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# Selective Catalytic Reduction NO by Ammonia Over Ceramic and Active Carbon Based Catalysts

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## 1. Introduction

The need for environmental protection is an indisputable objective. This is particularly important wherever environmental burden has become so high that the environment is no longer capable of self-purification. Such situation exists in our country. A major problem is the protection of the atmosphere.

The main pollutants emitted into the atmosphere include carbon monoxide (CO), sulphur dioxide (SO<sub>2</sub>), nitrogen dioxides (NO<sub>2</sub>), hydrocarbons (CH), and particulates.

Share of individual sectors of the industry in the total emissions is not identical. It is demonstrated by Fig. 1.

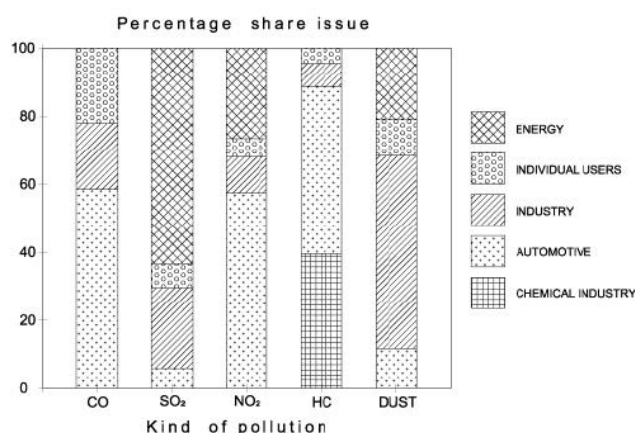


Fig. 1. Share of primary industries in emissions of toxins and particulates.

Although it is difficult to compare the harmfulness of each of the toxins to one another, it is assumed that the relative impact of NO<sub>x</sub> : CO : HC on the human body is like 100 : 1 : 0.1. It follows that nitrogen oxides are the most harmful for the human body. According to the data presented in figure 1, nitrogen dioxides are emitted mostly by transport, followed by the power industry and heavy and light industries. On the other hand, sulphur compounds are particularly dangerous for the environment. Here, the ratio is different because these compounds are emitted mainly by the power industry, followed by heavy and light industries, and then households.

The first method of combat is to reduce emissions by lowering energy consumption and fuel consumption per unit of energy produced. However, it is also obvious that although the above processes are essential, they are slow and demand constant disproportionate increase of expenses. In such case it becomes necessary to act in other directions, i.e. active and passive control of environmental pollutants.

Active methods include changes in the combustion process, but especially changes in the fuel, including its desulphurisation. However, fuel desulphurisation is an extremely expensive process and can only be used in the situations where fuel consumption is relatively small and there are practically no other methods of solving the problem.

Fuel desulphurisation does not solve the second problem, which is emission of nitrogen oxides. Here, the most adverse effects are produced by coal-burning devices. This is due to high combustion temperatures occurring in the process. In this case design changes (active methods) do not provide major results.

Much better results are obtained by the introduction of design changes in the processes of combustion of hard and brown coal in the so-called dry processes. The obtained results are not as good as in the case of newly built systems, but they are still significant (particularly with respect to hard coal combustion).

Changes with active methods do not result in achievement of target values – present and future emission standards. Therefore, passive methods must be used, particularly catalytic methods.

Composition of exhaust gases, including their concentrations of toxic components, varies widely. It depends on the type of fuel and the combustion process.

While emissions of sulphur oxides depend on its content in the fuel, nitrogen oxides produced in the combustion process depend, among other, on the following factors: combustion temperature, concentration of reagents (oxygen and nitrogen) during the combustion, contact time of reagents, especially in the high temperature zone, type of furnace equipment and fuel type and the quality of its mixture with air.

At present nitrogen oxide emissions can be limited by means of:

- processing and refining of fuel,
- limiting the amount of nitrogen oxides produced in the combustion process,
- removing nitrogen oxides from exhaust gases.

The first direction is feasible when it comes to crude petroleum, but in the case of coal it is unlikely to be used in the near future, because it is ineffective and requires building of a fuel refining industry.

The next two directions are currently being used and developed on a large scale in many highly industrialised countries. Nitrogen oxides are reduced by 10 to 80% depending on the type of fuel, type of boiler, and the applied method. The third direction is very effective since it reduces the nitrogen oxide content in exhaust gases by 70 to 95%.

At present the methods of catalytic selective reduction with the use of ammonia as a reducing factor are the most widely used. The process is described as a selective one because ammonia has greater chemical affinity to nitrogen oxides than to oxygen.

In this method nitrogen oxides are converted to nitrogen and water, i.e. neutral components of the atmosphere. Yield of reaction depends on: the temperature, type of catalyst, ratio of ammonia to nitrogen oxides and gas flow rate through the catalyst layer. The effectiveness of the process is primarily determined by the catalyst activity.

Nitrogen oxides are reduced by ammonia selectively on catalysts prepared with the use of noble metals (Pt, Rh, Pd) and metal oxides ( $V_2O_5$ ,  $TiO_2$ ,  $MoO_3$ ). Effective catalysts used in

SCR reactors are catalysts deposited on honeycomb ceramic monoliths, containing longitudinal ducts with square or round cross-section [1-4].

The main advantages of such solution are:

- low resistance of gas flow through the catalyst bed,
- small catalyst volume,
- storage of ammonia in catalysts, which ensures high flexibility of operation under variable load conditions,
- small losses of ammonia,
- resistance to poisoning,
- possibility of using spent catalysts as a raw material in the ceramic industry.

## 2. Nitric oxides

Depending on the combustion process, waste gases differ in chemical composition, concentration of toxins, dispersion of particulate matter, and temperature. The composition of exhaust gases may differ, just as there may also exist differences in the techniques of removal of their toxic components.

The primary toxic components of exhaust gases that must be removed are nitric oxides and sulphur dioxide.

Removal of nitric oxides is facing two major difficulties arising from the very nature of the process.

Nitric oxides created in the processes of industrial combustion consist almost entirely of nitrogen oxide NO (90%). Nitrogen oxide is very poorly soluble in water. Consequently, the methods of waste gas scrubbing face the problem of conversion of nitrogen oxide to oxides (by oxidation), which, on the other hand, dissolve better.

The second problem is the presence of oxygen in exhaust gases. Oxygen is present in the combustion process in excess (3-12%), ensuring optimum fuel combustion and preventing formation of carbon monoxide, soot, and boiler corrosion. However, excess oxygen hinders reduction of nitrogen oxides obtained with the use of chemical reducing agents because they react more readily with free oxygen than with oxygen from nitrogen oxides. Still, that problem can be resolved by means of catalysis.

Selective Catalytic Reduction (SCR) – enables reduction of nitrogen oxides using ammonia in the presence of a catalyst to form nitrogen and water. At the entrance to the reactor the exhaust gases must be mixed to the maximum possible extent with ammonia.

Nitrogen oxide (NO) is formed from water and nitrogen, present in fuel and atmospheric air. During the combustion of pulverized coal, over 80 % of nitrogen oxides are formed from nitrogen present in fuel. Natural gas contains approx. 0.5% nitrogen, fuel oils – approx. 0.1-0.2% nitrogen, and carbon – up to 2 % nitrogen.

Nitrogen oxide (NO) turns into nitrogen dioxide (NO<sub>2</sub>) in the presence of oxygen in the air, with the speed of reaction depending on the concentration of nitrogen oxide.

Combustion processes produce nitrogen oxide (NO) whereas nitrogen dioxide (NO<sub>2</sub>) is formed by oxidation of nitrogen oxide in atmospheric air. In addition to nitrogen oxide (NO) and nitrogen dioxide (NO<sub>2</sub>), boiler flue gases also contain nitrous oxide (N<sub>2</sub>O). The greatest amount of nitrous oxide is formed during combustion of coal, and the least amount – during combustion of natural gas. Nitrous oxide participates in reactions destroying the ozone layer of the Earth, thus contributing to the formation of the greenhouse effect. Specifically, it absorbs infrared radiation, preventing cooling of the Earth during the night.

Some of nitrogen oxides formed during combustion are decomposed into oxygen and nitrogen by coke formed at the same time in the process of pyrolysis. This process occurs with high intensity during fluidal combustion and, in addition to low combustion temperature, contributes to the generation of minimum amounts of nitrogen oxides in this type of combustion. Boiler flue gases containing  $\text{NO}_x$  consist of approx. 95% nitrogen oxide (NO) and approx. 5% nitrogen dioxide ( $\text{NO}_2$ ). Concentration of nitrogen oxides in boiler flue gases depends on the type of furnace, the temperature inside it, the method of fuel combustion, the type of fuel, the excess air ratio, and the boiler load.

Nitrogen oxides formed in the boiler combustion chamber can be divided into:

- thermal,
- fuel,
- fast.

Thermal nitrogen oxides are formed from nitrogen contained in atmospheric air during the combustion of each fuel at very high temperatures. Fuel nitrogen oxides are formed from nitrogen contained in fuel and their formation depends on the type of fuel and the method of its combustion. Fast nitrogen oxides are formed from nitrogen contained in atmospheric air, primarily during combustion of gaseous fuels, and their formation depends mainly on the excess air ratio.

Fluidal combustion at a temperature of 800-1000°C is accompanied by formation of fuel nitrogen oxides. Spatial combustion (in pulverized-fuel boilers) at a temperature of 1300°C is also accompanied by formation of mainly fuel nitrogen oxides, but with an increase in temperature their amount diminishes whereas thermal nitrogen oxides appear, which above the temperature of 2100°C constitute the only oxides. In the temperature range of 1300-2100°C fast nitrogen oxides are also produced in the amount of 7-10% of the total amount of formed nitrogen oxides. At temperatures above 2300°C (low-temperature plasma) thermal nitrogen oxides are formed.

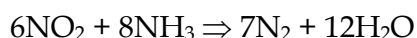
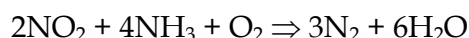
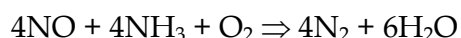
In order to reduce formation of nitrogen oxides, temperature of the flame cone must be lowered, oxide content in the combustion zone must be reduced, and the duration of fuel staying in the high-temperature zone must be shortened.

With the above methods, the amount of formed nitrogen oxides can be reduced by no more than 40-50% which, however, is insufficient to meet the requirements of European standards. To comply with the standard, two methods are used: selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR).

### 3. Methods of denitrification of exhaust gases

Catalytic reduction of nitrogen oxides by ammonia in the presence of a catalyst

The reduction results in the formation of nitrogen and water:



The catalyst load is measured according to the exhaust gas flow rate, i.e. the amount in  $\text{Nm}^3$  passing through 1  $\text{m}^3$  of catalyst over 1 hour. Obviously, the lower the load, the higher the



effectiveness of the process of exhaust gas denitrification. Catalysts can be plate type or honeycomb type.

A plate catalyst is made of high-grade stainless steel with active mass, consisting of titanium oxides (TiO<sub>2</sub>), vanadium (V<sub>2</sub>O<sub>5</sub>), tungsten (WO<sub>3</sub>) or molybdenum (MoO<sub>3</sub>).

It is highly resistant to erosion, has high mechanical and thermal strength, causes small pressure losses, and has a low propensity for clogging. It can operate in areas with high particulate concentrations, i.e. in front of an installation for particulate removal and desulphurisation of exhaust gases.

Ceramic honeycomb catalyst has an identical active layer, but it works well in areas of low particulate emissions. Consequently, it must be placed behind the installation for particulate removal and desulphurisation of exhaust gases. However, in order to ensure proper operating conditions for the catalyst, exhaust fumes must be additionally heated up because they are cooled down in the desulphurisation installation. The optimum operating temperature of the catalysts is 300-450°C if they are connected in front of an air heater, and 280-380°C if they are connected in front of the flue. A catalyst operates between 2 to 3 years in an area with high particulate concentration, and between 4 to 5 years in a clean area. 1 MW of power plant capacity requires approx. 1 m<sup>3</sup> of catalyst. With up to 95% effectiveness, it is the most effective of all the methods in use. However, this is the most expensive method in terms of investment and operation. Sizes of commercial catalysts with honeycomb structure and square meshes (grid cross-section) are shown in Table 1. Additionally, various manufacturers offer catalysts in the form of corrugated plates.

Determination	Sizes (mm)	
	mesh	wall thickness
Gas-fired boiler	3 to 6	0.5 to 1.6
Oil-fired boiler	6 to 8	1 to 1.5
Coal-fired boiler	6 to 10	1 to 2

Table 1. Dimensions of industrial catalysts with the honeycomb cross-section.

After passing through the electrostatic precipitator, the particulate content in exhaust gases does not exceed 50 mg/m<sup>3</sup> Although catalyst holes practically never become clogged, fine particulate matter deposits on the surfaces of its walls, deactivating the device. The problem is solved by selection of a catalyst with proper resistance to abrasion, mesh sizes, and wall thickness.

Selective non-catalytic reduction (SNCR) of nitrogen oxides by ammonia.

It is a variation of the first method but without the use of a catalyst.

It has 50% effectiveness but it is cheaper in terms of investment and operation than the previous one. Ammonia reacts with nitrogen oxides at a temperature of 800-1000°C without a catalyst, producing nitrogen and water. At other temperature ranges the reaction occurs very slowly and ammonia enters the flue. When the boiler load changes, it is accompanied by changes in the temperature of the exhaust gases and its distribution in the boiler.

If ammonia is injected at a certain point where the existing temperature is suitable for the occurrence of the reaction, then with a change in the boiler load – and thus a change of the temperature at that point – the reaction will not occur.

Irradiation of hot exhaust gases (at a temperature of 900 °C) by electron beam.

Free radicals formed during irradiation of exhaust gases by electron beam react with  $\text{NO}_x$  and  $\text{SO}_2$  molecules, creating ammonium nitrate and ammonium sulphate.

The DESONOX method of combined desulphurisation and denitrification of exhaust gases.

The essence of the method is catalytic oxidation of sulphur dioxide to sulphur trioxide, of which sulphuric acid is produced, while nitrogen oxides are also catalytically reduced to nitrogen (with the SCR method). This method offers 95% desulphurisation and 90% denitrification of exhaust gases. It is free of sewage and waste while the produced sulphuric acid is of commercial grade.

The Bergbau Forschung-Uhde method.

In this method sulphur dioxide is absorbed from exhaust fumes by special active coke, obtained from hard coal. Ammonia is fed to the absorber and reacts with nitrogen oxides without a catalyst. Active coke is regenerated at a temperature of  $400^\circ\text{C}$  in the desorber, from which gas rich in sulphur dioxide outflows and is used in sulphuric acid production.

Exhaust gases that passed through the desulphurisation installation and electrostatic precipitators for the capture of particulate matter have a temperature below  $100^\circ\text{C}$ . This temperature is too low for effective operation of the catalyst. It follows that exhaust gases must be heated up to appropriate temperature. However, in the case of old system designs there is often not enough place to incorporate the appropriate heating devices (not to mention the energy costs of such heating).

Therefore, there is no choice but to use catalysts that could operate efficiently at waste gas temperatures, particularly considering the fact that the amounts of gases that must be heated up pose a serious energy problem that puts into question the efficiency of the power acquisition system.

Low-temperature catalysts could also be used in the removal of nitrogen oxides from various technological processes [1-11].

## 4. DeNO<sub>x</sub> carriers and catalysts

### 4.1 The process of selective catalyst reduction (SCR) of nitric oxides with ammonia

Catalysts of denitrification of exhaust gases from power boilers must meet several requirements relevant to users. They should be characterised by:

- **Stability**

- a. thermal resistance:

The catalyst should maintain its activity at a temperature up to  $500^\circ\text{C}$  for a long period of time under the operating conditions of an industrial boiler.

