to the stack. In the glass tubes, the remaining SO_3 is hydrated, and the sulphuric acid vapour condensed and concentrated to 95% strength of the product acid. The formation reaction of the sulphuric acid is:

$$H_2SO_4 \text{ (gas)} + 0.28\ H_2O \leftrightarrows H_2SO_4 \text{ (95\% conc.)} + 80 \text{ kJ/mol}$$

The acid is collected in the bottom part of the condenser, from where it flows to the acid cooling system (16) where the acid is cooled to about 30 – 40°C in a water cooled plate heat exchanger, as seen in Fig. 1.

The WSA condenser contains a number of modules with vertical glass tubes. The cooling air is delivered by the air fan (14) and heated in the condenser. It is cooled in the boiler/trim cooler (17) to 150 – 160°C before it is further heated in the air pre-heaters (2) and used as combustion air in the boilers. Excess air is (through line 18) passed to the stack (15). The boiler (17) is used to keep the temperature of the flue gas entering the SNOX plant at about 200°C. Any acid droplets in the stack gas are completely removed in a simple guard demister installed in the duct upstream the stack.

Formation of aerosol in the condenser is avoided by heterogeneous nucleation control, "Mist Control", patented by Topsøe.

The SNOX treated stack gas is normally invisible even against a blue sky, as seen in Fig. 2. It corresponds to < 5% opacity.

Operating & Maintenance Experience

The results of the performance test run in February 2000 are summarized in table 1.

Inlet flue gas flow		Nm^3/h	971,000
SO_2 inlet		ppm-vol	2885
NOx inlet		ppm-vol	337
SOx removal efficiency		%	96.5
NOx removal efficiency		%	90.5
Acid mist in stack gas (prior to air dilution)		ppm-vol	< 3
Product acid concentration		%-wt	95
Ammonia consumption		kg/h	238
Natural gas consumption		kg/h	328
Total power consumption (blowers, pumps etc.)		MW	10.4
Flue gas pressure drop across the SNOX plant		mbar	45
Stack gas opacity		%	< 5 (invisible)
Product acid quality (recent measurements)	Fe	ppm	2
	HCl	ppm	< 10
	SO_2	ppm	< 10
	Hg	ppb	< 5
	Ni	ppb	65
	V	ppb	35
	Cr	ppb	< 30
	As	ppb	90

Table 1. Test run performance of SNOX plant at Agip Petroli SpA, Gela, Italy

The SNOX plant has operated with more than 98% availability (including planned stops for inspection), and practically no decrease in performance from the first start-up in September 1999 until now (mid 2006).

The plant has been shut down for about two weeks every year for inspection and ordinary maintenance. The catalysts have not been touched, apart from topping up the SO_2 catalyst panels with totally 4% of the total volume of sulphuric acid catalyst from 1999 until now (mid 2006) to compensate for catalyst settling in the panels. The plant was always found to be in excellent shape. All the catalyst was clean, apart from signs of slight dust accumulation in the SO_2 oxidation reactor found during the latest inspection.

The condenser top hoods and all the ducts leading the flue gas from the condenser to the stack are in perfect shape with no signs of corrosion or degradation of the polymer coating. The internal stack brick lining has remained in perfect shape, confirming that essentially no acid droplets are present when the flue gas enters the stack.

Fig. 2: The SNOX plant treating the flue gas from three boilers burning high sulphur petroleum coke at the Agip Petroli SpA refinery in Gela, Sicily, Italy. The banded stack seen on the left emits 1,000,000 Nm^3/h of SNOX treated flue gas. The chequered stack seen on the right emits flue gas from the 4th boiler before it was connected to the SNOX plant.

New SNOX Project

A new SNOX plant treating 820,000 Nm^3/h flue gas from combustion of heavy residue in the steam and power plant of the OMV refinery in Schwechat, Austria is in the construction phase and scheduled for start-up in 2007. The plant is designed with by-pass free gas-gas heat exchanger for achieving 98% SOx removal.

Comparison with Alternative Processes

Delayed coking is a common way to convert residual oils to more valuable, lighter petroleum products in refineries that are then left with petroleum coke (petcoke) as a low value by-product. Handling petcoke is a significant challenge because it contains all of the vanadium and nickel and most of the sulphur in the coker feed streams. With the increasing demand for light products, the world production of petroleum coke is expected to increase from 50 million tons per year (Mt/y) in 2000 to more than 100 Mt/y during the next 10 – 15 years.

An increasing fraction of this forced coke production has to be used as fuel in power plants. However, petcoke cannot in practice be burned in ordinary boilers equipped with FGD scrubbers, unless blended with minimum 80% coal. Use of up to 100% petcoke as fuel is only possible either in Circulating Fluid Bed (CFB) boilers with injection of large excess of limestone in the combustion zone, or in down-shot fired boilers. Gasification of petcoke in integrated gasification plants (IGCC) plants seems to be too expensive for power production.

