UDK 621.311.182

PRESENT CONDITION OF FLUE GAS CLEANING AT THERMAL POWER STATION

Theodor Vlassopoulos[1], Sergey Vysotskey[2]

1 – Kantor Consulting, Athens, Greece.
2 – Donetsk national technical university, Ukraine

АНОТАЦІЯ: Розглянуті основні компоненти забруднення довкілля при спалюванні органічного палива на теплових електростанціях. Мокра вапнякова технологія є основним методом очищення димових газів від діоксиду сірки. Показані основні напрямки використання відходу процесу десульфуризації – гіпсу. Розглянуті також проблеми забруднення довкілля ртуттю при спалювання палива в котлах

АННОТАЦИЯ: Рассмотрены основные компоненты загрязнения окружающей среды при сжигании органического топлива на тепловых электростанциях. Мокрая известняковая технология является основным методом очистки дымовых газов от диоксида серы. Показаны основные направления использования отхода процесса десульфуризации – гипса. Рассмотрены также проблемы загрязнения окружающей среды ртутью при сжигании ископаемого топлива в котлах.

ABSTRACT: Maine component of environment pollution by burning of fossil fuels at power plants are considered. The basic technology of flue gas cleaning is wet limestone desulphurization. Main directions of desulphurization wastes are shown. Problems of environment pollution by mercury from power plant also considered.

Main problems existing power plants operation in the world are concerned with the environment pollution. There are four main types of environment pollution from power plants: emission of SO_x, NO_x, mercury and CO_2.

The emission of SO_2 mainly result from the combustion of sulfurons fuels. The major share of these emissions comes from the use coal and oil in:
- fossil fired power plants;
- industrial combustion units;
- small combustion units in households and small business;
- traffic sources (use of diesel).

The emission in the traffic sector remained nearly constant despite the rise in vehicles and mileage, due to the reduction of the sulphur content in diesel. In the household and small business sector the emission decreased due to the use of lower sulphur fuels (including switch to gas) and decrease in energy consumption. The emission of industrial sources and public power plants are strongly diminishing due to wide application of desulphurization technology of flue gas.

Most widely applicated scheme of flue gases desulphurization is shown on fig. 1.

The limestone systems installed during last time were mostly forced oxidation systems (LSFO), which demonstrated the ability to achieve similar performance and reliability as lime systems. Although capital costs for limestone systems were higher than lime systems by 10 percent to 15 percent, their lower operating costs have given them a lower life-cycle cost advantage. This has resulted in virtually all wet FGD systems in the United States since the early 1990s being limestone-based.

The early dry FGD systems suffered from a combination of low SO_2 removals and lower reagent utilizations than wet systems; but even so, the dry systems have proven to be the choice for many low sulfur coal-fired boilers due to their lower lifecycle costs.
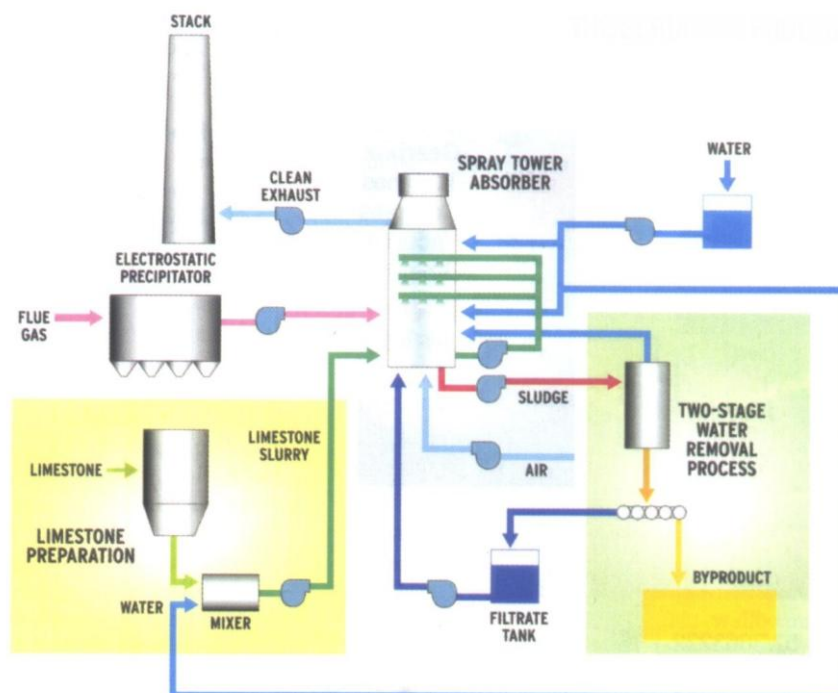

Fig. 1. The scrubber process for SO_2 removal from flue gas leaving the boiler.