- b. resistance to poisoning:

Acid centres are poisoned mostly by alkali metal ions while centres in oxidation reactions are poisoned mainly by arsenic oxide. Therefore, catalysts should be selected that are resistant to the above poisons. Active components, e.g.  $\text{CuO}$ ,  $\text{Fe}_2\text{O}_3$  or carriers react with gas components ( $\text{SO}_3$  etc.). That problem was resolved through the use of catalysts based on vanadium pentoxide deposited on titanium dioxide. The results of some studies have shown that vanadium-titanium catalysts can be promoted with some alkali metal salts, e.g. sodium sulphates and lithium sulphates, whereas potassium sulphate content had a negative impact on their activity. On the other hand, it was determined that the negative impact of some poisons on catalytic activity occurred only in the absence of  $\text{SO}_2$  and disappeared in its presence. Also of note is the observation that a catalyst can be completely regenerated by washing it with water.

c. resistance to abrasion:  
In the case of gases containing large amounts of particulates, a catalyst is subject to abrasion. In general, abrasion resistance is inversely proportional to catalytic activity. Therefore, it is important for industrial catalysts to be resistant to abrasion, and when a catalyst is poisoned especially in its surface layer, catalytic activity is maintained with gradual abrasion of the surface (poisoned) layers.

- **High activity over a wide range of temperatures of the process**  
The temperature of exhaust gases depends on changes in the boiler load but, despite this, the effectiveness of denitrification must be maintained at the same level. Vanadium catalysts deposited on TiO<sub>2</sub> show highest activity at lower temperatures, in the range of 300 - 400 °C, whereas WO<sub>3</sub> on titanium dioxide or V<sub>2</sub>O<sub>5</sub> WO<sub>3</sub> on titanium dioxide show highest activity at somewhat higher temperatures.

**Low conversion of SO<sub>2</sub> to SO<sub>3</sub>**  
Composition of the gases depends on the type of burnt fuel. Gases from the burning of coal and heavy heating oils contain SO<sub>2</sub>, SO<sub>3</sub>, and particulates. The denitrification catalyst should cause minimum oxidation of SO<sub>2</sub> to SO<sub>3</sub>. In the course of this reaction there is increased corrosion of the apparatuses and deposition of acid ammonium sulphate, as a result of reaction of SO<sub>3</sub> with ammonia below the crystallisation temperature at the subsequent apparatuses of the system. For this reason, vanadium pentoxide is being partially replaced in the catalyst by other metals, e.g. tungsten trioxide. Thanks to this, catalysts are obtained that enable acquisition of large conversions of nitrogen oxides at minimum oxidation of sulphur dioxide.

Small pressure drop and low particulate retention on the catalyst bed  
Despite the use of different types of electrostatic precipitators to remove particulates from exhaust gases, they contain from a few tenths of a milligram to several grams of particulates per cubic meter of exhaust gases. This causes clogging of catalyst bed in the form of various types of granulates, extrudates, or spheres [12].

**Selection of DeNO<sub>x</sub> catalyst carrier**  
Over the course of more than a dozen years, many types of catalysts have been tested in a number of laboratories and in some cases the method of their manufacture was patented. For example, according to Japanese researchers [7] the examined denitrification catalysts can be classified by the type of carrier used, as shown in Table 2.

Determination	Type of carrier		
Activity	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>
Resistance to SO <sub>2</sub>	high	average	average
Selectivity	high	low *	low **
Oxidation of SO <sub>2</sub>	low	high	high
Regeneration	possible	impossible	impossible

\*formation of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>      \*\* formation of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>      \* \* \* removal of deposited NH<sub>4</sub>HSO<sub>4</sub>

Table 2. Comparison of DeNO<sub>x</sub> catalyst carriers.

The presented data suggest that the best DeNO<sub>x</sub> catalyst carrier is titanium dioxide. Titanium carrier can be prepared with the use of several methods. A commonly used method is precipitation of TiO<sub>2</sub> by TiCl<sub>4</sub> hydrolysis with water [13].



Inomata and associates prepared both crystallographic forms of titanium dioxide: anatase and rutile by hydrolysis of, respectively, titanium sulphate or titanium chloride. Mixed anatase and rutile compositions are obtained by calcination of commercial titanium dioxide. In general, titanium dioxide has a small specific surface area. As a result of the so-called flame hydrolysis of  $\text{TiCl}_4$ , a high-purity (over 99.5%) carrier is obtained, with crystallite size of the order of 10-30 nm., specific area of approx. 55  $\text{m}^2/\text{g}$ , and approx. 75% anatase content (the rest consists of rutile). This is a commercial product by Degussa [14]. Rhone-Poulencs, on the other hand, produces  $\text{TiO}_2$  by precipitation from titanium sulphate solutions. The product obtained this way, with the surface area of approx. 100  $\text{m}^2/\text{g}$  and the crystallite size of the order of 300 nm., consisted exclusively of contaminated anatase with approx. 2% sulphate ions. Table 3 shows physicochemical properties of carriers formed from the two types of titanium dioxide discussed above. As we can see, compared to the carrier obtained by the flame method, the carrier obtained from precipitated titanium dioxide is characterised by almost twice as big specific surface area, somewhat greater porosity, and bimodal character of the porous structure.

$\text{TiO}_2$	flame	precipitated
Crystalline phase	75% anatase, 25 % rutile	100% anatase
Specific surface area [ $\text{m}^2/\text{g}$ ]	48	92
Pore volume [ $\text{m}^2/\text{g}$ ]	0.34	0.40

Table 3. Comparison of the properties of carriers formed by extrusion from different types of titanium dioxide (Shape: cylinders; Diameter: 4 mm; Length: 4 mm).

Carriers from titanium dioxide obtained by the flame method maintain their properties up to the temperature of approx. 400°C, after which there is a gradual reduction of the specific surface area and porosity as well as recrystallisation of anatase to rutile and an increase in the size of pores. At a temperature of approx. 700°C the carrier contains only rutile, the specific surface area shrinks to under 20  $\text{m}^2/\text{g}$ , and porosity does not exceed 0.1 ml/g. By choosing the calcination temperature of the carrier, the ratio of anatase to rutile content can be regulated. Also, use of calcination temperatures higher than 400-500°C may lead to significant changes in its properties and the porous structure. The duration of calcination also exerts some influence on the properties of the carrier, but it is less significant. Carriers from precipitated  $\text{TiO}_2$  are more stable, they maintain anatase structure up to approx. 900°C, but starting from approx. 400°C there is also a gradual reduction in porosity and the specific surface area, although this process is much slower than previously. Above the temperature of 800°C there is a clear sintering of pores, the bimodal structure disappears – sintering occurs in smaller pores (8 nm.) while bigger pores shrink in diameter (300 nm.). Haber and associates [15] developed a method for obtaining very fine crystalline anatase with the specific surface area of the order of 120  $\text{m}^2/\text{g}$  by hydrolysis of titanium butoxide (IV). Aluminium and silicon carriers initially used to produce catalysts of nitrogen oxide reduction came mainly from typical industrial production and then techniques were developed for homogenous precipitation, i.e. carrier precipitation from solutions, when the process takes place simultaneously in the whole mass. For example, Shikada et al. [16] used that method to produce a silicon-titanium carrier. Urea dissolved in acidified solution of sodium metasilicate and titanium tetrachloride decomposes during heating and the released ammonia increases the pH of the solution in a controlled manner and causes precipitation.

Those so-called mixed carriers are characterised by higher mechanical strength and thermal stability as well as exhibit interesting properties due to their diversified surface acidity.

The activity of the DeNO<sub>x</sub> catalysts used in the installations can be improved by a reduction of diffusion resistance in the catalyst pores [17]. This new type of catalyst is based on a titanium-silicon carrier. Although other researchers also used a titanium-silicon carrier [18], it emerged that catalyst activity can be increased thanks to the acquisition of a bimodal structure and provision of adequate mechanical strength of the monolith. According to Solar et al. [19] a titanium-silicon carrier combines the benefits of both types of oxides: introduction of silica ensures acquisition of the appropriate porous structure, while titanium oxide layered on pores makes the carrier exhibit its surface properties. After deposition of vanadium the obtained V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>/SiO<sub>2</sub> catalyst maintains its properties at a temperature much higher than its normal operating temperature, i.e. in the range of 350 to 380°C.

There are also reports [20] of high activity of DeNO<sub>x</sub> catalysts whose carrier is silica, on which a few percent of TiO<sub>2</sub> were deposited by impregnation in order to stabilise vanadium oxide on the surface of carrier (prevention of agglomeration). A catalyst of this type shows high activity in the reaction of reduction of nitrogen oxides by ammonia. At a temperature below 200°C they are excellent catalysts of the DeNO<sub>x</sub> process [21, 22], may form compositions with a titanium-vanadium catalyst, are active in a wider range of process temperatures, and are more resistant to deactivation [23]. The method of production described above is very similar in the case of catalysts without zeolites. An important difference is the deposition of active metal on zeolite by means of exchange. The applied metals are mostly copper and iron, but also other transition metals, including noble metals. The zeolites most commonly used for this purpose are mordenite and ZSM-5, but other zeolites are also appropriate and cited in the literature.

Ion exchange of zeolite should be made before zeolite is mixed with other components in the first stage.

According to Boer et al. [24] the main components of the DeNO<sub>x</sub> catalyst carrier are titanium dioxide and zeolites, which constitute a homogenous structure. Attempts were also made to deposit the active layer on the carrier surface, the so-called "washcoat", but this solution did not find wider practical application [25]. Apart from TiO<sub>2</sub>, which is the primary carrier component, preferably in the form of anatase, and the previously-mentioned silica [19, 26], transition metal oxides are also added to the formed carrier. [27]. An important role is fulfilled by various types of inorganic additives introduced together with TiO<sub>2</sub>, e.g. fibreglass and glass powder, diatomaceous earth, silica gel, aluminium oxide, and titanium dioxide in the form of sol or gel. Those additives reduce the propensity of extruded monoliths to crack during the subsequent thermal operations and ensure its adequate mechanical strength. Organic additives may contain polyvinyl alcohol, starch, polymers, and waxes as binding and surface-active agents. Some of TiO<sub>2</sub> may be thermally pre-treated (calcinated), which also prevents monolith cracking. During the mixing of those carrier precursors, vanadium compound may also be introduced. Only after thorough dry homogenisation water is added and the mixture is kneaded until a uniform mass is obtained [25]. The next stages of the carrier production are slow drying, thermal decomposition of organic binders, and final calcination at a temperature in the range of 400-650°C if it already contains vanadium pentoxide to prevent its deactivation by sintering, or to more than 700°C for maximum mechanical strength.

## Deposition of the active phase

### Impregnation

Active metals can be deposited on the carrier during the process of kneading of the carrier precursor mass by the introduction of appropriate metals to their salt solutions, followed by formation of the mass prepared in that way. This ensures uniform distribution of the active phase in the whole catalyst mass. The simplest way of depositing the active phase on the finished carrier is impregnation. Impregnated carriers are most often solutions of nitrates or metal acetates.

Much attention was devoted to the preparation of vanadium-titanium catalysts. Such catalysts can be prepared e.g. by wet impregnation of titanium carrier with titanium metavanadium in oxalic acid solution, followed by calcination at a temperature in the order of 500°C [28, 29]. Vanadium pentoxide was deposited in the same way on aluminium oxide carrier [30]. Saleh et al. prepared  $V_2O_5/TiO_2$  (anatase) catalyst by dissolving vanadium pentoxide in aqueous solution of oxalic acid and saturating titanium carrier [31].

A comprehensive review of the methods of deposition of various active metals on carriers and preparation of DeNO<sub>x</sub> catalysts was presented by H. Bosch and F. Janssen in their work on the catalytic reduction of nitrogen oxides [32]. In that publication the authors mention a number of methods of applying vanadium on a monolithic carrier by means of vanadium oxalate [11] and other vanadium salts, e.g. ammonium metavanadate from aqueous solutions [33, 34]. On the other hand, catalysts containing tungsten,  $WO_3/TiO_2$ , are prepared by impregnation of the carrier with aqueous solution of ammonium paratungstate, followed by drying and calcination.

Vanadium catalysts on silica were prepared by its impregnation with solution of ammonium metavanadate. In the case of commercial silica gels, titanium dioxide was first deposited on their surface in such way that in the first stage the carrier was saturated with titanium sulphate solution and then immersed in ammonia solution, thereby precipitating titanium hydroxide on the surface of pores. After washing and thermal treatment vanadium pentoxide was deposited by impregnation [35].

In some studies attempts were made to prepare vanadium-titanium catalysts using non-aqueous solutions of  $VOCl_3$ . In this method vanadium oxychloride reacts with surface OH groups. Bond and König deposited  $VOCl_3$  dissolved in petrol on anatase with small surface [36]. Vanadium catalysts on titanium oxides, silicon oxides, and aluminium oxides were also prepared by impregnating the appropriate carrier with  $VOCl_3$  solutions in  $CCl_4$  [10] or by passing gaseous  $VOCl_3$  over the carrier,  $TiO_2$  [28].

### Single-stage preparation

Catalysts can also be prepared by simultaneous precipitation of the carrier and the active phase. Catalysts of the  $WO_3/TiO_2$  type or the  $WO_3/Fe_2O_3$  type were prepared by mixing hydrogel of titanium hydroxide or ferric hydroxide with aqueous solution of ammonium paratungstate, followed by thermal treatment [37]. Vanadium catalyst on titanium dioxide was prepared with the sol-gel method using hydrolysis of their organic derivatives of tetra-1-amylenes of titanium and vanadium [38]. This group of methods can also include the previously discussed ways of preparation of vanadium-titanium and other catalysts involving the introduction of salts of active metals to the mixture of carrier precursors before their kneading and formation.

### Types of catalysts used

It has been established that some catalysts deposited on carriers made of aluminium oxides or iron oxides e.g.  $Fe_2O_3 - SnO_2$ ,  $Fe_2O_3$ ,  $WO_3$  or  $Fe_2O_3$  deposited on  $Al_2O_3$  or  $V_2O_5$  deposited

on  $\text{Al}_2\text{O}_3$  were characterised by high activity in reaction of denitrification of exhaust gases. However, those catalysts were losing their activity due to formation of sulphates during research on pilot systems for the purification of exhaust gases containing sulphur oxides. On the other hand, catalysts on titanium oxide as the carrier demonstrated not only high activity and selectivity, but also resistance to sulphur poisoning [39].

Indeed,  $\text{TiO}_2$  does not react with either  $\text{SO}_3$  or  $\text{SO}_2$  at a temperature above  $200^\circ\text{C}$  and because of this it maintains its structure for a long time in an environment of gases containing those oxides. On carriers made of titanium oxide, the active components are mainly  $\text{V}_2\text{O}_5$ ,  $\text{MoO}_3$ , and  $\text{WO}_3$  and in some cases also  $\text{Fe}_2\text{O}_3$ ,  $\text{CoO}$ ,  $\text{NiO}$ ,  $\text{MnO}_2$ ,  $\text{Cr}_2\text{O}_3$ , and  $\text{CuO}$  [40]. Catalysts of this type are active in DeNO<sub>x</sub> reactions at a gas temperature of between  $200$  and  $500^\circ\text{C}$ . For example,  $\text{V}_2\text{O}_5/\text{TiO}_2$ , a typical DeNO<sub>x</sub> catalyst, ensures under specific process conditions almost 100% reduction of nitrogen oxides with ammonia in the temperature range of  $220$ - $425^\circ\text{C}$ . After the temperature on the catalyst bed exceeds  $430^\circ\text{C}$ , reduction of nitrogen oxides rapidly decreases. Under the same conditions of the reduction process, the use of another monolithic catalyst, but with a completely different composition, containing zeolite -  $\text{TiO}_2 + \text{SiO}_2/\text{Fe}_2\text{O}_3 + \text{Fe}$  - mordenite, a 95% reduction of oxides can be obtained at catalyst temperature range of between  $375$  -  $600^\circ\text{C}$ . Significant differences can also be observed in the activity of zeolite catalysts, which differ from each other only by the type of replaced metal [25].