CFB boilers are the prevailing technology for use of petcoke for power production today in spite of its many disadvantages: very high consumption of limestone; production of a correspondingly large production of waste contaminated with all the vanadium and nickel from the petcoke; and the necessity of subsequent FGD (flue gas desulphurization) of the off gas to achieve 98% SO_2 removal with high-sulphur fuels. To put it in perspective: 1 ton of fuel with 6% sulphur requires injection of 0.4 – 0.5 t calcium carbonate ($CaCO_3$) and produces 0.6 – 0.7 t heavy metal contaminated solid waste per ton of fuel. Use of SCR also seems necessary in order to achieve less than 40 ppm NOx in the stack gas.

The lower heating value (LHV) of the petcoke is in the order of 32 MJ/kg. Petcoke is difficult to burn and is usually burned in down-shot (arch) boilers. They typically give higher net electric efficiency than CFB boilers with the same steam data. However, the use of wet scrubbing technologies for flue gas treatment is hampered by problems with corrosion, plugging and mist formation, which requires installation of WESP (Wet gas ESP) upstream of the stack. The problems are mainly caused by the high content of SO_3 and vanadium rich fly ash in the gas. The high consumption of high quality limestone for achieving 98% SOx removal also implies significant costs when scrubbing flue gas with very high SO_2 concentration. Furthermore, usual "high dust" SCR NOx reduction is hampered by rapid fouling of the DeNOx catalyst, caused by the high vanadium content in the fly ash.

None of these problems are encountered with SNOX flue gas treatment, which works in excellent synergy with boilers fired with petcoke and other petroleum residue products.

The SNOX lay-out with new down-shot boilers will be similar to that shown in Fig. 1 with the modifications noted earlier. Only one large ESP will be necessary, the support heat upstream of the SCR reactor will be supplied by heat exchange with superheated steam recycle from the boiler/steam turbines, and no catalyst cleaning system will be required. Up to 98% DeSOx and 96% DeNOx can be achieved by using a leak free (recuperative) gas-gas heat exchanger in place of a conventional rotating heat exchanger, as used in the Gela plant. The total investment costs per unit of net power production of a SNOX-equipped petcoke fired down-shot boiler are about the same as that of a CFB boiler with the same SO_2 and NOx emission, while the operating costs of the SNOX equipped boiler alternative will be substantially lower, even before credit for the sales of the produced sulphuric acid.

Conclusions

After more than six years of operation, the SNOX plant treating the flue gas from three (now four) petcoke fired boilers at the Agip Petroli refinery in Gela, Italy has demonstrated 92% NOx removal and 96 % SOx removal. There have been no significant corrosion problems or problems with plugging or fouling, and no other decrease in performance of the SNOX plant. The treated stack gas is invisible and essentially free of heavy metals. SO_2 and SO_3 are recovered as commercial grade 95% H_2SO_4 of high purity. Plant availability has been more than 98% since the first start-up.

SNOX-equipped boilers seem to be a technically, economically and environmentally superior solution for power plants burning petcoke and other high sulphur petroleum residue products.

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HALDOR TOPSØE A/S

The Catalyst and Technology Company

www.topsoe.com

The Topsøe Group, Haldor Topsøe A/S and its subsidiaries, is a private sector organisation devoted to research and development in heterogeneous catalysis, production and sale of catalysts, as well as licensing, engineering and construction of catalytic units.

The company was founded in 1940 by Dr. Haldor Topsøe, and today the staff is about 1500. Headquarters, central research laboratories and engineering offices are located near Copenhagen, Denmark. Manufacturing of catalysts is carried out in Frederikssund, Denmark and in Houston, Texas, U.S.A.

CATALYSTS

The wide range of Topsøe catalysts are used in a variety of catalytic process units in the following industries: ammonia, methanol, hydrogen, sulphuric acid, formaldehyde, petrochemicals, oil refining and power generation.

Topsøe's product line includes environmental catalysts for cleaning of off-gases from various industries and of flue gases from power plants and process units.

All Topsøe catalysts have been developed in-house. Topsøe catalysts are supported by technical service, and are also backed by the know-how and resources of the Technology Division and the R&D Division.

TECHNOLOGIES

The process technologies available from Topsøe may be divided into a number of broad groups, as follows:

- Steam reforming, i.e. adiabatic pre-reforming, tubular reforming, air and oxygen-fired secondary reforming, autothermal reforming, and heat-exchange reforming
- Shift conversion and Methanation
- Synthesis, i.e. production of final products, such as ammonia and methanol, from intermediates
- Purification of off-gases, i.e. removal of sulphur compounds, nitrogen oxides, and organic compounds from flue gases and off-gases from industrial plants
- Hydroprocessing and hydrocracking

ENGINEERING SERVICES

Topsøe's range of engineering and technical services includes:

- Process and basic engineering
- Detailed design and critical equipment and plant sections
- Procurement and inspection services
- Supervision during construction, pre-commissioning and start-up
- On-going technical assistance to optimize operation

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