Over the past decade, significant process improvements have been made to the dry systems such that process guarantees of 95 percent SO_2 removals are being offered for spray dryer systems and up to 98 percent for circulating dry scrubbers. Even with these improvements dry scrubber applications still have typically been limited to boilers firing coals with sulfur concentrations of less than 2 percent. At higher sulfur levels, wet scrubbers typically became the defacto technology selection.

The recent FGD selections basically have been made along the lines of coal sulfur levels; that is, dry systems (either spray dryer or circulating bed absorbers) are being selected for boilers that burn a low sulfur coal and wet LSFO systems are being selected for boilers that burn coals with 2 percent or greater sulfur levels.

Allegheny Energy Inc. reported the cost of installing scrubbers at two facilities has increased from $888 million to over $1.2 billion. And NRG Energy said its cost estimates for emission control spending by 2010 have increased from $275 million to over $900 million. American Electric Power Co. also said it would defer some installations until after 2010 when it expects costs will be lower.

In a technical paper presented at POWER-GEN International in Orlando in November 2006, Sargent and Lundy reported that 2003/2004 FGD project costs were typically $175–$225/kW, whereas in 2005/2006 they ranged from $275–$400/kW and higher. In an effort to control project capital cost increases and stay within an appropriated budget, some utilities have decided to outsource portions of their FGD systems to third parties.

The large capital cost increases seen over the past couple of years are due to a combined effect of increases in the cost of raw materials needed to build corrosion resistant vessels, increased demand for key system components such as ball mills and pumps, a labor constrained work force and a full workload for many system vendors. This last factor has allowed vendors to selectively bid on those systems that offer the most favorable terms. In addition to these factors are ever-tightening SO_2 emission standards. These require more robust system designs with higher liquid pumping rates, which increases capital costs and parasitic power requirements. A movement also exists toward more stringent water discharge standards (even zero discharge), which is adding still more complexity and further increasing the costs of LSFO FGD systems.
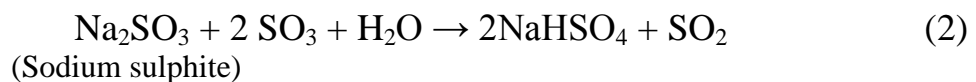
Control of sulphur trioxide (SO_3) emissions from coal fired power plants has recently been the subject of attention from utility management, the public living near the plants, and environmental regulators. What once was an aggravating problem of sulphuric acid corrosion of ducts and electrostatic precipitators (ESP) has become a problem of visible plumes, plume touchdowns, increased operating costs, and increased scrutiny from regulators and the public. Ironically the main cause of the recent attention has been the advent of selective

catalytic reduction (SCR) for control of nitrogen oxides (NO_X). These SCR units actually reduce the amount of air pollution coming from the plants. However, they also increase SO_3 concentrations in flue gas enough to make significant changes in the sulphuric acid dew point and in the visible plume.
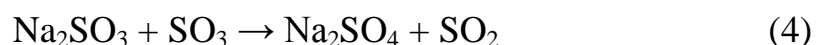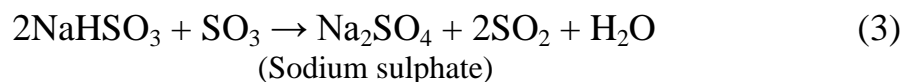
When burned, about one per cent of the sulphur in coal is oxidized in the boiler to form SO_3. The installation of SCR units for NO_X control can more than double the amount of SO_3 in the flue gas by oxidation of sulphur dioxide (SO_2) across SCR catalysts. When the flue gas is subsequently cooled, the SO_3 in the gas is converted to sulphuric acid. This sulphuric acid can condense in air heaters, in ducts and ESPs, and it can become a very fine mist or aerosol in the plume from the stack. Depending on atmospheric conditions, the visible plume appears as a blue-white haze, or a brown cloud carried for miles downwind. At elevated SO_3 concentrations, plume buoyancy can be influenced to the extent that touchdowns of the plume in the vicinity of the plant have occurred at several plants upon startup of the SCR units, leading to public outcry and some regulatory concerns.

