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Iveta Pandová, Anton Panda

**ZEOLITES AND THEIR USE AT ENVIRONMENT  
PROTECTION  
WITH A FOCUS ON THE AUTOMOTIVE INDUSTRY**

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The objective of the monograph is to review literature on the use of zeolites in the environmental field as well as to present the experimental results on natural clinoptilolite zeolite application. This publication intends to address researchers involved in the use of sorption materials in the environmental area as well as university teachers interested in new trends in the area.

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### **ZEOLITES AND THEIR USE AT ENVIRONMENT PROTECTION WITH A FOCUS ON THE AUTOMOTIVE INDUSTRY**

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RNDr. Iveta Pandová, PhD., prof. Ing. Anton Panda, PhD.

**ISBN 978-3-942303-65-1**

**Iveta PANDOVÁ, Anton PANDA:**

**ZEOLITES AND THEIR USE  
AT ENVIRONMENT PROTECTION WITH A FOCUS ON  
THE AUTOMOTIVE INDUSTRY**

**Abstract:**

Phenomenon of industrial production development and automobile transportation is the formation of gaseous emissions and waste water. Air pollutants accrue mainly in energy production as well as technology and transportation. Combustion engines produce exhaust gases containing carbon monoxide, nitrogen oxides and various types of hydrocarbons. All of these ingredients are toxic to living organisms. Moreover, nitrogen oxides are a group of gases and contribute to climate changes as well as greenhouse effect. In order to reduce pollutants in exhaust gases, zeolites that have a crystalline porous structure, ion exchange and catalytic properties, can be used. The nature provides us with a material which after suitable chemical treatment as a selective effect on certain molecules, cations and anions as well as catalytic properties useful for the conversion of toxic components in exhaust gases into nontoxic. This material is natural zeolite. The peculiarity of its structure is of great interest nowadays. Due to its chemical and physical properties it has a wide range of applications in ecology, industry and technology as well as in agricultural production. In Slovakia, there are significant deposits of zeolites in Nižný Hrabovec and Majerovce, where the main rock-forming mineral is clinoptilolite. Natural zeolite clinoptilolite is ranked among the most widely used zeolite minerals. In addition to the significant physical and chemical properties such as adsorption, ion exchange and catalytic properties, its non-toxicity and affordability is very important for environmental and industrial purposes. In the following sections, the authors characterize zeolites in general. The results of the research on the use of natural clinoptilolite zeolite for reducing toxic components of exhaust gases produced by internal combustion engines as well as the results of the research on the reduction of the content of some heavy metals in aqueous solutions are being presented in this publication.

## CONTENTS

<b>1</b>	<b>INTRODUCTION, BASIC TERMS, INTENTION AND THE OBJECTIVES OF THE MONOGRAPH</b>	<b>1</b>
<b>2</b>	<b>CHEMICAL AND PHYSICAL PROPERTIES OF ZEOLITES</b>	<b>3</b>
<b>3</b>	<b>NATURAL ZEOLITES PROPERTIES</b>	<b>8</b>
3.1	Selectivity	9
3.2	Regeneration – desorption of sorbents	9
3.3	Survey of the best known zeolites types	10
3.4	Physical and chemical properties of clinoptilolite	13
<b>4</b>	<b>METHODS OF THE NATURAL ZEOLITE MODYFING</b>	<b>18</b>
<b>5</b>	<b>WAYS OF USING NATURAL ZEOLITES IN PRACTICE</b>	<b>24</b>
5.1	The use of zeolite in agriculture	25
5.2	Water treatment	27
5.3	Use of zeolites in construction industry	28
5.4	Gas separation using the modified zeolites	29
5.5	Reduction of harmful emissions	30
<b>6</b>	<b>EFFECT OF INTERNAL COMBUSTION ENGINES ON ENVIRONMENT</b>	<b>32</b>
<b>7</b>	<b>OPERATION PRINCIPLES OF SORPTION AND CATALYTIC DEVICES</b>	<b>37</b>
<b>8</b>	<b>THE THEORETICAL BASIS OF ADSORPTION AS A MAJOR PROPERTY OF ZEOLITES</b>	<b>43</b>
<b>9</b>	<b>CLINOPTILOLITE TESTING TO REDUCE TOXIC COMPONENTS OF COMBUSTION ENGINES EXHAUST GASES</b>	<b>46</b>
9.1	Samples treatment	48
<b>10</b>	<b>REDUCTION OF TOXIC EXHAUST COMPONENTS FOR INTERNAL COMBUSTION ENGINES</b>	<b>50</b>

10.1	Reduction of nitrogen oxides in exhaust gases using the filter-sorption device with differently modified samples	51
<b>11</b>	<b>THE USE OF THE ZEOLITES IN WASTE WATER TREATMENT</b>	<b>70</b>
11.1	Copper cations removal using natural and synthetic sorbents	71
11.2	Removal of nickel cations from the waste water on the zeolite – clinoptilolite	76
<b>12</b>	<b>CONCLUSION</b>	<b>79</b>
<b>13</b>	<b>REFERENCES</b>	<b>81</b>