Copper catalyst [9.2% Cu-mordenite/6.92%  $\text{CuO}$ /+ 8% silicon binder] enabled obtainment of over 95% conversion of nitrogen oxides in the temperature range of  $225$ - $440^\circ\text{C}$ , whereas a catalyst of the composition, but containing 4.70 %  $\text{Fe}_2\text{O}_3$  instead of copper, showed a similar degree of conversion at a temperature range of  $310$ - $560^\circ\text{C}$ .

In industrial installations of DeNO<sub>x</sub> there are certain operational problems. At a process temperature of under  $200^\circ\text{C}$  there is a noticeable deposition of acid ammonium sulphate in the catalyst pores. Therefore, in the case of exhaust gases containing sulphur oxides, the process temperature must be maintained at over  $230^\circ\text{C}$ . On the other hand, at a temperature over  $400^\circ\text{C}$  there is a noticeable increase in oxidation of  $\text{SO}_2$  to  $\text{SO}_3$ . Since  $\text{V}_2\text{O}_5$  is the main promoter of the reaction of  $\text{SO}_2$  oxidation, at such time mainly the  $\text{TiO}_2$  -  $\text{MoO}_3$  or  $\text{TiO}_2$  -  $\text{WO}_3$  catalysts are used with minimum content or even elimination of  $\text{V}_2\text{O}_5$  from the catalyst. In such arrangement, a catalyst operating mostly in the gas temperature range of the order of  $300$  -  $400^\circ\text{C}$  can be operated for a long time without disturbances caused by deposition of acid ammonium sulphate on its surface and pores.

It should be noted that catalysts containing only vanadium show the highest activity, approx. 95 % conversion of nitrogen oxides at a temperature of  $300$ - $350^\circ\text{C}$ . The maximum activity of DeNO<sub>x</sub> catalysts containing small amounts of  $\text{V}_2\text{O}_5$ , of the order of 1%, and approx. 10%  $\text{WO}_3$  occurs in the temperature range of  $380$  -  $450^\circ\text{C}$  [7]. Catalysts containing only 3% of vanadium pentoxide on titanium dioxide offer 95% conversion of nitrogen oxides at a temperature of approx.  $380^\circ\text{C}$ . Further increasing of the active phase content no longer increases conversion of nitrogen oxides, but causes a few percent increase in  $\text{SO}_2$  oxidation to  $\text{SO}_3$ . In the case of catalysts containing tungsten (e.g. 10%  $\text{WO}_3$ ) a 95% conversion at a temperature of  $380^\circ\text{C}$  can already be achieved at less than 1% content of vanadium pentoxide (in such case conversion of  $\text{SO}_2$  to  $\text{SO}_3$  does not exceed 1%). Tungsten catalyst deposited on titanium dioxide oxidises  $\text{SO}_2$  only to a small degree. With continued operation the scope of oxidation increases. According to Morikawa, this is caused by deposition of vanadium on the catalyst by exhaust gases together with ash [41].



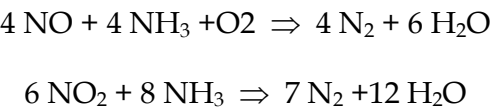
The relationships presented above concern only catalysts on a titanium carrier. According to Shikad et al. [35], over 95% reduction of nitrogen oxides on the V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>-SiO<sub>2</sub> or V<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> catalysts requires more than 10% content of the active phase (at a temperature of 200°C). The use of the first of those catalysts at a 20% content of V<sub>2</sub>O<sub>5</sub> enables almost complete reduction of nitrogen oxides at a temperature below 200°C. Much smaller activity was exhibited by vanadium catalysts on aluminium oxides or silicon oxides [32]. Similarly to titanium carriers, the optimum calcination temperature for mixed titanium and silicon carriers falls in the range of 350-400°C. A higher processing temperature gradually reduces catalyst activity, which is presumably due to a reduction of its specific surface area [16]. Table 4 shows the dynamics of development of the SCR systems, specifying the installations at power stations for hard coal and only for boilers with dry slag, situated in Germany.

No	Name of the power station	Power unit capacity	System	Provider
1	Reinhafen,	550 MW	High dust	Steinmüller (STM)
2	Reuter – West, Units D + E,	2 x 300 MW	High dust	Balcke - Diirr (B-D)
3	Reuter, Units 1 + 2 ;	2 x 50 MW	Tail End	Lentjes
4	Hannover – Stocken, Units 1 +2;	2 x 375 MW	Tail End	Uhde - Lentjes
5	GKM Mennheim –Neekarau, Unit 7,	475 MW	High dust	EVT
6	Heyden,	800 MW	High dust	Uhde - Lentjes
7	Farge,	325 MW	High dust	Uhde - Lentjes
8	Mehrun / Hannover,	642 MW	High dust	Uhde - Lentjes
9	Weiher,	707 MW	High dust	Steinmüller
10	Volklingen,	210 MW	High dust	KWU

Table 4. SCR installations at selected hard coal-fired power stations (Germany)

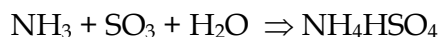
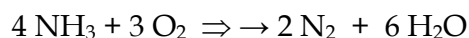
In some cases non-selective catalytic methods are also used. Here, the reducer can be hydrogen or methane. Those methods, referred to briefly as NSCR, are associated with considerable consumption of the reducer, because it also reacts with oxygen present in exhaust gases. This leads to disproportionately large consumption of the reducer, which is not economically viable.

In general, SCR are optional equipment – an addition to the primary methods. Such solution allows for a significant reduction of the amount of ammonia fed to exhaust gases, it reduces contamination of the catalyst, air heater, etc.; it also reduces the speed of catalyst poisoning. In the SCR method the evaporated ammonia at a temp. of approx. 200°C is blown into boiler exhaust gases by air. Reduction of NO<sub>x</sub> in catalysts proceeds according to the following major reactions:



In the case of large boilers, problems may arise in connection with introduction of sprayed ammonia to the exhaust stream in order to obtain uniform concentration and direct the exhaust stream so that the catalyst is uniformly loaded. Apart from the main reactions, there are also adverse associated reactions:





The first two reactions occur after the temperature of the exhaust gases goes above 400°C and result in increased demand for ammonia. At temperatures below 330°C and in the presence of SO<sub>3</sub>, a third reaction takes place in the exhaust gases, where acid ammonium sulphate is formed that deposits in pores of the catalyst surfaces, causing a reduction of the catalyst activity. Acid ammonium sulphate has the dew point at a temperature of 150°C and deposits in liquid state on the rotating elements of air heaters at a temperature range of 150°C to 250°C, which may primarily lead to the clogging of LUVO, but also to its corrosion. To mitigate the negative effects, special solutions are used in revolving heaters (specially shaped plates) as well as effective cleaning devices.

## 4.2 Preparation of ceramic carriers and catalysts

### Preparation of the carrier

Fig. 2 shows schematic diagram of production of a monolithic catalyst carrier

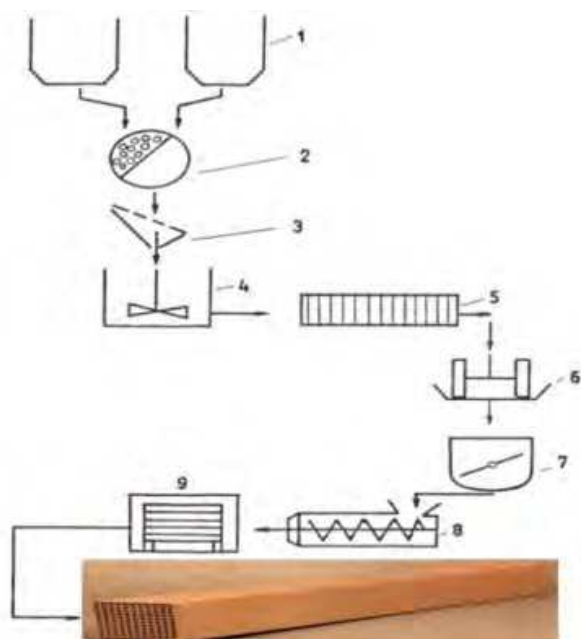


Fig. 2. Schematic diagram of production of monolithic carriers. 1-Raw material dispensers, 2-Grinder, 3-Sieve, 4-Tank with agitator, 5-Press, 6-Crusher, 7-Agitator, 8-Belt press, 9-Dryer.

Manufacturing of a carrier involves preparation of aluminosilicate mass, fragmentation, and selection of appropriate sieve fraction (aluminosilicate desludged and fragmented under 0.05 mm.). Degree of fragmentation of raw material affects the forming properties of the mass. It will also affect the quality of the final product – monolithic carrier. The next stage is mixing of aluminosilicate with additives such as lubricants and plasticizers, followed by forming of the obtained mass.

Forming of the carrier after mixing of the mass in a z-shaped mixer. Such method of preparation of the mass ensured uniform saturation with plasticizers of grain agglomerates

and de-aeration of the mass. Kneaded mass was directed to the forming operation. Fig 2 shows a diagram of the extruder die for forming a monolithic carrier.

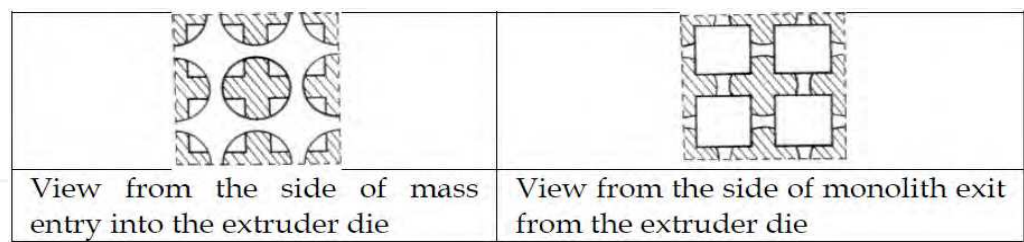


Fig. 2. A diagram of the extruder die for forming a monolithic carrier

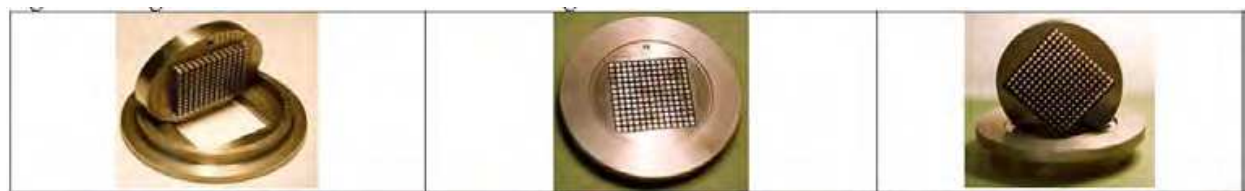


Fig. 3. A view of the extruder die for forming a monolithic carrier [42]

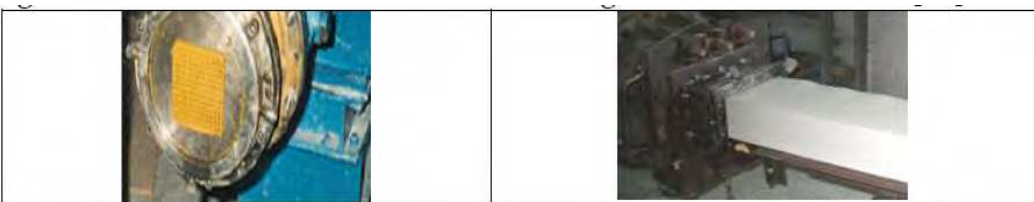


Fig. 4. A view of the exit of a monolithic carrier profile from the press.

The extrudate coming out of the extruder die was cut off after it achieved the appropriate length, giving the formed material its final shape. After pre-conditioning at room temperature, but no later than after 1 hour, honeycomb-structured profiles, the so-called “green monoliths”, were subjected to the appropriate process of drying in a microwave dryer. Microwave action enables taking of water molecules to the carrier surface while blowing hot air carries the emitted water away from the monolith surfaces.

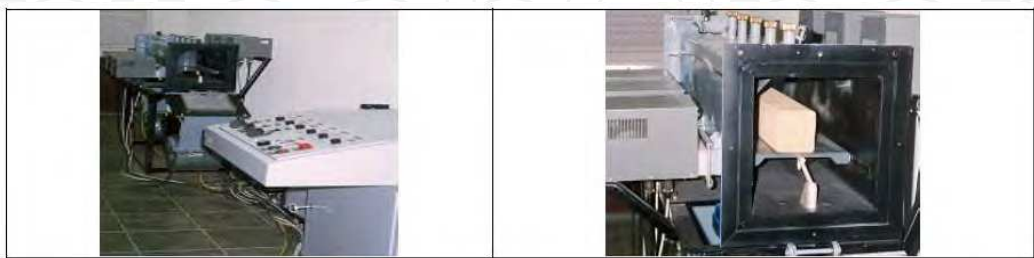


Fig. 5. Drying of creaming carrier in a microwave dryer.

The obtained dried profiles are then subjected to the process of calcination. In the conducted experiments monolithic carrier was put into a furnace and subjected to calcination at a temperature of 800°C with the temperature increase of 50 deg/h. After the final temperature was achieved, they were kept in it for 4 hours. The obtained monolithic carrier was characterised by good mechanical properties.

### Preparation of the catalysts

The method of preparing catalysts:

- Determination of carrier absorptiveness.
- Preparation of the appropriate amount of solution of salts of a given metal for saturation.
- Deposition of the salt solution of a given metal on the carrier.
- Drying at room temperature in the open air for 24h.
- Drying at a temperature of 110°C for 12h.
- Calcination of the catalyst to a temperature of 500°C and maintaining it at that temperature for 4h.

### 4.3 Testing of catalysts

The basic characteristics examined by manufacturers and users of catalysts are the activity and/or the so-called flashpoint, pressure drop, resistance to abrasion and crushing, lifetime, chemical composition, resistance to poisoning, grain shape and size, bulk density, porosity, specific surface area, and thermal stability. Some of those properties, e.g. grain shape and size or pressure drop on the bed are of secondary importance in the case of use of catalysts on a honeycomb-shaped carrier, while others concern all types of heterogeneous catalysts, and description of the methods of their determination is available in the standardisation literature.

From the user's perspective, of greatest importance is the activity of the catalyst. Determination of that property is relatively challenging because this is a speedy and strongly exothermic reaction, which causes huge temperature changes in the catalyst sample. Therefore, it is difficult to determine the reaction speed (or activity) as a function of temperature. Additionally, the catalyst exhibits changes in activity characteristic of hysteresis, i.e. differences in reaction speed depend on the direction from which we arrive at selected parameters of the process. This phenomenon is particularly evident at a temperature of the order of 450°C and sometimes several days of tests are required to determine the actual balance. The activity is generally determined as conversion under certain conditions and with a fixed catalyst volume or as an activity relative to a standard catalyst.

A measurement connected with the activity is the flashpoint or the threshold temperature of the catalyst reaction. This is a very important property of the catalyst because it shows the minimum gas temperature at the inlet to the reaction, below which the reaction slows down or stops. At working installations this property is also a function of gas speed, reactor geometry, characteristics of heat exchange, catalyst operation stage, and accuracy of temperature measurement.

Under laboratory conditions the activity of catalysts is usually determined by using model mixtures. Composition of gas, i.e. SO<sub>2</sub>, NO, O<sub>2</sub>, and N<sub>2</sub> content is determined at the inlet and outlet from the reactor, e.g. with the chromatographic method etc.