Control of SO_3 emissions can be achieved by contacting the flue gas with a clear solution of sodium bisulphite and/or sodium sulphite (SBS solution). The technology is patented by Codan Development LLC and is offered, in conjunction with URS Corporation, Codan's engineering partner.

Ideally the clear SBS solution is injected into the duct before the flue gas is cooled below the acid dew point for sulphuric acid. The sprayed solution dries upon contact with the hot flue gas and forms millions of small alkaline particles that react with the SO_3 in the flue gas according to the following chemical reactions:

$$NaHSO_3 + SO_3 \rightarrow NaHSO_4 + SO_2 \qquad (1)$$
(Sodium bisulphite)   (Sodium bisulphare)

$$Na_2SO_3 + 2\,SO_3 + H_2O \rightarrow 2NaHSO_4 + SO_2 \qquad (2)$$
(Sodium sulphite)

When the sodium to SO_3 molar addition ratio exceeds 1.0, the reactions become:

$$2NaHSO_3 + SO_3 \rightarrow Na_2SO_4 + 2SO_2 + H_2O \qquad (3)$$
(Sodium sulphate)

$$Na_2SO_3 + SO_3 \rightarrow Na_2SO_4 + SO_2 \qquad (4)$$

Alternately, Codan has developed and patented a process known as In-Situ SBS Injection. In this process, a clear solution of a variety of sodium-based reagents (carbonate, bicarbonate or hydroxide) is injected into the duct where it is converted to sodium sulphite or bisulphite by reaction with SO_2 in the flue

gas. Then the same chemical reactions listed above occur to replace SO_2 in the SBS particles with SO_3 absorbed from the flue gas. The end result is the removal of SO_3 and the formation of particles of sodium sulphate and sodium bisulphate, which are then removed with the fly ash.

In all cases, the alkali used for SO_3 control is not consumed by reacting with SO_2. Since SO_2 is not absorbed, very low molar ratios of active sodium to SO_3, typically 1.3 to 2.5, can produce the desired SO_3 removal results. Other chemicals such as lime, limestone and magnesium hydroxide must be used at very high molar ratios, since SO_2 in the flue gas consumes most of the alkali.

Figure two indicates the various potential locations for injecting the SBS solution. Since a solution is being injected, it is necessary to have a three to eight metre section of duct downstream of the injection point and free of obstructions, to allow adequate drying time before the solids contact any surfaces to prevent solids deposition. The duct work and objectives at each plant must be evaluated to select the most desired injection location.
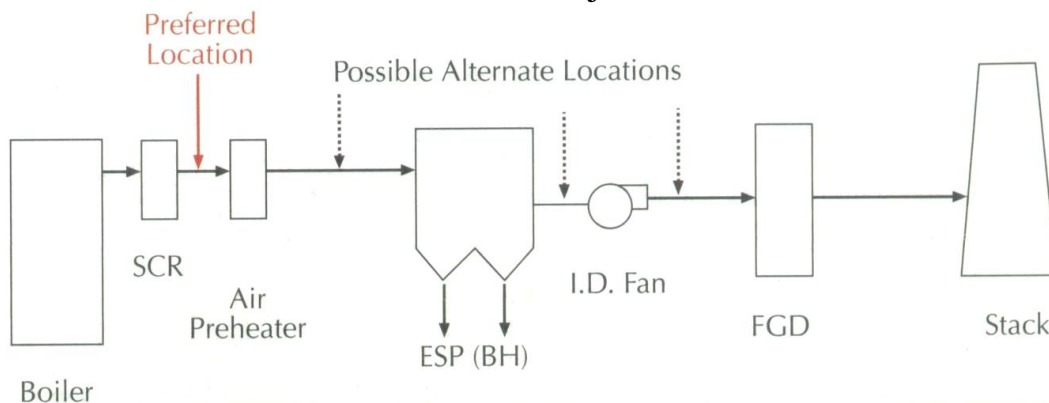

Fig. 2. The optimum SBS injection point is dependent on many parameters, which differ from plant to plant

Fig. 2 is a simplified illustration of the equipment required for the SBS Injection technology. The heart of the system is the injection grid itself. SBS reagent solution is injected into the flue gas through a series of lances with a number of dual-fluid nozzles on each lance. Each nozzle is supplied with both SBS solution and compressed air. The lance itself is cooled by an internal flow of ambient air that is forced into the lance shroud by the differential pressure between the duct and the shield air supply.