# **1 INTRODUCTION, BASIC TERMS, INTENTION AND THE OBJECTIVES OF THE MONOGRAPH**

Accompanying phenomenon of industrial production development and automobile transportation is the formation of gaseous emissions and waste water. Air pollutants accrue mainly in energy production as well as technology and transportation. Combustion engines produce exhaust gases containing carbon monoxide, nitrogen oxides and various types of hydrocarbons. All of these ingredients are toxic to living organisms. Moreover, nitrogen oxides are a group of gases and contribute to climate changes as well as greenhouse effect. In order to reduce pollutants in exhaust gases, zeolites that have a crystalline porous structure, ion exchange and catalytic properties, can be used. The nature provides us with a material which after suitable chemical treatment has a selective effect on certain molecules, cations and anions as well as catalytic properties useful for the conversion of toxic components in exhaust gases into nontoxic. This material is natural zeolite. The peculiarity of its structure is of great interest nowadays. Due to its chemical and physical properties it has a wide range of applications in ecology, industry and technology as well as in agricultural production. In Slovakia, there are significant deposits of zeolites in Nižný Hrabovec and Majerovce, where the main rock-forming mineral is clinoptilolite. Natural zeolite clinoptilolite is ranked among the most widely used zeolite minerals. In addition to the significant physical and chemical properties such as adsorption, ion exchange and catalytic properties, its non-toxicity and affordability is very important for environmental and industrial purposes.

In the following sections, the authors characterize zeolites in general. The results of the research on the use of natural clinoptilolite zeolite for reducing toxic components of exhaust gases produced by internal combustion engines as well as the results of the research on the reduction of the content of some heavy metals in aqueous solutions are being presented in this publication.



**Figure 1: Natural clinoptilolite zeolite**

## 2 CHEMICAL AND PHYSICAL PROPERTIES OF ZEOLITES

Rising demand for environmental protection requires to increase the proportion of usage of non-toxic and unexpensive materials at the same time. Such materials include zeolites of natural and synthetic origin. These materials are useful, inter alia, in environment protection. Since the fifties of the 20th century, zeolites have been used in this area. In the last decade it has become known how to use zeolites in the purification of exhaust gases and in waste water treatment. In terms of water treatment, their sorption and ion-exchange capabilities resulting from their structure are of great interest. The three-dimensional structure of zeolite is formed by a regular arrangement of tetrahedrons  $[\text{SiO}_4]^{-4}$  and  $[\text{AlO}_4]^{-5}$ . In the network of tetrahedrons  $[\text{SiO}_4]^{-4}$  a portion of silicon is isomorphically replaced by aluminum atoms. The occurring negative charge of zeolitic lattice is compensated by cations which are located in the off grid-positions. The most common are alkali metal cations and alkaline earth metals [1,2]. These cations may be replaced by means of sorption and ion exchange with the other cations. In the late sixties, the first high silicate zeolites, which enabled the development of highly selective processes in the chemistry of aromatic hydrocarbons, were prepared. Natural zeolite was discovered in 1756 when the term "zeolite" was used for the first time by the Swedish mineralogist Cronstedt for mineral stilbite. The most recently discovered natural zeolites include tsernichite which is a natural analogue of synthetic zeolite Beta and mutinait which is a natural analogue of the synthetic ZSM-5 [3]. Under the glaciers of Antarctica, Yugawaralite was discovered. Zeolites are minerals of great importance and wide application in environmental engineering. Their unique structure, characterized by a regular system of channels and chambers, determines their properties such as ion exchange, molecular-sieving, catalysis and adsorption. Natural zeolites are represented by over 80 minerals but only a few of them (clinoptilolite, mordenite, philipsite and chabazite) occur in forms accessible for mining. So far, over 150 types of synthetic zeolites have been obtained using laboratory procedures and various starting materials, such as clay minerals, silicate group minerals and chemical reagents or coal combustion by product like flyash [4].

The chemical composition of zeolites can be described by the following general formula:



Inside the crystal structure of zeolites, the channels are positioned in precisely defined dimensions. The input windows are in the range from 0.3 nm to 1 nm. This defines the

size of molecules which can enter the channel of zeolite structure. This regular structure containing channels separates zeolites from amorphous microporous materials such as carbon or active alumina. In most of porous zeolite, about 50% of each crystal is the pore volume accessible to water or other guest molecules. Sorption of the guest molecules is based on physical phenomena such as surface adhesion, the action of the Van der Waals forces and the electromagnetic force field. Zeolites can bind various substances, metal ions, groups of atoms, polar and non-polar molecules. Zeolites with large cavities, for example faujazit (zeolite of X and Y type) can adsorb whole clusters of molecules. Barrer dealt with detailed study of sorption equilibrium of zeolites [6]. According to the results with the increasing temperature, the degree of saturation in the sorbed component decreases and the volume of sorbed molecules increases. Sorbed components bound in groups are not so strongly bound to each other. An important mineralogical and chemical characteristic of zeolites is the ratio Si/Al.