Based on this method (Preparation of the catalysts) 3 manufactured units of a monolithic catalyst have been produced in industrial conditions (approx. 1m<sup>3</sup> each), based on an aluminosilicate carrier: Cupric catalyst - Cu/natural aluminosilicate, Manganic catalyst - Mn/natural aluminosilicate, Mixed cupric manganic catalyst-CuMn/natural aluminosilicate.

Active metals were placed on the carrier by impregnation of water solutions of cupric nitrate and manganic acetate. Chemical composition of natural clay used for carrier prepared is presented in Table 5.

Chemical composition	Parameters
SiO <sub>2</sub>	54 – 56 wt. %
Al <sub>2</sub> O <sub>3</sub>	37 – 39 wt. %
TiO <sub>2</sub>	max. 1,0 wt. %
Fe <sub>2</sub> O <sub>3</sub>	2,2 – 2,7 wt. %
CaO	max. 0,4 wt. %
MgO	max. 0,6 wt. %
Na <sub>2</sub> O + K <sub>2</sub> O	1,5 – 2,1 wt. %

Table 5. Chemical composition of natural clay from deposit of Lower Silesia Poland

Mineralogical composition: Kaolinite-min. 72 wt. %; Illite- max. 23 wt. %: Quartz- max. 3,0 wt. %; Colour -Light beige

The laboratory apparatus for testing the activity prepared catalysts is presented on Fig 6. The research was conducted on the laboratory flow equipment using the model gas of determined chemical composition corresponding to that of a waste gas from power plant. Tests of activity were performed with the apparatus shown in figure 6 (apparatus for denitrating tests).

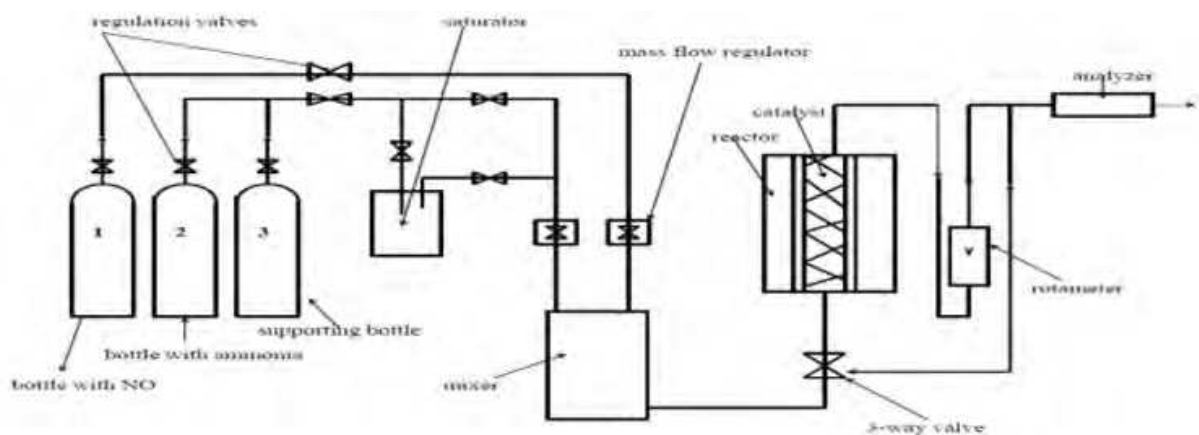


Fig. 6. Schematic diagram of laboratory apparatus for testing catalyst

The apparatus consisted of model gas feeding system and dosage system, catalytic reactor and analyzer for determining the content of nitric oxide in the gas. The reactor was supplied with the mixture of nitrogen and air enriched with water steam. The mixture contained, depending on the type of test, a specific amount of nitric oxide. The concentration of NO was measured at the entrance and exit of the reactor.

10 cm<sup>3</sup> of the tested catalyst (grain fraction 0,6 – 1 mm) was put in the electrically heated reactor (Fig. 6). The mixture of gases from the mixer was directed into the SCR reactor. The reactor was equipped with an electrical heating jacket powered by auto transformers. The temperature of the reactor at the entrance and at the exit of the catalyst bed was measured by means of thermocouples connected with the temperature regulator. Additionally, the reactor was equipped with an isolation mantle in order to provide isothermal conditions inside it. Gases coming out of the reactor went into an analyzer through the filters. Nitric oxide contents at the entrance and at the exit of the catalyst bed was determined with using of MSI 2500 analyzer.



Activity of catalyst – reaction of denitridding the combustion gases – is determined according to the following formula:

$$\alpha = 100(c_o - c_k)/c_o \quad [\%]$$

c<sub>o</sub> concentration of NO<sub>x</sub> before reactor

c<sub>k</sub> concentration of NO<sub>x</sub> after reactor

The conditions of the process were: temperature range from 150 °C to 500 °C, volume speed of the gas flow was GHSV=3000 m<sup>3</sup>/m<sup>3</sup>•h<sup>-1</sup>, oxygen content in the model gas = 6 %, NO content within the range ~ 500 ppm, ratio NH<sub>3</sub>/NO equal to 1, water vapor content in the model gas ~ 1 %, Model gas and gas leaving the reactor was analyzed using the MSI 2500 analyzer.

The results of investigation of catalyst activity of 8,78 wt% CuO; 3,63 wt% MnO; and 8,78 wt% CuO with 3,63 wt% MnO catalysts are presented in Fig.7.

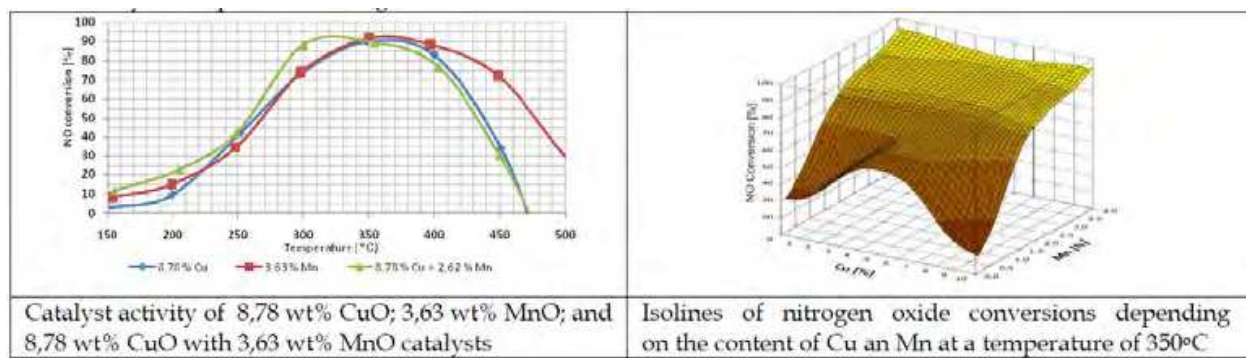


Fig. 7. Catalyst activity

As we see ( Fig. 7- left) in range of temperatures above 400°C take places ammonia combustion reactions and take place decreasing of NO conversion.

4.4 Catalyst deactivation

The aging of the catalyst is caused by several mechanisms acting simultaneously, which can be divided into three groups:

- thermal deactivation,
- mechanical deactivation,
- chemical deactivation.

Thermal deactivation is caused by raising the catalyst temperature to about 600-650°C, which causes irreversible degradation of the carrier. Presumably this is connected with a change of the porous structure of the catalyst as well as blocking of some of the pores by molten components of the active phase. There is no doubt that the porous structure of the catalyst changes, and its specific surface area diminishes while the average pore radius increases. There are also crystallographic changes: amorphous silica crystallises to form a-cristobalite.

Mechanical deactivation is caused by blockade of the gaps between catalyst granulates (or channels in the monolith) by particulates carried by gas. This type of deactivation depends mainly on the purity of the gas fed to the reactor. Chemical deactivation or catalyst poisoning are usually regarded as rapid loss of activity caused by reaction of trace impurities with the catalyst. However, there are many substances that react with its



components resulting in a reduction of the activity or deterioration of its mechanical strength. Most known catalyst poisons, such as arsenic oxides, nitrogen oxides, carbon monoxide, lead, and mercury are harmless in small quantities. Hydrogen chloride and chloride acting for a longer time can cause a loss of catalyst activity [23].

#### 4.5 Methods of installing catalysts

The level of the required catalyst temperatures determines where catalysts are incorporated. Generally speaking, catalytic systems can be installed on boiler exhaust gas lines irrespective of other installations, e.g. desulphurisation of exhaust gases (DESOX). However, in practically all exhaust gas purification solutions, the DENOX and DESOX systems are designed in a comprehensive manner. This creates various possibilities for locating SCR installation in the exhaust gas line downstream the boiler.

Fig. 7-12 shows installation options for the SCR systems. Fig. 7 shows the most common version of SCR installation, the so-called high dust (with high ash content in exhaust gases).

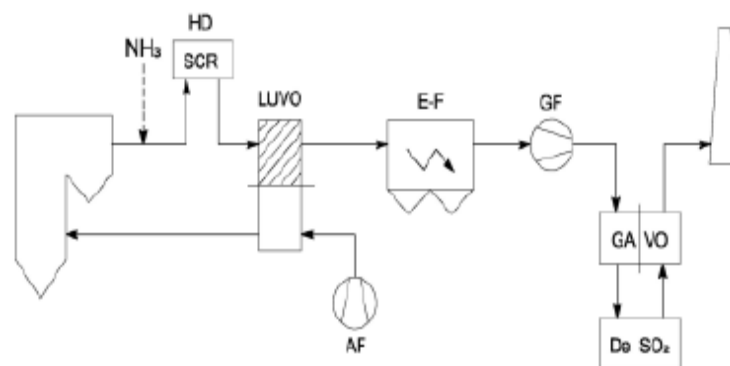


Fig. 7. "High dust" system with desulphurisation and denitrification.

Fig. 8 presents a "Low dust" only for organisation purposes. It is used exclusively in the USA, in boilers with hot electrostatic precipitator.

The systems presented in Fig. 9 and 10 also constitute "low dust" solutions but due to their incorporation at the end of the exhaust gas line they are commonly referred to as "Tail End". Fig. 9 shows a very interesting "High dust" concept with the so-called DENOX - LUVU, in which heating elements in special execution have catalytic properties.

The use of RAH (LUVU) as a two-function device by extending its heat-exchanging function to include a catalyst function, would result in a considerable reduction in the cost of implementing the SCR method.

The proposed [43-45] way of using the regenerative air heater (RAH-SCR) as a catalyst would eliminate the necessity of building a SCR reactor, as the existing RAH could then be used. The trials will enable to compare the activity levels of industrial-scale manufactured catalysts in reduction of  $\text{NO}_x$  using ammonia. A series of trials is also anticipated, during which fly-ash from boilers will be added to flue gas. It will enable researchers to assess durability and time-based changes of reduction efficiency of the catalysts at variable ash loads (fly-ash which may 'pollute' the catalyst).

Figures 12 show detailed diagrams of the most interesting SCR systems. Ammonia injection is placed at least 3 m upstream of the catalyst.

Fig. 13 shows balance of ammonia at the individual devices of the HD system. It is very important that sulphur oxides are removed from exhaust gases prior to the process of

selective catalytic reduction, because it prevents the formation of ammonium sulphates that can form in the following reactions:

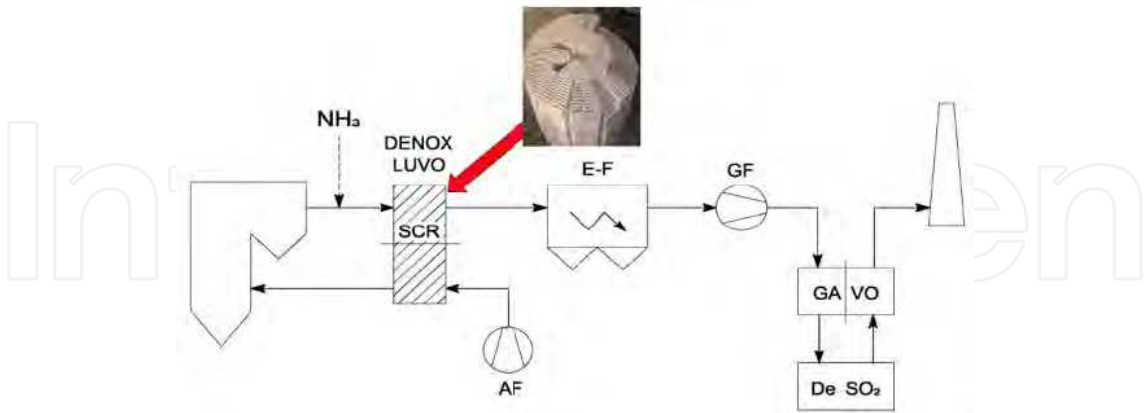


Fig. 8. “High dust” system with DENOX LUVU.

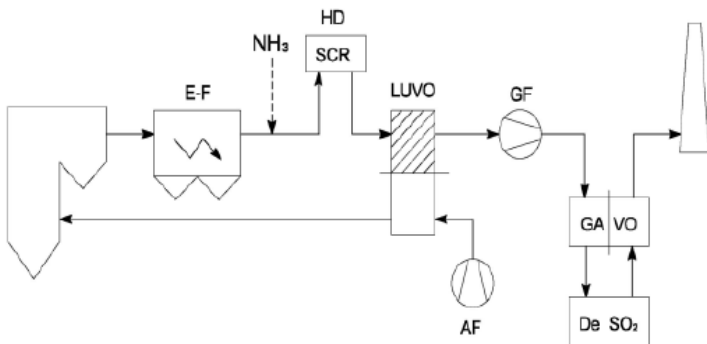


Fig. 9. Classic “Low dust” system of SCR with desulphurisation.

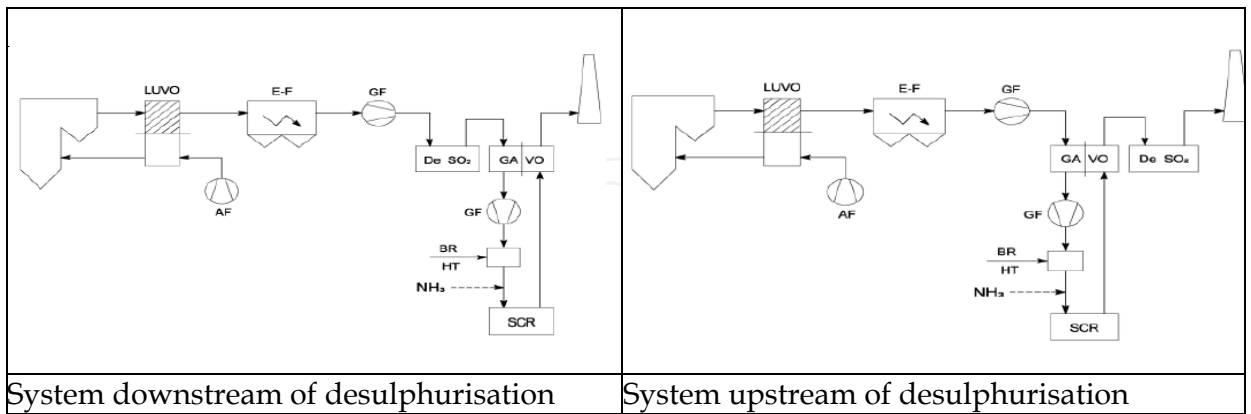
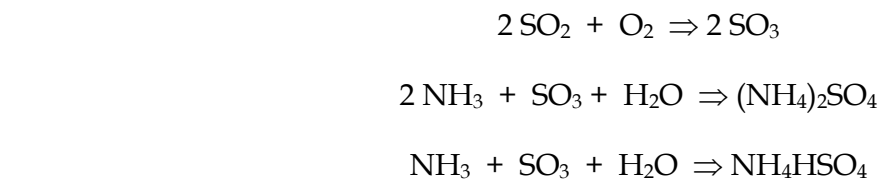


Fig. 10. “Tail end” system





- catalysts based on transition metal oxides ( $V_2O_5$ , NiO) deposited on carriers ( $TiO_2$ ,  $Al_2O_3$ ,  $SiO_2$ ,  $ZrO_2$ ),
- zeolites containing Cu,
- metals such as Fe, Mn, or Cu deposited on carbon and mineral-carbon carriers.