After initial pilot testing of the SBS injection process on simulated flue gas in 2000 and 2001, a 265 MW demonstration test was conducted at the AB Brown station Unit 2 of Vectren Corporation, Indiana, USA. The Electric Power Research Institute (EPRI) studied the process in two phases between August and December 2002. URS Corporation directed all aspects of process application, including nozzle and lance development.

Three additional full-scale demonstration programmes were conducted in 2002, at 400 MW, 430 MW, and 750 MW scales, leading to the first commercial systems starting up in 2003.

The first permanent SBS Injection system was installed at the Bruce Mansfield plant of FirstEnergy, which began operation at Unit 1 in March 2003. A total of eight full-scale systems (totaling 5300 MW) are now operational, and several additional full-scale systems (totaling 4000 MW) are being planned for installation in 2005. Some of the SBS Injection systems are installed ahead of the air heater, while others are installed between the air heater and the ESP. The injection point is selected based on evaluation of many parameters, including duct configuration, residence time ahead of major obstacles and major equipment, balance of plant impacts, cost of reagent and objectives for additional process benefits at the plant.

Capital costs for the technology are inversely related to unit size, and have ranged from \$4 to \$10 per kW. Operating costs are highly dependent on the level of SO_3 in the flue gas, the SO_3 removal required, and the reagent contract. Although site specific, operating costs in the US are estimated to fall between \$250 to \$600 per ton of SO_3 removed.

Data from full-scale demonstration tests and many of the permanent installations show that over 90 per cent removal efficiency can be achieved at molar ratios of 1.0 and above, and removal efficiencies above 95 per cent are possible at higher reagent ratios (Fig. 3). Full-scale installations have generally achieved reliable, consistent operation at molar ratios of sodium to SO_3 of about 1.3 to 2.5, depending on site-specific considerations. The reagent cost is by far the largest component of the annual operating cost for the SBS Injection technology. Commercial products are available for reagent (sodium bisulphite solution, sodium sulphite solution, and sodium sulphite solids), but are relatively expensive compared to the use of a flue gas desulphurisation (FGD) byproduct solution. Since the product of the scrubbing of SO2 with caustic or sodium carbonate is a solution of sodium sulphite and bisulphite, a low cost reagent for the SBS Injection process can be made at any plant site willing to install and operate a scrubber for the purpose of producing their own reagent for SBS Injection. Alternatively, the In-Situ SBS process using soda ash or caustic can be considered. If a utility elects to produce its own SBS reagent or use the In-Situ SBS process, the reagent cost could be reduced by 30 to 70 per cent.

The effective removal of SO_3 from the flue gas can provide valuable operation and maintenance (OScM) benefits, in addition to the highly desirable environmental benefit of eliminating the plume opacity aspects of sulphuric acid aerosol emissions. Removal of 90 to 95 per cent of the SO_3 will reduce the acid dew point of the flue gas by somewhere between 4°C and 16°C (depending on the pre-injection SO_3 level), thereby providing significant protection against acid corrosion for all equipment and ductwork downstream of the injection point.

This lower acid dew point allows for flexibility in the temperature of operation of the air heater, and in some cases can result in substantial savings by improving heat rate.

SBS Injection technology is promising for effectively and selectively removing SO_3 from flue gas. The technology is currently being applied at eight power plants totaling approximately 5300 MW, and is being considered for a number of additional applications in the US utility sector. Demonstrations are planned for SO_3 mitigation applications for a utility oil fired boiler and a petrochemical industry fluidized catalytic cracker unit (FCCU). The capability to effectively remove SO_3 has been consistently demonstrated. As the commercial applications accumulate operating experience, it will be possible to better document long-tem reliability, maintenance and operating costs as well as the potential for other plant benefits like reduced corrosion and improved heat recovery.

Wet method of cleaning is assosiated with production of significant quantity of gypsum (by-product). The amount of the by-product (gypsum) is proportional to the SO_2 mass flow separated from the flue gas.

FGD and limestone utilization has some peculiarities.