This value indicates the acidity and basicity of zeolites as well as their thermal and chemical stability. Zeolites with higher value of ratio Si/Al are more acidic and more stable. Generally, zeolites with a higher proportion of Si/Al are more hydrated. Boundary of the thermal stability with different types of zeolites varies. The thermal stability is also influenced by cationic composition. Synthetic zeolites are prepared as primary products usually in a sodium form. Modifications of zeolites derived from the primary type of zeolites by cation exchange and introducing other metal ions in zeolite structure. Ion exchange is affected by contacting zeolite with a salt solution containing prevailing ion or salts combination. Electron neutrality principle of zeolite lattice shows the lower ratio between silicon and aluminium. This principle is supported by greater number of cations which neutralize the negative charge of the lattice [7]. This exchange cannot always be taken at 100%. Therefore, even if the exchange is done only by one ion in relation to the original structure, resulting zeolites may contain a combination of both. The equilibrium adsorption capacity (EAC) is one of the basic physical characteristics of the adsorbent which can be represented on a particular state, that is, for a pressure or relative humidity and temperature.

EAC is a complex of characteristics of several adsorption isotherms for the adsorbent and the adsorbate in the interval of the pressures of adsorbates. EAC in the form of powder zeolites without a binder for the same types and modifications have the minimal differences. EAC of granular zeolites is affected by the amount of binder which is inert in relation to adsorption capacity. Typically, the EAC granule is about 20% lower than that of pure zeolite powder. It is equivalent in relation to a binder. The equilibrium adsorption capacity of syn-

*CHEMICAL AND PHYSICAL PROPERTIES OF ZEOLITES*

thetic zeolites is determined in relation to water at 25° C and a relative humidity of 43%. It is generally introduced by a complex of curves of adsorption isotherms for water and certain selected adsorbates.

**Table 1:**  
**The base structural characteristics of some types of zeolites [5]**

Zeolite type	Pore size [nm]
Beta zeolite	0.76 x 0,64
Boggsite	0.52 x 0,58
Chabazite	0.38 x 0,38
Erionite	0.36 x 0,51
Ferrierite	0.42 x 0,54
ZSM- 11	0.53 x 0,54
ZSM-5	0.53 x 0,56
Mordenite	0.65 x 0,70
Clinoptilolite	0.4 x 0,54

**Table 2:**  
**Physical and chemical characteristics of some synthetic zeolites [4]**

Zeolite sort					
Characteristics	Potasite	Nalsite	Calsite	Y-site	Y-site/P
Type	3A	4A	5A	13Y	13Y
Effective porous diameter [ $10^{-10}$ m]	3	4	5	9	9
Ratio Si:Al [mol/mol]	1.9 – 2.1	1.9 – 2.1	1.9 – 2.1	4.5 – 5.5	4.5 – 5.5
Dominant cation	K <sup>+</sup>	Na <sup>+</sup>	Ca <sup>2+</sup>	Na <sup>+</sup>	Na <sup>+</sup>
Dominant cation change proportion [%]	50 - 70	90 - 100	70 - 80	90 - 100	99 – 100
Sorptive capacity for water near 25°C [g/100g]	17	19	18	23	23

## CHEMICAL AND PHYSICAL PROPERTIES OF ZEOLITES

Nalsite is synthetic zeolite of 4A type with pore size of 0.4 nm. Its chemical composition in dehydrated state is expressed by the following formula:



It is utilized as ecological softening element in detergents as well as it can be used for drying of some gases.

Potasite is synthetic zeolite of 3A type with pore size of 0.3 nm.

Potasite has 50 – 60 % of sodium ions replaced by potassium ions. Its chemical composition in dehydrated state is expressed by the following formula:



Its utilization is as follows:

- drying unsaturated hydrocarbon in gaseous or liquid phase;  
(ethylene, propylene, butadiene, acetylene);
- drying alcohol (methanol, ethanol);
- cleaning the air from CO;
- drying the polar fluid with small molecules diameter.

Y-site is synthetic zeolite of Y type with pore size of 0.9 nm. Its chemical composition in dehydrated state is expressed by the following formula:



It is used for adsorption and desulfurization.

Wear resistance and stability of the grind of granulated zeolite must be of a certain level. The stability of the grind regarding its application is influenced by the integrity of its particles.

Zeolite strength is expressed as a force influencing the destruction of the molecular sieve particles. A measure of stability to abrasion is time in which a total disruption of the granules occurs. Both mechanical characteristics are determined by the molecular sieve under certain conditions of these standards.

An important quality characteristic is bulk density which indicates the weight of the unit volume of dry powder or granular zeolite. According to standardized procedures, volume density of zeolites is determined as the ratio of weight of freshly dried zeolite and its volume.

Thermal stability is a characteristic feature of zeolites. Calcination of the finished granules is performed at the final stage of production of zeolites at temperatures from 500 °C to 650 °C but within an environment with a low concentration of water vapor. Resistance to

## *CHEMICAL AND PHYSICAL PROPERTIES OF ZEOLITES*

action of water vapour current and temperature is called hydrothermal stability. Module zeolite is higher, the higher the temperature and hydrothermal stability. Therefore, among the basic zeolites, zeolite of Y type possesses the highest thermal and hydrothermal stability.

### 3 NATURAL ZEOLITES PROPERTIES

Cations and water molecules are placed in all the internal pores of natural zeolites [8]. Adsorption and desorption of water from all zeolites is described by continuous and smooth isotherms, which are divided by the stepped adsorption - desorption curve characteristics of hydrated salts. This specificity explains the considerable strength of their skeletons which practically do not change during the sorption and desorption of water. Skeletons of silicate structures are different. Their larger structural unit is formed by a small amount of tetrahedrons.