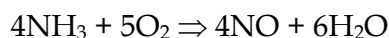


Fig. 14. View of a catalyst SCR.

Currently, more and more attention is devoted to carbon materials and their use in catalytic processes. Especially strong interest is generated by active carbon as a carrier of the active phase of catalysts. It has several important benefits thanks to which it has been widely used in different fields of chemistry. Active carbon is characterised by a very well-developed surface (from 1000 to 1500  $m^2/g$ ), diverse pore diameters, and high adsorption capacity. For these reasons, it is used as a component of water purification filters or as the main component of canisters in gas masks, capturing such hazardous substances as: some organic compounds, sulphur oxides, hydrogen chloride, ammonia, hydrogen cyanide, or nitrogen oxides. Active carbon is also used in medicine, administered by the oral route in some cases of poisoning. As a carrier of the active phase of catalysts, it is used e.g. in organic chemistry. In industrial processes, such as SCR, active carbon can be connected with mineral compounds, which significantly increases its mechanical strength as an active phase carrier.

The catalytic method with the use of ammonia was developed by Englehard Corporation in the United States in 1957. The first SCR installations used platinum catalyst for nitrogen oxide reduction. However, its use was abandoned due to the fact that the reduction reactions took place at temperatures similar to the flashpoint of the ammonia and air mixture. Currently, most catalysts in use are made of a carrier – titanium oxide ( $TiO_2$ ) and the active phase – tungsten oxide ( $WO_3$ ) and/or vanadium oxide ( $V_2O_5$ ).

In the process of selective catalytic reduction of nitrogen oxides, in addition to the active phase the temperature of the process is also important. It is recommended to use temperatures in the range from 300°C to 400°C, so optimum conversion of nitrogen oxides can be obtained. At temperatures above 450 °C ammonia is burnt to NO.



On the other hand, too low process temperature (under 200 °C) may lead to the formation of ammonium nitrites and nitrates. When exhaust gases contain a lot of particulates (approx. 20 g particulate per 1  $m^3$ ) a reactor is used, in which the fuel jet is directed vertically downwards to the catalyst bed. Typically, three or four catalyst layers are used, placed over each other (Fig.16). Each layer consists of certain number of buckets containing catalysts, which facilitates ongoing replacement of spent catalysts starting from the top of the reactor. This way each bed is periodically subjected to the process of cleaning of deposits by means of overheated water vapour.

The technique of manufacture of catalytic monoliths was first perfected in Japan. For dusty exhaust gases two types of flow profiles were developed: plate and honeycomb.

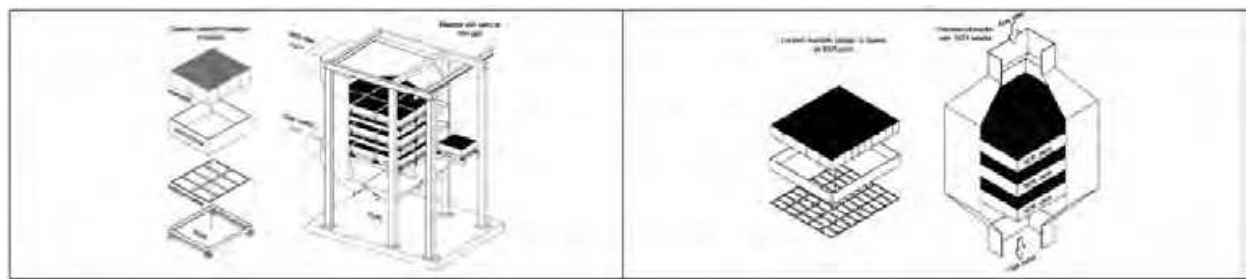


Fig. 16. Diagram of the SCR reactor (right - the element and package of ceramic catalysts)

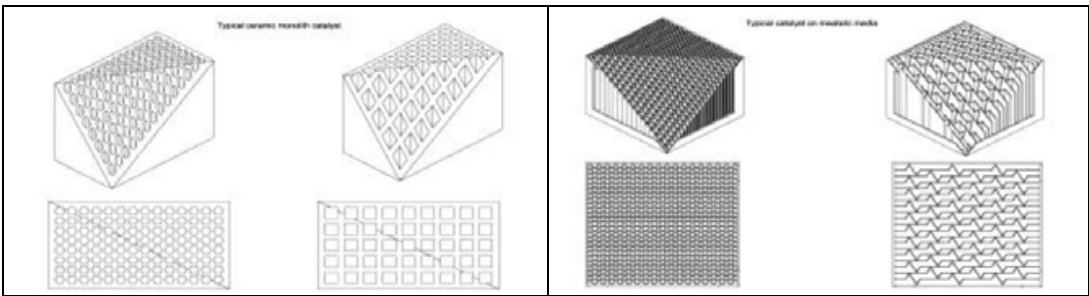


Fig. 17. Types of industrial catalysts in use.

In Japanese metal catalysts the primary material is titanium oxide  $\text{TiO}_2$  mixed with glass fibre, covered on the outside with tungsten and vanadium pentoxide. Besides high investment costs, catalysts containing those heavy metals also create serious problems connected with their storage after they are spent. Catalysts have a lifetime of 2 to 7 years. In their search for cheaper solutions, German companies developed their own iron-chrome (Didier) and ceramic (Mannesman) catalysts. Spent ceramic catalysts are powdered and used as a raw material for the production of new catalysts.

Plate catalysts are made in the form of blocks similar to the so-called baskets of heating elements of rotating air heaters. Plate catalyst blocks are assembled as packages (modules), as shown in Fig. 17.

Honeycomb catalysts are made in the form of small-scale elements, which are then assembled into modules.

Catalysts are installed in the exhaust duct in 3 or 4 layers, with a gap between them to incorporate cleaning devices (blowers).

Table 5 shows SCR device suppliers to illustrate the dynamics of development of the catalyst manufacturing industry in Germany supplying the power industry. Table 6 shows types of catalysts used in the Japanese power industry. In table 5 of note are unmentioned catalysts based on carbon chemistry (active carbon, active coke). This technology will be presented later in the text.

Catalytic methods, included among non-waste methods, due to lack of waste are an alternative to the waste methods. They are characterised by a high degree of exhaust gas purification (simultaneous removal of  $\text{NO}_x$  and  $\text{SO}_2$ ) and achievement of a commercial product in the form of concentrated sulphuric acid, sulphur, or other products. They involve catalytic oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  and three-stage condensation of exhaust gases: at the first



stage - with condensation of concentrated sulphuric acid, at the second stage – after moistening of sulphuric acid of a lower concentration, at the third stage – after moistening of hydrogen chloride and hydrogen fluoride.

Supplier	Licence	Type of catalyst
Deutsche Babcooc	Kawasaki (Jap.)	Honeycomb-type based on titanium oxide (TiO <sub>2</sub> )
Deutsche Rauchgas	Babcoc- Hitachi (Jap.)	Plate-type based on titanium oxide
Dider	own (Germany)	Iron-chrome
EVT	Mitsubishi (Jap.)	Honeycomb-type based on titanium oxide (TiO <sub>2</sub> )
Flakt	Hitachi - Zosen (Jap.)	Plate-type based on titanium oxide
GEA	Engelhard	Honeycomb-type based on titanium oxide (TiO <sub>2</sub> )
Linde	Norton (USA)	Powder catalyst
Knauf Research Cottrel	USA	Plate-type or honeycomb-type based on titanium oxide (TiO <sub>2</sub> )
Steinmuller	Ishikawajima	Honeycomb-type based on titanium oxide (TiO <sub>2</sub> )
Mannesmann	own	Molecular sieve, ceramic
Holter- Lurgi	Hitachi - Zosen (Jap.)	Plate-type based on titanium oxide
Thyssen	MHI	Honeycomb-type based on titanium oxide (TiO <sub>2</sub> )
Uhde	Bergbau-Forschung	Active coke
Uhde- Lentjes	Babcoc - Hitachi (Jap.)	Plate-type based on titanium oxide

Table 5. Companies offering SCR devices

Name of the power station	Power unit capacity Mw	Type of catalyst	Concentration of NO,[mg/Nm³]		SCR effectiveness, %
			input	output	
Takehara	2x250; 700; 2x250;	plate	700-500	134-96	81
Shimono Seki	175	honeycomb	840	360	57
Shin Ube	156	honeycomb	800	280	65
Mizushima	156	plate	700	240	65
Saijo	156; 250;	honeycomb	760-660	260-180	65-70

Table 6. SCR systems in larger carbon units in Japan

It should be emphasized that those are the methods of the future and they already have their applications in the world, e.g. Münster in Germany and Vendsyssel power station in Denmark. However, they are characterised by an extensive centre of catalytic oxidation and reduction of gas contaminants as well as centres of condensation of separated contaminants with complex devices. They do not require the use of sorbents and they provide end-products with specific commercial properties.

## 5. DENOSOX method of simultaneous removal of $\text{SO}_x$ and $\text{NO}_x$ from exhaust gases by catalysts

The DESONOX method was devised and developed as a relatively simple method of treatment of exhaust gases, in which the end-product is sulphuric acid. The method was used for desulphurisation and denitrification of exhaust gases at power unit No 3 of the heat and power generating plant in Münster (Germany) (Heizkraftwerk der Stadtwerke Münster GmbH).

The DESONOX method was devised and developed with the following objectives:

- removal of sulphur dioxide and nitrogen oxides,
- generation of sulphuric acid from the removed sulphur dioxide, which can be used in industry.

Figure 18 shows a simplified diagram of the DESONOX installation. The DESONOX technology includes utilisation of two toxic components of waste gases in installations:

- nitrogen oxides (using the DENOX technology),
- sulphur dioxide (using the DESOX technology).

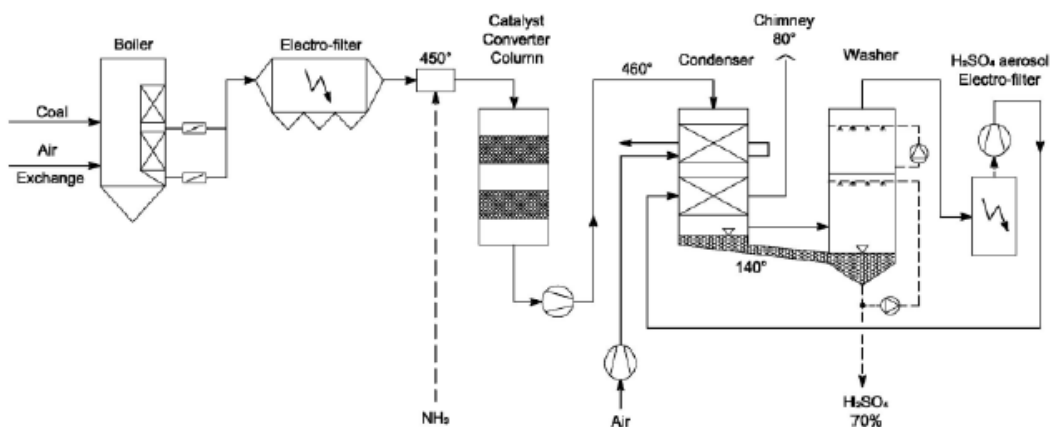


Fig. 18. DESONOX installation diagram.

### The DENOX technology

The DENOX technology utilises the phenomenon of selective catalytic reduction (SCR). It uses catalysts in whose presences – by means of ammonia, forming a reducing atmosphere – nitrogen oxides are reduced to pure nitrogen and water, i.e. components neutral to the atmosphere. The temperature of waste gases, after passing through the heat exchanger and the electrostatic precipitator, amounts to approx. 160°C. This temperature is too low for the work of the catalyst. Therefore, waste gases pass through a recuperator where they are heated up to 450°C. In some cases, in order to obtain that temperature, it is necessary to use an additional flame heater, powered e.g. by natural gas. Heated gases are enriched with ammonia. The mixture of warm exhaust gases and ammonia is directed to the catalytic converter. The catalyst is deposited on ceramic monoliths arranged in 1-2 layers.

Above the monolith layers there is an element for uniform distribution of gases throughout the cross-section of the converter. The converter has a modular structure. A single module often consists of up to 100 monoliths. The number of monoliths depends on the size of the system. For example, a boiler with the capacity of 200 MW requires approx. 200 m<sup>3</sup> of catalytic bed.

The degree of conversion of nitrogen oxides varies between 85 and 98% while the degree of conversion of sulphur dioxide remains at the previous level of approx. 90%. The effectiveness of the DESONOX process depends primarily on the temperature of exhaust gases. If we assume at least 80% degree of conversion, then the reduction of nitrogen oxides with such efficiency is already present at temperatures above 390°C, whereas the same degree of SO<sub>2</sub> conversion is obtained at a temperature above 440°C.

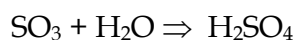
Hence, the working temperature of the catalyst in the DESONOX system is assumed to be equal to 450°C. Raising of that temperature has a positive effect on the efficiency of the process. The only adverse effect of lowering the temperature below the adopted value is a reduction of the process effectiveness, starting with a reduction of the SO<sub>2</sub> conversion. A positive effect, which makes it possible to maintain the process temperature at a set level, is the fact that the oxidation of SO<sub>2</sub> to SO<sub>3</sub> is an exothermic reaction. It also goes to show that the higher the concentration of sulphur in carbon, the greater the amount of heat generated during oxidation of sulphur dioxide and the easier it is to maintain the adopted parameters of the process. One drawback of the technology is the need to feed ammonia to the system.

#### **The DESOX technology**

Utilisation of sulphur dioxide occurs at the second stage of the catalytic converter in the DESOX process. After waste gasses pass through the first bed, they still contain approx. 8 % of excess oxygen. Therefore, in the second bed, sulphur dioxide can be oxidised in the presence of a catalyst – at temperatures of the order of 450°C – to sulphur trioxide, according to the following reaction:



Unlike sulphur dioxide, sulphur trioxide is readily soluble in water, which is present in exhaust gases in the form of vapour arising during reduction of nitrogen oxides with ammonia, and binds to it to form sulphuric acid.



Sulphuric acid is taken from the gaseous form to liquid form in the heat exchanger through which exhaust gasses pass, and is stored in a settler. Exhaust gases then pass to the washer, where the remaining sulphuric acid is removed by sprinkling with a shower of sulphuric acid, previously collected in the settler of the heat exchanger.

Any residue of the sulphuric acid deposits on this electrostatic precipitator. The waste gases upstream the electrostatic precipitator have a temperature of approx. 50°C. This temperature may be too low, therefore waste gases are additionally heated to a temperature above 80°C. Sulphuric acid may be derived either directly in concentrated form (concentration over 70 %) or taken to gypsum after reaction with lime.

## **6. Methods of simultaneous removal of sulphur and nitric oxides on adsorbents and carbon catalysts**

At the current state of technology, the methods whose process include carbon sorbents seem to be the easiest, the most technologically mature, and the most economically promising solution.

A precursor of these technologies is believed to be the UNITIKA method developed in Japan in the 1970s, which uses sorption of sulphur dioxide by active carbon with simultaneous

reduction of nitrogen oxides to free nitrogen. The reducer was ammonia and the process was taking place in the temperature range of 200-250°C. The catalyst used in the form of fixed bed was regenerated by gas at a temperature of 300-350°C. Sulphur dioxide was recovered from regenerated gases in a separate device by means of absorption. The applicability of that method was limited by the required low particulate content in purified gases (under 0.2 g/m<sup>3</sup>).