Limestone is only slightly soluble in water. In the presence of acid, calcium carbonate reacts much more vigorously and it is the acid generated by absorption of SO_2 into the liquid that drives the limestone dissolution process.

$$CaCO^3 + 2H^+ \rightarrow Ca^{+2} + H_2O + CO_2 \uparrow \qquad (5)$$
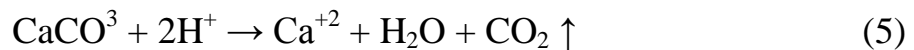
Equations when combined illustrate the primary scrubbing mechanism.

$$CaCO_3 + 2H^- + SO_3^{-2} \rightarrow Ca^{+2} + SO_3^{-2} + H_2O + CO_2 \uparrow \qquad (6)$$

$$Ca^{+2} + SO_3^{-2} + \tfrac{1}{2} H_2O \rightarrow CaSO_3 \cdot \tfrac{1}{2} H_2O \downarrow \qquad (7)$$

In the absence of any other factors, (for example, oxygen in flue gas) calcium and sulfite ions will precipitate as a hemihydrate, where water is actually included in the crystal lattice of the scrubber byproduct.

However, oxygen in the flue gas has a major effect on chemistry, and in particular on byproduct formation. Aqueous bisulfite and sulfite ions react with oxygen to produce sulfate ions (SO_4^{-2}).

$$2SO_3^{-2} + O_2 \rightarrow 2SO_4^{-2} \qquad (8)$$
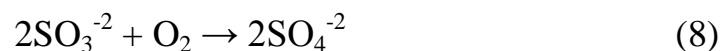
Approximately the first 15 mole percent of the sulfate ions co-precipitate with sulfite to form calcium sulfite-sulfate hemihydrate

[(CaSO$_3$·CaSO$_4$)·½ H$_2$O]. Any sulfate above the 15 percent mole ratio precipitates with calcium as gypsum.

$$Ca^{+2} + SO_4^{-2} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O \qquad (9)$$

Calcium sulfite-sulfate hemihydrate is a soft, difficult-to-dewater material that previously has had little practical value as a chemical commodity. Gypsum, on the other hand, is much easier to handle and has practical value. These factors are driving utilities to install forced oxidation systems for gypsum production. Three major markets exist for gypsum: wallboard manufacture, cement production and soil stabilization. Wallboard manufacture currently leads the way by far. According to the United States Geological Survey (USGS) in 2006, almost 91 percent of domestic consumption, which totaled 41.6 million tons, was accounted for by manufacturers of wallboard and plaster products. Some 3.0 million tons was used for cement production, 1.1 million tons for agricultural applications and small amounts for a range of industrial processes such as smelting and glassmaking. At the beginning of 2006, the capacity of operating wallboard plants in the United States was about 37.6 billion square feet per year.2 At present, synthetic gypsum from FGD systems supplies about one quarter of the wallboard industry's needs.

For process of wallboard manufefacture original gypsum must be rather pure, with a CaSO$_4$·2H$_2$O content of 92 percent or better. Precursors in FGD systems to meet these requirements include the use of high-purity limestone (93 percent or greater calcium carbonate content) and sufficient air compressor capacity to convert all sulfite in the scrubber to sulfate. Obviously, the compressors must be able to introduce at least the stoichiometric amount (1:1 ratio) of oxygen required for the SO$_2$ being removed, but typically the ratio must be at least 1.5:1 and often higher to ensure complete conversion of sulfite to sulfate. Under-designed air compressor capacity results in byproduct quality that cannot meet required standards.

Moisture content and an interrelated issue of dissolved salt concentration (chlorides in particular) are also very important. Typically, calcining plants require the moisture content of raw material to be at or below 10 percent. Gypsum as it is first produced in the scrubber is a slurry. The common method of moisture reduction, and in part slurry density control in the scrubber, is to route the slurry through one or more banks of hydrocyclones to remove moisture by centripetal action, followed by drying either via vacuum drum or, for consistent solids of 90 percent dryness, belt filters. Even at 10 percent moisture, solids can contain significant chloride concentrations, as often the chloride levels in the scrubber process slurry can reach or exceed as much as 30,000 parts-per-million (ppm). This is particularly true at plants burning eastern bituminous coal. So, even with moisture reduced

to 10 percent, the byproduct chloride concentration can easily exceed the common 100 ppm maximum guideline for wallboard production. This can easily be overcome by installing a freshwater wash at the beginning of either the vacuum drum or the belt filter process. Calcium chloride, and the much smaller concentrations of magnesium chloride, are soluble and quickly wash out of the filter cake.