Natural zeolites due to their specific physical and chemical properties are used as raw materials in various industries, in environmental protection and agriculture. Natural clinoptilolite zeolites are used more frequently in environmental area. Topology of clinoptilolite is made up of 4 to 5 membered rings of tetrahedrons in parallel layers forming right angles to each other. Each ring consists of 8 to 10 ring members of tetrahedrons. In terms of IUPAC and IZA nomenclature, clinoptilolite is the structural type heulandite (HEU). Periodicity of HEU zeolite structure is created according to the latest IZA classification of construction T9 units.

Application possibilities of natural zeolites such as ion exchange, sorption and derived properties of the molecular sieves depend on the specific physicochemical properties. These application possibilities of natural zeolites also depend on density and size of pores. Actual natural zeolite is a natural form of composite based on porosity as well as on the multi-phase mineral composition. Composite materials are composed of two or more chemicals, the components of which (at least one of them) referred to as the matrix (metal, ceramic or polymer). The continuous phase and the other components form discontinuous phase (dispersed in the matrix). Zeolites are also defined as macromolecular matter or clathrates or inclusive compounds which contain great number of channels able to absorb hosting elements to the outside of the skeleton. Hosting elements are subjected to weak intermolecular interactions [5, 9].

Clinoptilolite from the deposit in Nižný Hrabovec is the K-Ca type zeolite with little Fe, Mg, Na ions and other ions in trace amounts. This mineral is shown in Figure 1.

Natural zeolites are hydrated aluminosilicates having the ability to absorb heavy metal cations from aqueous solutions. Heavy metals are immobilized by two mechanisms of ion exchange and chemisorptions [9].

### 3.1 Selectivity

One of the important characteristics of zeolites from the point of view of their practical use is their selectivity for the adsorbate. Selectivity of zeolites manifests itself in various forms. Dimensional selectivity is the result of different diameters of effective pores which are characteristic for the different types and modifications of zeolites. Selectivity is based on dimensional network effect which is so precise that it allows quantitative separation of some molecules of the critical diameter. Another form of selectivity is different zeolite affinity to molecules that have penetrated the surface of sieve adsorption dimensional selectivity.

Heterogeneous zeolite surface and electrostatic fields induced by metal cations prefer adsorption of polar molecules before non-polar molecules. This form of selectivity applies when removing polar impurities from gaseous or liquid technology flows. Kinetic selectivity is an expression of a different rate of diffusion of molecules through the pores of the molecular sieve. Molecules with less critical diameter diffuse faster than larger molecules creating a kinetic separation effect which has a practical application, for example in separation and final purification of air components. Zeolites are formed as a conversion product of volcanic glasses of impact origin, plagioclase, nepheline, biogenic silica, aluminosilicate gels and others by effect of capillary, hydrotherma or leaking atmospheric water at various physico-chemical environmental conditions. Currently, the term zeolite refers to a large group of inorganic materials more than 80 of which are natural [9]. The number of new syntheses is continually growing. From an industrial point of view, natural zeolites may be used as clinoptilolite, heulandite, mordenite, ferrierite, chabazite, erionite, filipsite, laumonite and analco. Natural zeolites contain additive minerals such as volcanic glass, cristobalite, feldspar, quartz, mica, etc., based on aluminum and silicon which adversely affect their quality.

### 3.2 Regeneration – desorption of sorbents

The majority of adsorption processes works with cyclic operating system with the fixed bed of adsorbent. It means that it alternates the phase of sorption and the phase of regeneration. The regeneration phase is technically demanding and usually has a decisive influence on the efficiency of the separation. The principle of regeneration is to set the parameters of such technological process, which from a thermodynamic point of view prefers desorption before adsorption. From the curve of the adsorption isotherms it is obvious that the adsorption capacity of zeolites is decreased by reducing the partial pressure of the adsorbate or by its

concentration and temperature increase. The real process usually combines several procedures desorption. For example, with thermal desorption, which is carried out at temperatures of 180° C - 300° C, the adsorbent bed is heated by a hot gas which generally acts also as stripping medium by reducing the partial pressure of the adsorbed components. If the process of sorbed elements release, the adsorbent is heated by a stream of gas, which acts as eluent, to reduce the concentration of the adsorbate. The adsorption-desorption cycle is reversible. Re-generation is carried out by using the inorganic acid diluted to such a concentration that it does not disrupt the crystalline structure of zeolite.