A more technologically mature method, brought to the stage of an industrial solution, was also developed in Japan by SUMITOMO Heavy Ind., and involved simultaneous disposal of SO<sub>2</sub> and nitrogen oxides on a fixed bed of appropriately prepared coke and in the presence of ammonia supplied to the gases. The process takes place at significantly lower temperatures than in the UNITIKA method, of the order of 120-150°C, where sulphur dioxide is oxidised to trioxide, and then is retained in sorbent pores in the form of sulphuric acid and its ammonium salts. Simultaneously, nitrogen oxide is reduced with ammonia to nitrogen and water vapour.

Because adsorbed sulphuric acid or its ammonium salts reduce the catalyzing ability, sorbent is regenerated in a stream of inert gas, at temperatures of 350-600°C, with emission of sulphur dioxide and carbon, water vapour, and nitrogen. Gases containing 10-30% SO<sub>2</sub> are converted to sulphuric acid or elemental sulphur.

The process was implemented on a large industrial scale at the Matsushima installation, where removal of 95% of sulphur dioxide and 40-50% of nitrogen oxide was achieved. That method became the starting point for the development of a similar process under the name Bergbau-Forschung (BF). The primary sorption factor is active coke while gaseous ammonia is the reducer of nitrogen oxides. In accordance with this method an installation was built (by UHDE) for two brown coal-fired power units at the Arzberg power station.

The main benefits of catalysts based on carbon sorbents are their sorption of sulphur dioxide to a technically usefully degree as well as the ability to realise the process of reduction of nitrogen oxide with ammonia under relatively low temperatures 80-130°C. In this scope, typical of energy waste gases, these catalysts are characterised by high efficiency. Their adsorption and catalytic properties were used in the process of removal of nitrogen oxides and sulphur from gases in practically one operation, at one reactor, and at similar parametric conditions.

The raw materials used to obtain active carbons contain carbon and include hard coal, brown coal, peat coal, charcoal, coconut shells [46], industrial waste [47] and organic compounds containing nitrogen, polyacrylonitriles, and melamine and urea resins [48-51]. The initial mechanical processing of the raw material involves: grinding of the output product; addition of binding agents, for example aluminosilicate [52], tar, and refinery waste [47, 53-55]; thickening; drying; initial thermal treatment; and giving the appropriate form, usually that of granulate. The obtained material is subjected to the process of activation, usually thermally at a properly selected high temperature by contact with inert gases or gases containing ammonia [50, 56-58] or water vapour [49].

The product obtained this way is a mixture of amorphous and microcrystalline structures, with the cavities formed inside it constituting a system of channels of different dimensions – micropores with a diameter of up to 20 Å, mesopores 20-500Å, and macropores of greater diameters. Macropores primarily determine the total volume of pores. The inner specific surface area formed this way usually amounts to between 500 and 1500m<sup>2</sup>/g.

Carbon sorbents should exhibit the following properties:

- inner volume as large as possible to ensure maximum absorptiveness of sulphur dioxide or sulphuric acid,
- high proportion of micropores, responsible for a large expansion of the specific surface area, of decisive importance in the process of catalytic reduction of nitrogen oxide with ammonia,
- low resistance to gas flow,
- high mechanical resistance to crushing and abrasion;
- defined quantitative and qualitative share of ash,
- high flashpoint together with low susceptibility to spontaneous combustion,
- selectivity with respect to catalysed reaction.

The patent literature usually provides very sketchy descriptions of the processes of production of appropriate carbon sorbents, mostly from hard or brown coal as starting raw materials [47, 52-55, 59, 60]. One of the patents describes [54] preparation of active formed coke by subjecting ground coal with the granulation of under 1 mm and containing 10-45% of volatiles to the process of fluidisation at a temperature of 180-270°C in the presence of 2-10% of oxygen. The product with the addition of binding substances is used to form granulate with the diameters of 4-9 mm, which is subjected to a temperature of 650-950°C.

Another method of obtaining sorbent [47] involves use of soot and waste from kerosene processing installations, which are mixed together with molasses as a binding agent, extruded, dried, carbonised, and thermally activated. Hard product, with the pore volume of the order of 60 cm<sup>3</sup>/100g, exhibiting high absorptiveness of nitrogen oxides (over 6% NO<sub>x</sub> by weight), was used to for their removal from waste gases. There are also reports [86-89] of preparation of a new type of sorbent by charring some nitrogenous organic compounds (polyacrylonitriles, urea and melamine resins) in a stream of air or inert gas, at temperatures of 300-1200 °C, and their subsequent activation by water vapour. The obtained sorbent, with the specific surface area of up to 1000 m<sup>2</sup>/g, additionally modified with vanadium compounds (up to 2% V), exhibited high purification efficiency of up to 90% for SO<sub>2</sub> and up to 100% for NO.

Many patents point to the advisability of modification of carbon sorbents by addition of ammonium salts of hydrohalic acids [61-66] or by metal oxides of Cu, Cr, Ni, Mn, Fe, Co, V, Mo and others. This increases the ability to catalyse NO reactions [51] and, as a result, most sorbents modified this way are used in the processes of exclusive removal of NO. Patent applications [67-71] suggest they may also be used in the processes of joint removal of sulphur and nitrogen oxides. Activation of such sorbents is carried out by prior contact with inert gasses containing ammonia at an elevated temperature of 500-950 °C, over a period of approx. 10 minutes [56-58].

Some patents demonstrate more research to increase efficiency of carbon sorbents, among others toward further lowering of the working temperature or improvement of their mechanical characteristics. An example of such efforts is the patent information [72] on preparation of network catalysts covered with carbon material by the introduction of coke into the cellular structure of the Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> type or isomorphic aluminosilicates. The currently obtained carbon sorbents have well-developed specific surface area up to 1500 m<sup>2</sup>/g [49, 73], bulk density in the range of 500-900 g/dm<sup>3</sup> [54, 73], specific volume of pores of 40 to 60 cm<sup>3</sup>/100 g [47, 54], and exhibit absorption of sulphur dioxide at a temperature of 120 °C from 10 to 15% in relation to the sorbent weight [53, 57, 59]. However, as previously mentioned, they are characterised by relatively low permissible gas load values, usually



amounting to 500-1000 m<sup>3</sup>/m<sup>3</sup>• h [58, 63, 74]. Their mechanical strength, especially if a movable bed is used, is also considered to be insufficient [75].

### 6.1 The Bergbau - Forschung/Uhde (BF) method

The process is carried out in a two-stage reactor with a movable bed of active coke by carrying out reduction of nitrogen oxide by ammonia with simultaneous adsorption of sulphur dioxide at temperatures of 120-150 °C. The installation is situated in the power production line after the air heater and electrostatic precipitators. The process consists of a three-stage procedure -adsorption, desorption, and the section of sorption gas processing.

The adsorber design is subdivided into two stages, which fulfil the functions of, respectively, SO<sub>2</sub> adsorption and NO reduction; the regeneration stage takes place in a separate reactor. Both reactors and the adsorber are connected by movable bed of active coke, forming a closed circuit. Adsorption: During the first stage of the adsorber, sulphur dioxide is stopped in the amount of approx. 90%, which in the presence of water vapour and oxide forms adsorptionally bound sulphuric acid. At this stage the sorbent also stops HCl, HF, heavy metals, and fly ash. At the second stage of adsorption, after ammonia is added to the gases, nitrogen oxide is reduced.

#### Desorption:

Coke from the adsorber is fed pneumatically or transported or mechanically transported to the desorption system. Heating through membrane by hot exhaust gases to 400°C causes desorption of sulphur dioxide; the resulting gases contain approx. 30% of SO<sub>2</sub>. After desorption coke is cooled by air, also through membrane, and returned to the second stage of the adsorber.

#### Gas processing for desorption:

Gases leaving the desorber and containing in addition to sulphur dioxide also CO<sub>2</sub>, water vapour, and nitrogen are subjected to separate processing into sulphuric acid, elemental sulphur, or liquid SO<sub>2</sub>.

Figure 19 shows a simplified diagram of the Bergbau-Forschung (BF) method with the omission of the section of gas preparation for adsorption and the section of sorption gas processing, containing up to 20% SO<sub>2</sub>.

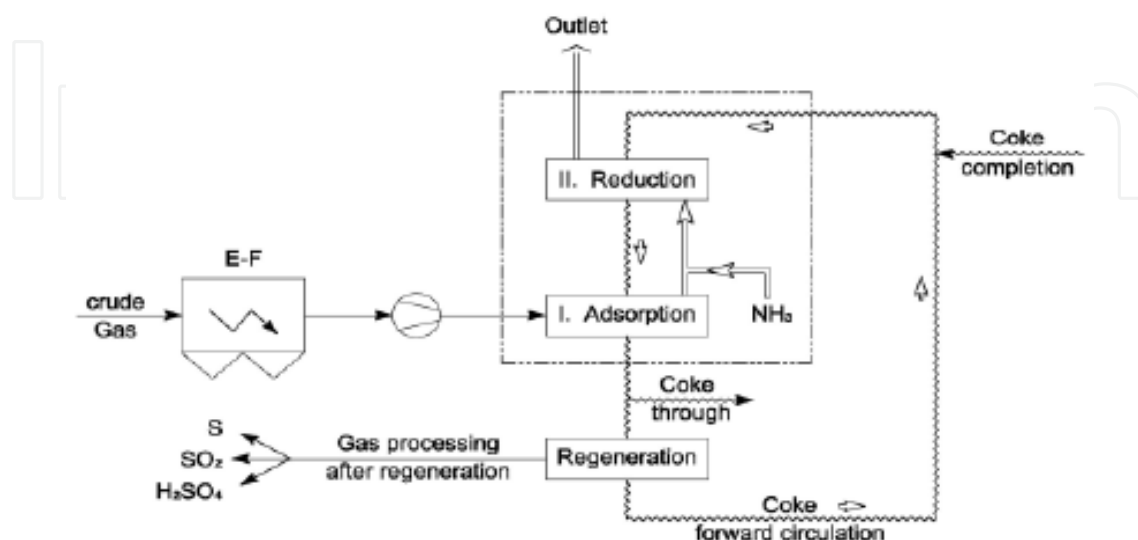


Fig. 19. Diagram of the Bergbau-Forschung process.

Purified gases leaving the electrostatic precipitator section of the power production line are sucked in by a blower and compressed to the pressure corresponding to the conditions in the adsorber. The optimum process temperature (120 °C) is set by water injection using compressed air or steam in the column not shown on the drawing, upstream the adsorber and in the additional steam exchanger. Gases introduced into a two-stage adsorber flow horizontally through movable bed of active coke, and then to the second stage of the process, selective reduction of nitrogen oxide with ammonia. On the other hand, regenerated coke from the desorber passes through the container situated at the top of the tower first to the second stage of the process of reduction, and from there it lowers gravitationally and passes to the first stage. Coke with SO<sub>2</sub> adsorbed on it is collected from the first stage at the bottom of the adsorber and is directed to desorber. In this way, the movable bed of active coke forms a closed circuit between the adsorber and the regenerating unit.

Purified gases, leaving the adsorber at a temperature of 120°C are discharged through the flue into the atmosphere. Heat losses due to emission through the adsorber walls and in smoke flues are offset by the heat of reaction. The dew point of the sulphuric acid is not exceeded anywhere along the exhaust gas line to the flue and reheating of the gases is unnecessary.

Gases leaving the regeneration system contain approx. 20% of SO<sub>2</sub>, water vapour, carbon dioxide, nitrogen, HCl and HF, and heavy metals. After purification of the gases by means of sorption with the so-called "Halex" mass, the gases are converted to sulphuric acid, elemental sulphur, or liquid SO<sub>2</sub>, depending on the variant of the procedure.

#### Chemical mechanism of the process

In the Bergbau-Forschung (BF) process, active carbon acts both as an adsorbent, and as a catalyst. In the absence of ammonia, sulphur dioxides as well as oxygen and water vapour contained in gases are adsorbed on the active surface of coke. Later in the process they undergo catalysed transformation to sulphuric acid, which remains adsorbed in pores of the sorbent:

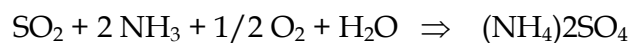


Simultaneously to this reaction, nitrogen dioxide which is present in gases in 5-10% of the total amount of NO<sub>x</sub>, is rapidly reduced:

After the addition of ammonia, favourable conditions are created for the reduction of nitrogen oxides to free nitrogen and water vapour:



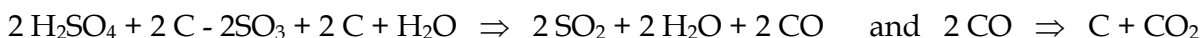
Sulphur dioxide in the presence of active coke reacts with ammonia to form ammonium sulphate:



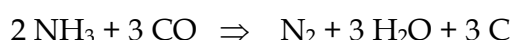
The individual salts are similarly formed, reacting with sulphuric acid adsorbed in pores:



In the process of thermal regeneration, at a temperature above 300°C, adsorbed sulphuric acid reacts with carbon to form carbon dioxide and sulphur dioxide. The reaction goes through surface-formed CO oxides:



Decomposition of ammonium salts goes in the opposite direction. On the other hand, ammonia reduces sulphur trioxide formed by decomposition of sulphuric acid and surface oxides of CO according to the following reaction:



thus reducing carbon losses.

#### **Process of adsorption on carbon sorbents**

Depending on the sulphur content in fuel,  $\text{SO}_2$  concentration in exhaust gases varies between 500 and 2000 ppm; depending on the type of boiler and the manner of conducting the process, the amount of nitrogen oxides in gases stays in the range of 500-1500 ppm.

The amount of chlorine and fluorine compounds is much lower; the amount of volatile particulates is of the order of  $150 \text{ mg/m}^3$ . These values and temperature in gases upstream the reactor affect the physical and chemical conditions of the execution of the purification process, with active carbon performing both adsorptive and catalytic functions.

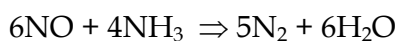
The mechanism of reduction of nitrogen oxide with ammonia in the presence of sulphur dioxide on active carbon, adopted by Richter [76], and the conclusions from laboratory-scale experiments in this area [77,78] clearly indicated the advisability of initial lowering of the  $\text{SO}_2$  concentration in purified gases, using excess ammonia with respect to the total of  $\text{SO}_2$  and NO, ensuring adequate contact time by increasing the height of the bed layer, and maximally lowering the temperature of the process.

In experiments referred to by Knoblauch [78], conducted on a fixed bed of active coal, attention was drawn to the distribution of sulphuric acid and its ammonium salts in the bed, as well as distribution inside it of areas of individual reactions, including the reaction of reduction of nitrogen oxide.

The mechanism of the process presented by Richter [76] and the results of experiments cited, inter alia, by Knoblauch, were the basis for the decision to use a two-stage model of the process of  $\text{SO}_2$  adsorption and NO reduction, carried out in a suitably designed reactor.

In the first stage of adsorption, the primary processes of sulphur dioxide sorption take place inside pores of active coke. At this stage over 90% of the total amount of  $\text{SO}_2$  is stopped, as well as HCl, HF, heavy metals, volatile particulates, and the total amount of  $\text{NO}_2$ . The middle part of the adsorber, designed in the form of a mixing chamber, ensures uniform concentration of  $\text{SO}_2$  in gases upstream the second stage. At the same time, nozzles supply ammonia, which, in order to prevent formation of streams, is pre-mixed at a ratio of 1:25 with purified gas.