As mentioned earlier, synthetic gypsum from FGD systems supplies only a portion of what is received by wallboard plants. However, with additional FGD units coming on line, the market may become saturated within five years or so. The housing market downturn in mid-2007 shows that demand can be variable, so utility personnel must give this idea careful investigation before assuming that their gypsum byproduct will find a market in the construction industry.

Calcium sulfate is used in the cement industry as a conditioning agent. Small amounts of the material improve cement's setting characteristics. I have no exact data regarding gypsum quality requirements for this market, but have learned that they are not as stringent as for the wallboard industry. This may be due to the fact that impurities in synthetic gypsum, such as un-reacted limestone, would not adversely affect cement properties.

Demand for gypsum in the agricultural industry is not nearly as great as for wallboard manufacture. However, reports indicate that some expanded use may be in the offing. Calcium and sulfur are two minor, but essential, elements for crop growth. Gypsum represents a ready and inexpensive source of each. Perhaps the emerging biofuels industry will generate an increased need for additional benign fertilizers. Impurities are much more tolerable in gypsum used for agricultural purposes. Even so, chlorides still must be washed from the solids as the high salinity would otherwise be detrimental.

The quality of the gypsum is determined by the share of impurities contained such as silicates, iron, aluminium and magnesia compounds. These compounds enter the by-product via fly ash and/or the absorbents.

Chlorides and fluorides in gypsum mainly result from the fuel used. Table 1 shows a mineralogical composition of a typical FGD-gypsum.

The quality of the gypsum is influenced by different parameters, such as:
- used absorbent (lime or limestone),
- share of fly ash dragged into the absorber and
- installations for separating gypsum.

There are several measures used the world for reduction of NO_x emission. They include combustion modifications (primary measures), noncatalitic and selective catalytic reduction (secondary measures). Combustion modifications to reduce: the combustion temperature; the oxygen level in the so-called primary zone and the residence time zones of high temperature.

The Selective Catalytic Reduction process is a secondary measure to reduce NO_x emissions. In nearly 95 % of all existing combustion installations in the world; this process is implemented.

In the Selective Catalytic Reduction process, NO_x is reduced with ammonia in the presence of a catalyst to nitrogen and water. The principle of the SCR process as well as the reactions at the catalyst are shown in Fig. 3.
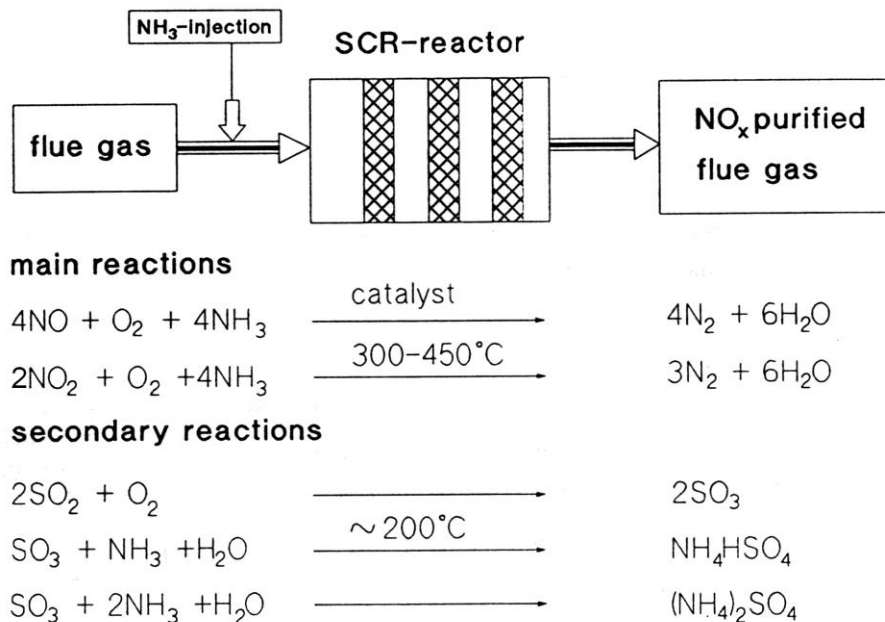

Fig. 3. Diagram of the SCR process.