### 3.3 Survey of the best known zeolites types

#### Chabazite

Chemical formula:  $\text{Ca}_2(\text{Al}_4\text{Si}_8\text{O}_{24}) \cdot 13\text{H}_2\text{O}$

**Table3:**  
**Physical properties of chabazite [10]**

Colour	white, grey, red, yellow, brown
Density	2.2
Hardness	4 - 4.5
Break	rough
Crystal structure	anorthic

#### Faujasite

Chemical formula:  $(\text{Na}_2\text{Ca})(\text{Al}_2\text{Si}_4\text{O}_{12}) \cdot 8\text{H}_2\text{O}$

**Table 4:**  
**Physical properties of faujasite [10]**

Colourless	colourless, white
Density	1.923
Hardness	5
Break	rough
Crystal structure	cubic

#### Heulandite (Stilbite)

Chemical formula:  $(\text{NaK})\text{Ca}_4(\text{Al}_9\text{Si}_{27}\text{O}_{72}) \cdot 24\text{H}_2\text{O}$

*NATURAL ZEOLITES PROPERTIES*

**Table 5:**  
**Physical properties of heulandite [10]**

Colour	white, yellow, pink, red, brown
Density	2.1
Hardness	3.5 - 4
Break	rough
Crystal structure	monoclinical

**Natrolite**

Chemical formula:  $\text{Na}_2(\text{Al}_2\text{Si}_3\text{O}_{10}) \cdot 2\text{H}_2\text{O}$

**Table 6:**  
**Physical properties of natrolite [10]**

Colour	white, yellow, pink
Density	2.2
Hardness	5 – 5.5
Break	rough
Crystal structure	orthorhombic

**Phillipsite**

Chemical formula:  $\text{KCa}(\text{Al}_3\text{Si}_5\text{O}_{16}) \cdot 6\text{H}_2\text{O}$

**Table 7:**  
**Physical properties of phillipsite [10]**

Colour	white, red,
Density	2.2
Hardness	4 – 4.5
Break	rough
Crystal structure	monoclinical

**Analcime**

Chemical formula:  $\text{Na}(\text{AlSi}_2\text{O}_6) \cdot \text{H}_2\text{O}$

*NATURAL ZEOLITES PROPERTIES*

**Table 8:**  
**Physical properties of analcime [10]**

Colour	white, red, green
Density	2.3
Hardness	5 – 5.5
Break	rough
Crystal structure	cubic

**Mordenite**

Chemical formula:  $(Al_2Si_{10}O_{24}) \cdot 7H_2O$

**Table 9:**  
**Physical properties of mordenite [10]**

Colour	gray, yellow, pink, red
Density	2.08 – 2.15
Hardness	3 - 5
Crystal structure	orthorombic

**Amicite**

Chemical structure:  $K_2Na_2(Al_4Si_4O_{16}) \cdot 5H_2O$

**Table 10:**  
**Physical properties of amicite [10]**

Colour	colourless
Density	2.94
Hardness	5.5
Crystal structure	monoclinical

### 3.4 Physical and chemical properties of clinoptilolite

The active component found in zeolites from the deposit in Nižný Hrabovec is clinoptilolite (Fig.2). Its appearance was first described in 1976 by workers at Comenius University in Bratislava. The average content of clinoptilolite in the rock accounts for 52-86%. A substantial part of clinoptilolite tuff consists of potassium-calcium type. The deposit is part of the compact sodium - calcium type. The composition of clinoptilolite is expressed by the following formula:  $(Ca, K_2, Na_2, Mg)_4 Al_8 Si_4O_{96} \cdot 24 H_2O$  [11, 12, 13].



**Figure 2: Natural clinoptilolite zeolite from Nižný Hrabovec**

The partial substitution of  $Si^{4+}$  ions by  $Al^{3+}$  ions causes the occurrence of a negative charge in the crystal structure and this charge is compensated with the alkali metal cations and alkaline earth metal cations. These cations occupy a certain position in the channel whose dimensions are large enough to enable to penetrate the molecule with dimensions of a few tenths of a nanometer. The total volume of the cavities is from 24% to 32%. Its adsorption capacity is influenced by the content of micropores in unit volume or mass of adsorbent. Adsorption of cations is affected by their different sizes, charge and concentration of solution [13].

Adsorption capacity can be influenced by changing a chemical composition through ion exchange properties of this mineral. Adsorption capacity is also influenced by the thermal activation, thus dehydrating zeolite, whereas the adsorption capacity change depends on the temperature. The literature review shows that clinoptilolite can be heated to the optimal temperature (450° C) [8]. Heat treatment at higher temperature results in change in the structure of zeolite. With a variety of different types of zeolites, their thermal stability is different. It is influenced by the  $\text{SiO}_2 / \text{Al}_2\text{O}_3$  and cationic composition. Based on low thermodynamic quantities, exothermic zeolite adsorption process is not a typical chemical sorption. The process is mostly of physical nature. Electrostatic interactions prevail [13]. After removal of water from the channels of clinoptilolite, organic and inorganic substances may be sorbed. Zeolites can bind metals in vapor or volatile substances such as metal carbonyls. After heating they decompose into metal or they are bound after hydrogen reduction. After hydrogen reduction, metals can be bound into the channels by ion exchange. Based on research done at the Center of Applied Technology in Kosice, clinoptilolite zeolite absorbs about 10 g  $\text{H}_2\text{O}/100$  g of zeolite in normal conditions at a relative humidity of 50%.

For reference only, silica gel adsorbs from 14g to 15g  $\text{H}_2\text{O}/100\text{g}$  of sorbent at the same humidity. Benzene adsorption amount was 4.1g/100g of rock at 0° C and 3 533 Pa [11]. The Si : Al ratio of clinoptilolite is between 4.25-5.25 which is the cause of its high heat stability and acid resistance. Reference [5] provides the kinetic diameters of the presence of some molecules in combustion gases as it is shown in Table 11. From these values it follows that the smallest dimension of the water molecules is preferably sorbed by clinoptilolite.