At the second stage nitrogen oxide is catalytically reduced at temperatures of 90 to  $150^\circ\text{C}$ . Ammonia is adsorbed and then reacts on the coke surface according to the total reaction:



Additionally, there is binding of residual sulphur dioxide; neutral and acid ammonium salts are formed and deposit on the surface layer of sorbent. Purified gases are discharged through the flue to the atmosphere.

Some solutions [79] provide for a three-stage adsorption system, where the first and second stages of  $\text{SO}_2$  adsorption and NO reduction have been supplemented with a third stage, adjoining the second one and powered with part (50%) of the sorbent leaving the first stage,

which contains mainly adsorbed sulphuric acid. Such solution is designed to limit ammonia losses in gases leaving the installation.

#### **Parameters of the adsorption process**

On the basis of numerous data, contained in patent information, findings of studies conducted on an increased scale on existing pilot installations, as well as on the basis of bidding information of Bergbau-Forschung [75], we can attempt to identify the parameters characterising the process using carbon sorbents. For example, patent information [80] provides some data about the process executed on a Japanese pilot installation for the amount of gas  $V=1400 \text{ m}^3/\text{h}$ , with the  $\text{SO}_2$  and  $\text{NO}_x$  content of, accordingly, 2900 and 500 ppm. Ammonia was supplied to gas prior to adsorbers. Inertness of active carbon bed in the adsorber was 4.6 and  $1.8 \text{ m}^3$ ; the process was carried out in two stages.

Based on these data and assuming an average bulk density of the sorbent  $d=0.700 \text{ kg}/\text{m}^3$ , the amount of sorbent can be estimated at the respective stages, sorbent load with the GHSV gas, and the duration of stay of active carbon [h] in the adsorber:

Duration of stay of coke in the adsorber approx. 200 hours, including on the second stage for 150 hours [75, 81, 82]. The flow rate of coke in the adsorber approx.  $0.1 \text{ m}/\text{h}$ .

The installation provides for the use of a third adsorption stage, whose task is to remove residual ammonia from gases leaving the adsorber. This stage, which is connected directly with the second one, is supplied with sorbent from the first stage in the amount of 50% of coke supplied to the adsorber.

#### **Regeneration of the carbon sorbent**

The process of regeneration of active coke, saturated with sulphuric acid and its salts, takes place mostly by means of thermal distribution at temperatures above  $300^\circ\text{C}$ .

Knoblauch presented [78] the results of experiments on thermal regeneration of active carbon, heating it in a stream of helium in a differential reaction at a rate of  $10 \text{ deg}/\text{min}$ . Initially, secretion of physically adsorbed water vapour is observed. As the temperature increases, desorption of sulphur dioxide and a two-stage decomposition of ammonium sulphate takes place according to the following reaction:



with some of the ammonia released at the first stage being oxidised with surface oxides. At a temperature of approx.  $500^\circ\text{C}$  acid ammonium sulphate decomposes with release of sulphur dioxide, ammonia, and water vapour to the gas phase. At temperatures above  $500^\circ\text{C}$  increasing amounts of nitrogen, carbon dioxide, and carbon monoxide start to appear in the exhaust gases.

There are several variants of the process depending on the form of contact of the solid phase with gas, mobile bed of sorbent or the fluidal system, and direct method of supplying heat energy. In the first solutions by Bergbau-Forschung [78], hot sand was used as the heating medium, heated separately to the temperature of  $600\text{--}650^\circ\text{C}$ , which was mixed with coke leaving the adsorption system. Under these conditions sulphuric acid and sulphates were reduced. Loss of carbon in the regeneration process, causing a change in the configuration of sorbent pores, simultaneously lead to an increase in its absorbing and catalytic capacity by an increase of the effective catalytic area. In another variant [83], thermal decomposition of sulphuric acid and sulphates was achieved by hot sorption gases, additionally heated in a separate exchanger to the temperatures of  $300\text{--}600^\circ\text{C}$ . The process was carried out in a fluidal system.

In a recently proposed solution, a three-section tube desorber was used on a large industrial scale [75, 81]. Active coke from the first adsorption stage, totally free of particulates, passes through an intermediate tank to the upper part of the desorber, which consists of three parts. In the actual upper desorption part, coke moves gravitationally through the tubes, heated through membrane to the temperatures of 400-450°C. The source of heat are hot exhaust gases, produced in a separate combustion chamber.

In the middle part of the apparatus, sulphur dioxide desorbs from the bed, passing to the gases discharged outside as a so-called "rich" (containing up to 30% of SO<sub>2</sub>) desorption gas. In the lower part coke is air-cooled through membrane to approx. 100°C. After subgrain is separated on the sieve and the missing content is filled in, coke is directed to the upper part of the second stage of the adsorber. The operation of thermal regeneration of sorbent constitutes a significant power load for the process. The literature signals [84-86] attempts at regeneration of the sorbent at a lower temperature by washing with water; however, this process results in very diluted solutions of sulphuric acid and sulphates.

Other attempts at regeneration of carbon sorbents by means of inert gases containing in their composition ammonia and at an elevated temperature of the order of 250-450°C usually concerned a process that realised only sorption of nitrogen oxides [50, 70, 87].

#### **Variants of the process**

In a classical system of simultaneous removal of sulphur and nitrogen oxides according to the Bergbau-Forschung method, the purification installation is located in the power production line directly downstream of the electrostatic precipitators and such system does not require additional heating of the gases.

Because active coke, in addition to catalytic properties, may provide sorption functions, nitrogen oxide will be removed together with "residual" sulphur dioxide, which leaves desulphurisation installation in the amount of approx. 400 mg/m<sup>3</sup>. The resulting ammonium sulphate has an adverse affect on the catalytic activity of coke. This necessitates periodic regeneration of the sorbent, but in very small amounts, therefore desorber dimensions may be only slightly decreased [88].

Gases containing sulphur dioxide emitted in the regeneration process are returned to the desulphurisation unit, thus increasing the total effect of SO<sub>2</sub> removal. With this solution and when desulphurising with lime milk, the system for processing of post-regenerated gases is not used, and the only product of the process is gypsum.

A similar solution is proposed by H. Petersen, which uses the Bergbau-Forschung licence. The purpose of the procedure is to obtain liquid SO<sub>2</sub> with the omission of gypsum production. Sulphur dioxide is absorbed by means of the NaOH solution, whose pH stabilises with the addition of appropriate organic compound. Blowing with air desorbs SO<sub>2</sub> from the post-absorption solution, resulting in gases where it is present in high amount. After drying and cooling the gases are subjected to separate processing. On the other hand, NO reduction is carried out on the bed of active coke in the same way as in the BF process, with periodic coke regeneration and returning of the gases to the desulphurisation stage after regeneration.

Despite obvious benefits, the presented variants have not as yet been implemented on a large industrial scale. The patent literature indicates a number of proposed changes to some fragments of this process. These changes concern supplementation of the sorbent composition to give it different qualities or properties, the method of conducting basic operations – adsorptions or the number of apparatuses on the technological diagram, and the search for reducers other than ammonia.



Some of the patents [73] suggest the possibility of obtaining much higher gas loads of sorbent than e.g. in the case of active coke without modifying additives, which is often associated with the need to use higher temperatures [70, 87, 89, 90]. It is also proposed that the composition of carbon sorbents is supplemented with substances having alkaline functions, for example hydroxides and alkaline earth carbonates [91-96], with the patent by Ishikawajima Harima Heavy Ind. [94] suggesting that a process of NO reduction can be conducted without ammonia.

One of the publications considers the advisability of NO reduction using active carbon saturated with urea [97]. Besides the most common form of operation with the use of a fixed or movable bed, there is perceived possibility of conducting adsorption in the fluidal phase [98, 99]. Similarly, the previously described methods of thermal regeneration – by mixing sorbent with hot sand [78], heating by inert hot gases in a fluidal system [70, 77, 83, 87, 100, 101] and by way of membrane heating [75, 88, 81], as well as the two-stage method described in one of the patents [102] and attempts at regeneration by washing with water or appropriate solutions [84-86] – may determine different shaping of the whole technological process. Different adsorber designs represent two patents [103, 104]. Several patents propose replacement of ammonia as an NO reducer by carbon monoxide or hydrocarbons [61, 89, 105, 106] as well as hydrogen sulphide [104].

## 7. The manufacturing of CARBODENOX catalysts on the basis of monolithic carbon carrier

Active carbon based catalysts elaborated by EKOMOTOR Ltd. (Poland) are sufficiently active to realise SCR reaction at low temperature, from 100 to 200°C. They are especially useful for application in these processes at which flue gases temperature is lower than 200°C. Above 200-220°C and in the presence of oxygen (in air) active carbon catalyst is oxygenated and therefore higher process temperature is limited. This type of carbon catalyst after exploitation can be easily utilised e.g. by combustion. In comparison to titania based ceramic SCR catalysts active carbon based catalysts are relatively cheaper. Active carbon based catalysts are capable to adsorb SO<sub>2</sub> and other chemical compounds from the flue-gases. It is necessary to say that they show appreciably higher specific surface area, from 200 to 800 m<sup>2</sup>/g and pore volume, from 0.2 to 0.8 dm<sup>3</sup>/kg. For instance titania based catalysts are characterised by specific surface area lower than 100 m<sup>2</sup>/g and pore volume 0.15 – 0.30 dm<sup>3</sup>/kg. **Active carbon based SCR catalysts should be operated after ESP or between preheaters and ESP but always after desulfurization process.** DeSONOX combined process is also possible with using the same active carbon based catalytic material but with using different active phases and different temperatures and **deSOx have to be the first step of the process.**

High efficiency of denitrification of flue gases can be accomplished as a result of utilisation of carbon catalysts within the temperature range 100-200°C. The possibility of a high efficiency of gas purification at relatively low temperature range, close to temperatures of flue gases exiting from the electrostatic precipitator, makes the process very attractive particularly for domestic power stations equipped predominantly with "cold" electrostatic precipitator. Therefore, the new carbon-based catalysts will result in elimination of preheating stage of flue gases prior to their classic SCR processes [107]. The economic advantages of application of these catalysts are very obvious.

The application of active carbons additionally enables an effective removal of halide species, which are particularly harmful for the environment. In comparison to the grain shaped catalysts the honeycomb monolithic catalysts exhibit appreciably lower pressure drop, the cleaning operations are easier and more seldom, in the end the plugging risk is lower than in the case of the grained catalysts.

Active carbon based catalysts and adsorbents which are commonly applied all over the world in the form of spherical tablets or granules create high pressure drop along the catalyst bed and require the dust separation and application of small gas flow rates.

Active carbon monoliths can be effectively utilised in all operations where active carbon is being applied as a granulate (adsorption in gases and liquids, catalysts, catalyst supports). In comparison to grain catalysts the "honeycomb" structure guarantees developing of high geometric specific surface of catalysts per volume unit while pressure drop (low flow resistance) is low. This structure assures also an uniform gas flow, appropriate temperature distribution and gives the possibility to apply high linear flow rate of flue gases without excessive pressure drop.

Monolithic form of catalyst ensures its resistance against deactivation by dust fines contained in the cleaned gas. Due to the fact that such catalysts can be easily regenerated, extending their period of exploitation (life time), assures the operation at relatively high dust concentration, and reduces the operation costs by limitation the number of demanded ventilation and gas conditioning equipment. Active carbon monoliths can be manufactured with using of the special types of coal (e.g. 34 type) or carbonaceous material which are susceptible for forming and retaining the monolithic form after thermal treatment. The additional specific property of the monolithic material is low thermal expansion coefficient.

On the basis of own technologies EKOMOTOR Ltd. (Poland) has manufactured carbon monoliths of "honeycomb" structure. It was found that the active carbon having such a structure exhibits unique properties both as a sorbent and as a support for catalysts. Its sorption properties can be fully utilized for gas and liquid purification. An active carbon can also be applied as a support in manufacturing of catalysts for low temperature selective catalytic reduction (SCR) of nitrogen oxides with ammonia and of catalysts for desulfurization as well.

In relation to other technologies of flue gases cleaning, the catalytic methods are recognized as wasteless and costs of their operation are low. Preliminary studies of catalytic cleaning of flue gases shown that the application of catalysts manufactured from active carbon leads to the apparent lowering of temperature of cleaning process. It was found that efficiency of flue gases desulfurization was within the range of 60 - 80% whereas efficiency of denitrification reached above 75% when active carbon catalysts were applied even within the range of temperature of 100 - 190°C. Such a high purification extent of flue gases at relatively low temperatures makes the process very attractive from the point of view of energy consumption. In the case of carbon-based catalysts it is not necessary to pre-heat flue gases prior to the desulfurization and denitrification as it has to be performed in the case of standard ceramic catalysts. In the later, required temperature of the process is in the range of 300 - 450°C. The remarkable reduction of economic costs is therefore obvious when carbon catalysts are used.

The manufacturing of novel catalysts of "honeycomb" structure from active carbon in the laboratory scale was the result of previously performed investigations. These catalysts

appeared to be an unique achievement even in the world scale. It is mainly due to the fact, that the elaborated and developed catalysts for low temperature gas purification are resistant to deactivation by dust fines contained in the cleaned gas. Such a form of a modified active carbon exhibiting thin wall structure with a longitudinal channels creates very low flow resistance. Due to the fact that such catalysts can be easy regenerated, extending their period of exploitation (life time), assures the operation at high dust concentration, and reduces the operation costs by limitation the number of demanded ventilation and gas conditioning equipment.

Catalysts and adsorbents based on active carbon are commonly applied all over the world in the form of spherical tablets or granules create high pressure drop along the catalyst bed and require the dust separation and application of small gas flow rates. Active carbon monoliths can be effectively utilized in all operations where active carbon is being applied as a granulate (adsorption in gases and liquids, catalysts, catalyst supports).

Geometry of fabricated catalyst of the "honeycomb" structure guarantees its highest developing of specific surface per a unit of volume. This structure assures also an uniform gas flow, appropriate temperature distribution and suitable residence time in the catalyst layer. Moreover, monolithic carbon catalysts except of being remarkably active have an essential virtue of being cheap. According to the preliminary cost analysis, these catalysts are expected to be considerably cheaper in relation to standard ceramic catalysts employed for high temperature catalytic desulfurization and denitrogenation of flue gases. High efficiency of desulfurization (60-80%) and denitrification (above 75%) of flue gases can be accomplished as a result of utilization of carbon catalysts within the temperature range as low as 120-190°C. The possibility of such high efficiency of gas purification within a relatively low temperature range, close to temperatures of flue gases exiting the electrofilter, makes the process very attractive particularly for power stations equipped predominantly with "cold" electrofilters. Therefore, the new carbon-based catalysts will result in elimination of preheating stage of flue gases prior to their desulfurization and denitrification processes. The economic advantages of application of these catalysts are very obvious.

The CARBODENOX catalysts are supported on the carrier of the same type - "honeycomb" structure monoliths of active carbon. As carbon plays a very important role in changes occurring on the catalyst when it is functioning, the division into the carbon carrier and the catalyst placed on the carrier must be regarded conventionally. Based on literature analysis, it was decided that the research should use hard gas-coke coal type 34 coming from the polish coal mine "NOWY - WIREK".

Tables 7 and 8 show the results of the technical and elemental analysis, of the petrographic composition, and of the carbon structure parameters determined from the X-ray diffraction method.