The required NH_3/NO_x ratio ranges between 0.8 and 1.0. The reaction of nitrogen oxides and ammonia is selective, which means that oxidation of ammonia and sulphur dioxide should not take place, but oxygen is essential for selective behaviour and secondary reactions and products may not always be excluded. The formation of ammonium sulphates $((NH_4)_2SO_2, NH_4HSO_4)$ may pose problems. Its corrosive and sticky nature may cause damage to downstream facilities. Using catalysts with SO_2/SO_3 conversion rates lower than 1 %, the formation of ammonium sulphates can be avoided or limited. In the FRG, the amount of unreacted ammonia, which leaves the reactor with the flue gases, known as ammonia slip, is limited to 5 vpm (3.8 mg/m3) due to ensure the utilization of the fly ash.

The efficiency of the Selective Catalytic Reduction process is determined by catalyst parameters such as: the high activity in wide temperature ranges; the high selectivity; the chemical resistance (e.g. against SO_2, halogenes and heavy metals); the mechanical stability (against erosion); the low pressure drop; the long service life and; the unoroblematic disposal.

The catalysts in use for Selective Catalytic Reduction are mainly parallel flow catalysts, of which there are two types, plates or extruded. In some cases the packed bed catalyst with active coke or zeolite pellets is implemented.

The extruded type, more often called honey comb is self-supporting and a mixture of carrier material and the active components. Characteristic of the honey comb catalyst is the pitch size or width of the catalyst opening, which can vary depending on the fly ash content of the flue gas.

The plate type catalysts have a metal (iron) net, on which the active substance is applied. Layers of corrugated plates or a mixture of corrugated and level plates are fitted together to a catalyst element. The main geometrical specification is the distance between two plates, which again varies for different flue gas compositions. Plate type catalysts have a higher resistance towards deposition and blockage than honey comb types.

From the end of 2000 the US Environmental Protection Agency (EPA) anounced its intent to regulate mercury emissions from coal generators. EPA initiated the Mercury Information Collection Request (MICR) to 84 plants to provide new information to assist in making future regulatory determinations on controlling mercury emissions from coal fired plants.

Based on these data, under the President's Clear Skies Act of 2003, mercury emissions from industry is planned to be limited in two phases - 26 tons by 2010 and a cap of 15 tons by 2018, corresponding to a 47 per cent and 69 per cent reduction respectively.

This corresponds to an annual emission cap of 5 tons.

The Clean Power Act does not have any provision for mercury allowances. It calls for a mercury emission limitation for individual units of no more that 2.48 grams/1000 MWh, and does not differentiate by coal type.

The affected units under the Clear Skies Act would be exempt from the New Source Review if they comply with the NSPS emission limit of 0.015 lb/GWh (6818 mg/GWh).

The US Department of Energy (DOE) has estimated that at 90 per cent mercury removal, the control cost may range between $25 000 and $70 000 per lb ($55 556 and $155 556 per kg) of mercury 'removed. At this rate mercury control could cost the coal fired utility industry some $2500-7300 million per year.

Fig. 4 shows the mercury control technologies under development - wet scrubbing, sorbent injection, corona discharge, catalyst, fixed/fluid beds and precombustion coal cleaning.
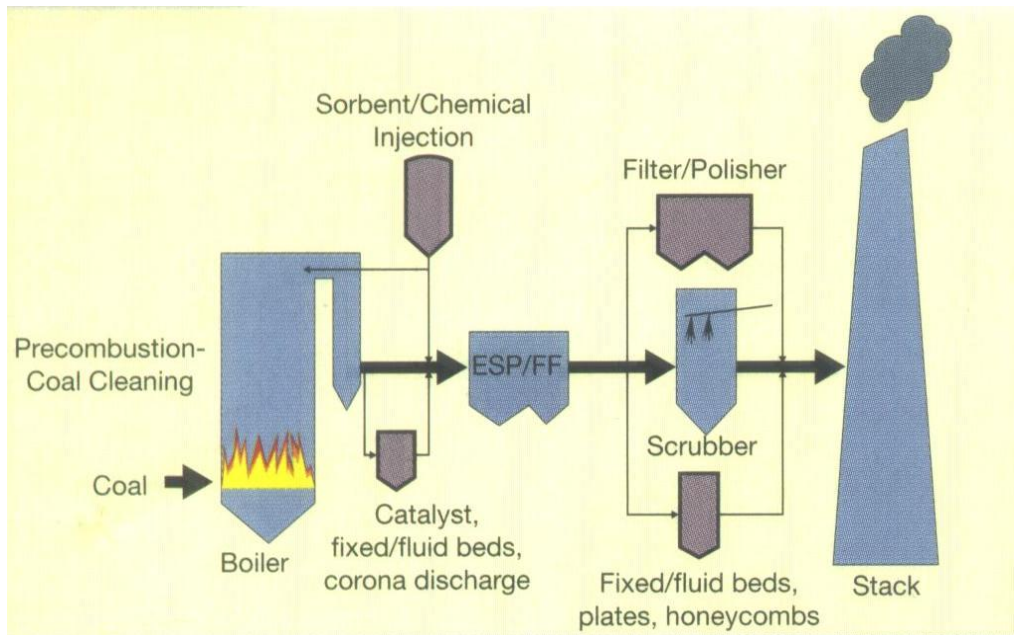
Fig. 4. Power plant mercury control.