**Table 11:**  
**Kinetic molecules diameters [5]**

Molecule	Kinetic diameter [nm]
CO	0.376
N <sub>2</sub>	0.364
NO	0.317
O <sub>2</sub>	0.346
N <sub>2</sub> O	0.33
H <sub>2</sub> O	0.265
SO <sub>2</sub>	0.36
CO <sub>2</sub>	0.33
NH <sub>3</sub>	0.36
CH <sub>4</sub>	0.4
Toluene, p-xylene	0.67
Benzene	0.68
Ethylene, ethyleneoxide	0.42
Methylmercaptan	0.45
1,3 butadiene	0.52
Chloride-difluoromethane	0.53
Cyclohexane	0.61
Triethylamine	0.84
m-xylene	0.71
o-xylene	0.74

An important characteristic feature of zeolites is their ability to exchange cations. For some types of zeolites as well as clinoptilolite, ion exchange properties are accompanied by its selectivity. The value of maximum ion exchange capacity depends on several factors such as pressure, environmental temperature, types of crystal lattice, the content of minerals in the tuff involved in uptake of ammonium ions, the starting concentrations of the ingredients in the solution, etc. Clinoptilolite from Nižný Hrabovec is a mineral of K- Ca type containing little amount of iron, magnesium and sodium ions. Other ions are present in trace amounts.

ZEOCEM a.s. Bystré mines and processes clinoptilolite zeolite. The annual production capacity of grounded zeolite is 200,000 tons and with granular zeolite it represents 20,000 tons. More than half of production is exported to European countries [1].

## NATURAL ZEOLITES PROPERTIES

Impurities cannot be separated from clinoptilolite by ordinary physical and chemical methods because of their mutual overgrowth with clinoptilolite. Therefore, the use of the rock can be realized applying the same ratio in which mineral components are located in certain places of the rock. Clinoptilolite crystals are isomorphic with heulandite. Determination of the quality of zeolite rock is currently done by scanning using electron microscope, X-ray diffraction analysis, infrared spectroscopy, thermal analysis, nuclear magnetic resonance and chemical analysis. The X-ray diffraction analysis is the basic method for obtaining data on the structure of rocks.

Zeolite rock composition is determined by X-ray diffraction analysis of infrared spectroscopy as well as thermal analysis, nuclear magnetic resonance and chemical analysis. To determine the content of zeolite rock, methods based on diffraction measurements from the X-ray record and their correlations with the correlation curve obtained by standard material have been developed. In case of clinoptilolite zeolite, tuff from Hector in California containing approximately 90% of clinoptilolite, have been used as a standard [14].

Chemical and physical characteristics are shown in the Tables 12 and 13.

**Table 12:**  
**The chemical composition of zeolite from Nižný Hrabovec [12]**

Types of chemicals	Percentualcomposition [%]	Types of chemicals	Percentualcomposition [%]
SiO <sub>2</sub>	65.0 - 71.3	Fe <sub>2</sub> O <sub>3</sub>	0.7 - 1.9
Al <sub>2</sub> O <sub>3</sub>	11.5 - 13.1	MgO	0.6 - 1.2
CaO	2.7 - 5.2	Na <sub>2</sub> O	0.2 - 1.3
K <sub>2</sub> O	2.2 - 3.4	TiO <sub>2</sub>	0.1 - 0.3
P <sub>2</sub> O <sub>5</sub>	0.02	Si/Al	4.5 - 5.4

**Table 13:**  
**Physical properties of natural zeolite from Nižný Hrabovec [12]**

Softening temperature	1260° C
Thaw point	1340° C
Flow temperature	1420° C
Porosnes	24 to 32 %
Porous effective diameter	0.4 nm
Fortress at pressure	33 MPa
Density	2200 to 2440 kgm <sup>-3</sup>
Volume weight	1600 to 1800 kgm <sup>-3</sup>

For indirect determination of clinoptilolite in the rock, the chemical analysis has been used.

The analysis determines the following:

- a content of exchange cations;
- an aluminum content by extraction;
- maximum ion exchange capacity.

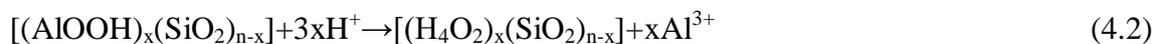
## 4 METHODS OF NATURAL ZEOLITE MODIFICATION

Sorptive and catalytic properties of natural zeolites can be influenced by appropriate chemical treatment. We understand chemical treatment either as dealumination by dilute acids or cations incorporation of metal elements into the structure of zeolite by ion exchange using appropriate solutions. Dealumination, decationization, amonization and ion exchange can be used as chemical treatment. The preparation of monoion forms is achieved either through direct or indirect way through  $(\text{NH}_4)^+$  form. By zeolite dealumination it is possible to achieve partial removal of aluminum from tetrahedral coordination of zeolite lattice resulting in increasing the proportion of silicon to aluminum. For the sorption of organic substances it is more suitable to use sorbent with high silicon content, i.e. the sorbent with the higher acidity. Dilute acid cause spartial dealumination and the alkali leaching. Consequently, the number of active centers is increased. Modification of natural zeolites is carried out under conditions that do not destruct zeolite. It results in the possibility of improving the sorption properties of zeolites. The action of dilute  $\text{H}_2\text{SO}_4$  takes place for partial or total removal of  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{K}^+$  cations. After application of 3%  $\text{H}_2\text{SO}_4$ , decationization and dealumination of clinoptilolite occur [15]. Clinoptilolite is completely decomposed by concentrated  $\text{HCl}$  during boiling process. As a result, aluminium gets into a solution.