W <sup>a</sup>	A <sup>a</sup>	V <sup>daf</sup>	C <sup>daf</sup>	H <sup>daf</sup>
1.9	6.1	33.4	85.9	5.0

Table 7. Technical and elemental analysis of the gas-coke coal from the coal mine "Nowy Wirek" [%]. The symbols show as follows: W<sup>a</sup> - analytic moisture, A<sup>a</sup> - ash content, V<sup>daf</sup> - volatile matter content counted as dry and ash-free matter, C<sup>daf</sup> - carbon content counted as dry and ash-free matter, H<sup>daf</sup> - ash content counted as dry matter

Vitrinite [%]	Exinite [%]	Micrinite [%]	Fuzynite [%]	Mineral matter [%]	R <sub>o mean</sub>	d <sub>002</sub> [nm]	L <sub>c</sub> [nm]	L <sub>a</sub> [nm]
66.1	6.3	3.8	20.6	3.2	0.92	0.36	0.87	1.36

Table 8. Petrographic composition and structure parameters of coal from the “Nowy Wirek” coal mine. The symbols show as follows: R<sub>o mean</sub>- average light reflecting power, d<sub>002</sub>- distance between crystal planes,L<sub>c</sub>- crystallites height, L<sub>a</sub>- crystallites diameter

Table 9 shows coke properties of the gas-coke coal from the “Nowy Wirek” coal mine, which was used in the research.

RI	SI	Dilatometric properties					Plastic properties			
		t <sub>I</sub>	t <sub>II</sub>	t <sub>III</sub>	a	b	t <sub>1</sub>	t <sub>max</sub>	t <sub>3</sub>	F <sub>max</sub>
		°C			%		°C			deg angle/min
63	4.5	373	417	435	28	15	370	338	454	178

RI - Roga agglomeration number (agglomeration capability), SI - free-swelling index, Dilatometric properties in the Arnu-Audibert method (t<sub>I</sub>- softening point, t<sub>II</sub>- contraction temperature, t<sub>III</sub>- dilatation temperature, a – contraction, b – dilatation), Plastic properties of the Griesler method

t<sub>1</sub> - softening point  
t<sub>max</sub> - temperature of maximal plasticity  
t<sub>3</sub> - temperature of the end of plasticity  
F<sub>max</sub> - maximal plasticity

Table 9. Coke properties of the gas-coke coal from the “Nowy Wirek” coal mine. The symbols are as follows:

Chemical composition of natural clay used for carrier prepared is presented in Table 5.

The technology of production of CARBODENOX catalysts covers two basic stages:

- manufacturing of the carrier,
- manufacturing of the catalyst on the produced carrier.

Active carbon based catalysts can be manufactured from type 34 hard coal and carbonaceous like additives which are susceptible for carbonisation. The carbon catalysts produced out of the basic types of materials: gas- coke hard coal type 34, natural aluminosilicate, active metals salts (for example: ferric, cupric and manganese nitrate).

Coal is a basic material used for obtaining monoliths out of active carbon shaped into block of “honeycomb” structure. The following substances are put on the surface area of monoliths depending on their use cupric oxide, ferric nitrate, manganese nitrate.

The block diagram of manufacturing of catalysts shaped into block of “honeycomb” structure used for low-temperature cleaning of combustion gases are presented below (Fig.20).

The three types of catalysts can be used in the process of low-temperature cleaning of combustion gases: ferric oxide (3,5 wt%) based catalyst, copper oxide (3, 5 wt%) based catalyst, copper (3,5 wt%) and manganese (3, 5 wt %) oxides based catalyst. The carrier is the same for all catalysts. Geometry of catalysts based on monoliths of honeycomb structure is presented in table 10.

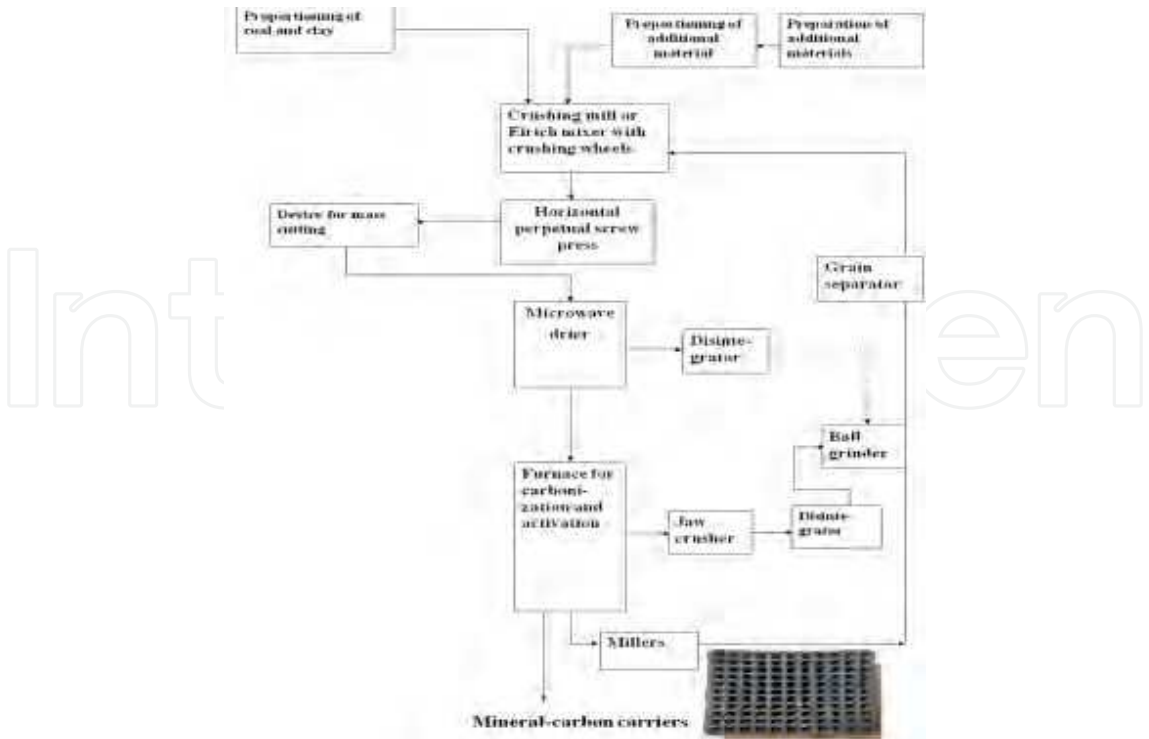


Fig. 20. Block diagram of manufacturing of the carrier

Parameter	Dimension	Typical monoliths
Determined draw hole	-	5.0
Dimensions of the cross-section (length of side)	Mm	98
The number of draw holes	-	11 x 11
External wall thickness	Mm	3,0 - 4.0
Internal wall thickness	Mm	2,2 - 2,8
Draw hole size	Mm	4.5
Open space	%	31,5
The development of the surface after carbonization and activation	m <sup>2</sup> / g	600 -800

Table 10. Geometry of catalysts based on monoliths of honeycomb structure.

Carbon monoliths of "honeycomb" structure were obtained with the following structural parameters: specific surface of micropores (for pore radius below 1.5 nm): 40-200 m<sup>2</sup>/g; specific surface of mezopores (for pore radius within 1.5-50 nm): 20 - 160 m<sup>2</sup>/g; specific surface of macropores (for pore radius above 50 nm): 20 - 80 m<sup>2</sup>/g; total porosity: 0.3 - 0.6 cm<sup>3</sup>/g.

The above mentioned catalysts were prepared by wet impregnation method. It means that carbon monoliths were dipped in the suitable concentration solution of active metal salts. Fe (NO<sub>3</sub>)<sub>2</sub>; Cu (NO<sub>3</sub>)<sub>2</sub>; Mn (NO<sub>3</sub>)<sub>2</sub>.

After each impregnation the monoliths were dried at ambient temperature and 110°C. Removal of water occurs at 100°C - 115°C. After the monoliths impregnated with nitrates are dried, they are calcined at 400°C in oxygen-free conditions. There is a possibility of using



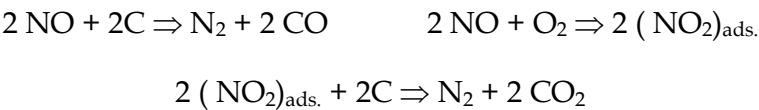
the furnaces (used for carbonisation and activation of the carrier) for calcination process of the catalyst. It must be remembered, however, that aggressive gassing waste containing huge amount of nitrogen oxide (NO<sub>x</sub>) are emitted during the calcination process of the CARBODENOX catalyst and it must be reduced. Calcination step was carried out at 400°C for 4 hours in nitrogen stream. In the case of Cu-Mn/C catalyst this operations was repeated twice. New, freshly-produced catalysts of the selective reactivity of catalytic reduction of nitric oxide with ammonia, require conditioning before the test starts. It is advisable to condition the catalyst for 72 hours in testing conditions. The quality of produced catalysts must be estimated by estimation of the geometric shape as well as regards activity of the catalysts. In order to estimate activity of the catalysts the monoliths selected from produced mass must be loaded into the testing flow micro-reactor reactor and undergo a test of activity. The activity of prepared catalysts was determined with testing method of a selective catalytic reduction of nitric oxide by ammonia. operating in the way shown in Fig. 6 was used to carry out the research. The conditions of the test (in temperature range: 100 - 200°C):

Oxygen content in the model gas: 8%  
Nitric oxide contents: 1000ppm  
GHSV: 3 000 m<sup>3</sup>/m<sup>3</sup>•h<sup>-1</sup>  
Mole ratio NO : NH<sub>3</sub> 1:1

The estimation of catalyst activity was carried out by determination of the conversion of nitric oxide on the surface of the tested catalysts in dependence on catalyst bed temperature. As catalyst activity indicator can be used NO<sub>x</sub> conversion at temperature 180 °C, (temperature of flue gases in the case of applying of cold electro-precipitator) [108- 113].The results of activity some prepared catalyst were presented in Fig. 21

Scheme of SCR reactions on active carbon catalyst:

1. Small quantity of NO is reduced by carbon support:



2. More of NO from exhaust gases is reduced by ammonia:

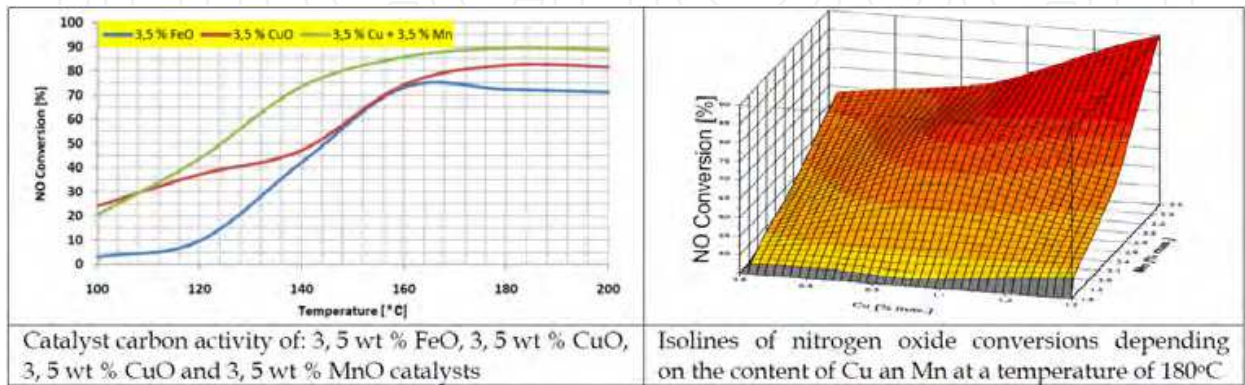


Fig. 21. Carbon based catalyst activity

## 8. Conclusion

The rapid development of industry results in an increase in the emission of sulphur and nitrogen oxides into the atmosphere. The issue becomes even more complex due to the gas temperature and dustiness. From among the currently known technologies used for simultaneous elimination of both sulphur and nitrogen oxides the dominant role seems to be played by the processes employing carbon sorbents. The methods for which it is not necessary to preheat combustion gases will always be more cost-effective. Their main advantage is the possibility of carrying out SO<sub>2</sub> adsorption and NO reduction at low process temperatures, approximately 90-130°C, namely within the range of gas temperatures behind electrostatic precipitators in the majority of boilers. It enables smooth incorporation of the purifying installation in the existing energy system, without the necessity of additional gas preheating. Concurrently, in connection with the positive thermal and catalytic effect, the thermal balance of the process is also positive and the temperature of purified gases is adequate for releasing them into the atmosphere. Therefore, the installation does not upset energy relationships in the existing system.

Another considerable advantage of the technologies based on carbon sorbents is the high effectiveness of their operation, in both sulphur (95-100%) and nitrogen removal processes (75-80%), where the sorbent activity increases with time. The Bergbau-Forschung method, representative of this group of technologies, is characterised by its flexibility in the case of a variable motion of the power unit (insensitivity to switching the unit on and off) and capacity for adaptation to variable concentrations of SO<sub>2</sub> in the purified gases, i.e. to a varying sulphur content in the fuel. In the case of high concentrations of SO<sub>2</sub> in gas, a two-stage adsorber system is used, which concurrently meets the requirement for the minimum ammonia consumption and reduces the negative impact exerted by SO<sub>2</sub> on the course of nitrogen oxide reduction. In the case of a low content of sulphur dioxide (gas fuel) a one-stage system is sufficient, and hence the dimensions of the installation and energy input can be significantly reduced.

Unlike the selective catalytic NO reduction methods, the technologies employing carbon sorbents are not sensitive to gas contamination with chlorine, arsenic and mercury compounds and alkalis, which in practice are removed completely.

Since no data are available from large-scale industrial installations it is difficult to present any reliable characteristics of these methods in terms of their cost-efficiency. In the SCR method a half of capital expenditure is related to the purchase of a catalyst. BF method is commensurate with the expenditure incurred for the SCR method. Disadvantages of the BF method include a high demand for active carbon, resulting from, among others, admissible gas loading on sorbents, which is significantly lower than in the case of the SCR methods, considerable consumption of active coke (up to 50% by weight) caused by subgrain formed when a movable bed is used, increased resistance of gas flow through moving beds and large dimensions of the adsorber and regenerator in the case of a two-stage system. The last one of the listed disadvantages, combined with difficult location problems, restricts the use of this method to single power units, with the power output up to 200 MW. The presented information, gathered from the literature review, concerning catalytic methods of combustion gas purification shows clearly that research on this problem goes in many directions and it is aimed at working out technological solutions tailored to the local raw material conditions as well as universal ones.

## 9. Acknowledgments

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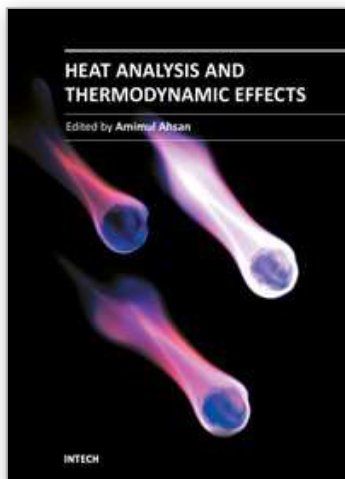
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The heat transfer and analysis on heat pipe and exchanger, and thermal stress are significant issues in a design of wide range of industrial processes and devices. This book includes 17 advanced and revised contributions, and it covers mainly (1) thermodynamic effects and thermal stress, (2) heat pipe and exchanger, (3) gas flow and oxidation, and (4) heat analysis. The first section introduces spontaneous heat flow, thermodynamic effect of groundwater, stress on vertical cylindrical vessel, transient temperature fields, principles of thermoelectric conversion, and transformer performances. The second section covers thermosyphon heat pipe, shell and tube heat exchangers, heat transfer in bundles of transversely-finned tubes, fired heaters for petroleum refineries, and heat exchangers of irreversible power cycles. The third section includes gas flow over a cylinder, gas-solid flow applications, oxidation exposure, effects of buoyancy, and application of energy and thermal performance index on energy efficiency. The fourth section presents integral transform and green function methods, micro capillary pumped loop, influence of polyisobutylene additions, synthesis of novel materials, and materials for electromagnetic launchers. The advanced ideas and information described here will be fruitful for the readers to find a sustainable solution in an industrialized society.

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