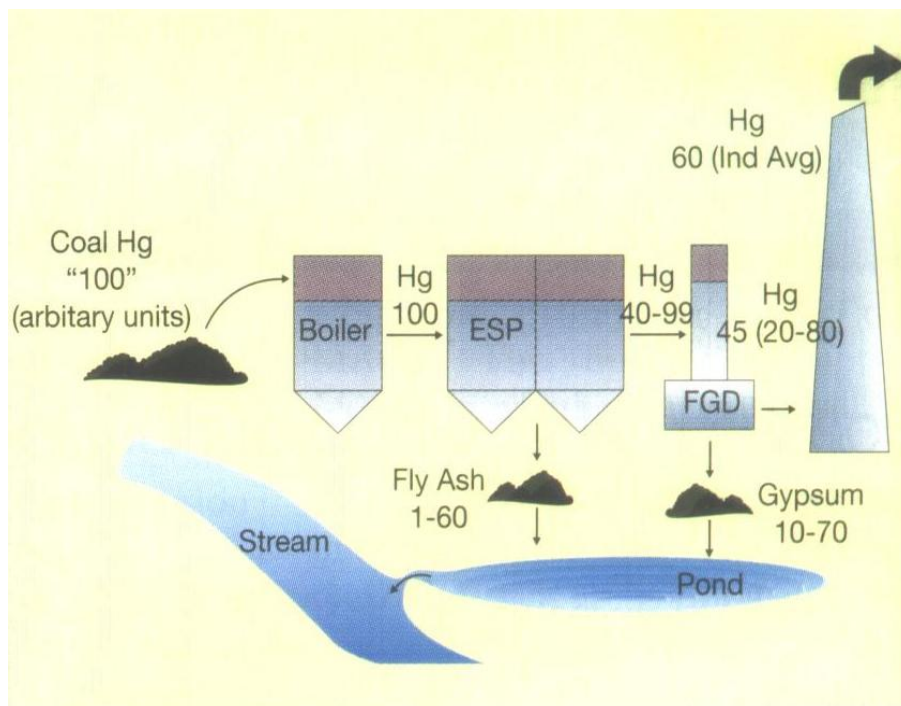Mercury distribution by different part of duct is shown on fig. 5.

Fig. 5. Fate of mercury (Hg) in power plants.

Some of the major development projects underway include:

• Full scale testing of enhanced mercury control in wet FGD by Babcock and Wilcox

• Full scale testing of mercury control by sorbent injection by ADA-ES.

• Pilot scale study of non-thermal plasma based technology by Powerspan Corporation.

• Pilot scale study of mercury removal in ESP at lower temperature by Consol Coal.

• Mercury removal by an advanced hybrid participate collector (AHPC) - combination of ESP and baghouse by Energy and Environmental Research Center (EERC).

• Development of cost effective carbon and other chemical based sorbents for mercury removal in ESP or baghouse.

• Development and improvement of effectiveness of calcium based sorbents and oxidizing catalysts. The developers include URS Group, Southern Research Institute, and Arcadis.

• Pre-combustion mercury removal from low-rank coals privately funded by KFx Inc. & Associates. This novel and cost-effective technology also achieves multi-pollutant control.

As far as carbon dioxide emission is considered we do not have acceptable technology for its capture from flue gases by burning of fossil fuels.