Exchange cations and  $\text{SiO}_2$  remain in insoluble form. When acid modification of clinoptilolite is achieved by change in its adsorption properties, an increase in porosity also occurs. The use of organic acids such as trifluoroacetic acid, adipic acid, fumaric acid, phthalic acid, concentration of glutaric acid from 0.02 to 12  $\text{mol dm}^{-3}$  is also appropriate. Dilute acid, partial dealumination and alkali leaching increase the number of active centers. The action of dilute mineral acids leads to the two degrees of acid decationization. The first stage was ion exchange expressed by the following equation [13]:



In the second stage, dealumination, represented by the following equation, takes place:



In the first stage, after cations exchange of the hydrogen from the acid, proton with the water in zeolite creates zeolite ion  $\text{H}_3\text{O}^+$  forming the so-called hydrogen form. Another interactions of protons with oxygen radicals leads to liquidation centers of cation exchange which is associated with a reduction in charges of the matrix and the creation of hydroxide form. This process is irreversible. Dealumination reduces the theoretical ion-exchange capacity of zeolite. The consequence of partial dealumination leads to complete decationization.

Dealumination is manifested by disturbance of the regular microporous structure of zeolite crystals and forming secondary mesoporous structure that contributes positively to the sorption of bulkier hydrated cations and larger molecules.

Treatment with alkali metal hydroxide is extracted from zeolite structure of the silicon. Depending on the solution concentration of the sodium hydroxide modifier there can occur a partial change or the surface and internal pore structure of zeolite. The change consists in the fact that silicon forming a part of the crystal lattice of clinoptilolite readily reacts with  $(\text{OH})^-$  anions as it is expressed by the following equations:



Silica extends in the form of silicic acid in the solution and the proportion of aluminium in zeolite increases and by silicon extraction it results in creating a new mesoporous structure. By using high concentrations of hydroxides there may occur recrystallization of zeolite structure to form a new material with a gismondine structure. Destruction accompanied by breach of the pore structure can also occur. Besides the impact on zeolite component there may occur hydroxides modification and dissolution of some non-zeolite components, for example cristobalite which can also positively influence the resulting surface and ion-exchange properties [16, 17].

Preparation of basic zeolites is carried out by the known ion-exchange techniques. Aqueous solutions containing salts of alkali metals cations and alkaline earth metals are used mostly in the form of nitrates, chlorides and sulphates using to treat zeolite with a sufficient time at a sufficient temperature. The exchange capacity of zeolite depends mainly on the content of active ingredient of zeolite (clinoptilolite), differences in affinity to the various cations exchange solution concentration, contact time of the solution, the temperature, pressure and particle size of zeolite.

As a further possibility of zeolites chemical modification, deamonization of ammonium form is applied. The ammonia form  $(\text{NH}_4)^+$  of zeolite is prepared by exchanging the cations originally contained in zeolite in ammonium ions and ammonium salts with a solution at the suitably chosen conditions. It is important that the majority of original cations of zeolite was removed without decomposition of its structure. Heat treatment of zeolite realized before chemical treatment shall not exceed the temperature of  $400^\circ\text{C}$  [8,13].

When using ammonium salt solutions, the amount of removal of zeolite original cations and at the same time the amount of bound ammonium cations increases with rising concentrations of the exchange solution, the temperature in the exchange, phase ratio and the duration of the exchange.

Ammonium forms are applied as intermediates for the preparation of monoionic and other ionic forms. For perfect exchange of cations presented in zeolite in  $(\text{NH}_4)^+$  ion, it is suitable to use ammonium salts, mainly chlorides and sulfates [8, 13, 15, 29]. Another method of zeolite treatment is hydrophobization of its surface the essence of which consists in bounding of organic compounds capable of binding the anions. Using aqueous solution of octadecylamine, adsorption of octadecylamine occurs allowing the uptake of anions from the aqueous solution [14, 15, 18, 28]. Organic ammonium groups may be immobilized by either single or bilayer layer. Organic amine monomers can effectively bound toxic metal anions from water (electrostatic binding character) [18].

Modification by magnetic particles will enhance zeolite with magnetic properties as well as increase its sorption capacity.

Modified zeolite offers the advantage of simple separation in a magnetic field, which is of great importance in terms of the adsorbent regeneration. The methods of modifying zeolites magnetic particles are as follows:

1. The surface treatment of zeolite using magnetic metal nanoparticles (Fe, Co, Ni).
2. Treatment of natural zeolite using colloidal particles of magnetite.

The advantage of a modification using magnetite  $\text{Fe}_3\text{O}_4$  and maghemite  $\gamma - \text{Fe}_2\text{O}_3$  is a relatively high chemical and thermal stability. It was reported in the literature that impregnation of zeolite using Y maghemite is performed in the following three steps [19]:

1. Incorporation of  $\text{Fe}^{3+}$  in the Na - form of zeolite Y by using  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}/\text{NaNO}_3$  melting exchange reaction.
2. Chemisorption pair of formic acid to  $\text{Fe}^{3+}$  centers.
3. Annealing of the resulting compound at  $400^\circ\text{C}$  in the air.

The modified clinoptilolite - clinoptilolite - magnetit-  $\text{Fe}(\text{OH})_3$  was used to remove  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  ions [20].

The literature review shows that magnetic modification is carried out at pH 6.5 at 70° C according to the following equation [21]:

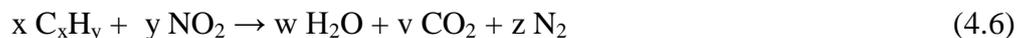


Ammonium form is suitable for the preparation of cobalt modification by cobalt solution in the form of chloride, nitrate, sulfate or acetate. The most efficient way is to modify zeolite by cobaltous salt so that the molar amount of the cobalt presented in zeolite was from 0.9 to 1.6 times of the molar amount of aluminum presence. The most suitable is zeolite in which the molar ratio of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  is at least 15 and the upper limit is not limited. Zeolite with a catalytic effect and satisfactory heat resistance and durability will be the result. Introduction of cobalt into zeolite structure can be performed in two ways: by impregnation or ion-exchange method. In both cases, cobalt is used in the form of its sodium salt, i.e. in the form of chloride, nitrate, acetate or sulphate. Ion exchange is required at least once again. The impregnation is carried out by dipping zeolite in an aqueous solution of the selected cobalt salt for one to two hours. Then zeolite is air-dried and finally, when the process is finished, it is calcinated at 500°C. Modified zeolite is subjected to high-adhesion cobalt ion only on external surface and therefore the access to the cobalt ion exchangeable area is insufficient.

Adjustment of ion exchange may be carried out in practice by adding cobalt salt to the slurry of zeolite and stirring the mixture. The most appropriate solution temperature is between 50°C - 100°C. The mixture should be stirred for at least 5 hours. The most appropriate concentration of cobalt salt to ion exchange is 0.01 mol·dm<sup>-3</sup> to 1 mol·dm<sup>-3</sup>. The adjustment cobalt can be combined by introducing alkali metal cations and cations of the lanthanide series or actinide. These cations can be incorporated into the structure of zeolites by impregnation [23].

Zeolite can also be modified by carbonization. Natural zeolite surface is enriched by nanometer layer of amorphous carbon organic type. Carbonisation of zeolite will provide more meso - and macropores which improve the sorption properties of zeolite. This original feature of the polar microporous carrier approaches the properties of the activated carbon, i.e., to the traditional non-polar hydrophilic adsorbent [17, 18].

Previous study has shown the possibility of adsorption of hydrocarbons contained in exhaust gas to zeolite with alkali metal followed by reduction of nitrogen oxides which are in contact with the bound hydrocarbons. This reaction is expressed by the following chemical equation [24]:



Modifying zeolites by salt solutions of metal cations zeolite acquires catalytic properties. Zeolite itself acts as an ion catalyst carrier. An example is cobalt cation zeolitic carrier. From all the metal elements, elements of the d-block of periodic system have the most characteristic catalytic properties. Catalytically active metals are characterized by the incomplete d-orbitals which determine their properties (tendency to complex) and physical properties (crystal structure, magnetic properties). The presence of the empty d-orbitals and transitions of electrons from p-orbitals in d-orbitals results in the fact that on the outer d-orbitals the unpaired electrons are formed resulting in increased catalytic activity of zeolite. Transition of electrons from the metal to the molecule is possible under the certain conditions [25].

Zeolites on the base of the microporous precise systems of channels are used as molecular sieves. It results in the synthesis of mesoporous molecular sieves.

Supramolecular templates in mutual interaction with self-templated organic and inorganic reactants produce regular crystal lattice. X - ray analysis, however, shows the irregularity at the atomic level.

In 1992, a new synthesis of MCM - 41 (Mobil Composition of Matter) was discovered. Six years later, the University of California in Santa Barbara prepared silica nanoparticles with pore sizes from 4,6 to 30 nm and called them SBA - 15. The structure was made of parallel channels rod hexagonal cross-section with a hexagonal arrangement resembling a honeycomb. Synthesis of MCM is closely related to biomimetic chemistry of inorganic materials, which was already mentioned by the Dutch chemist Pieter Harting in 1872.

With supramolecular templates, inorganic ingredients form oligomeric silicate anions  $(H_nSi_8O_{20})^{(8-n)}$  and the organic phase of a micelle of surfactants of type  $C_nH_{2n+1}(CH_3)_3N^+A^-$ , where  $A = (OH)^-, Cl^-, Br^-$  is formed at very low concentrations.

Pore size determines future product surfactant concentration and the geometry of the hydrocarbon chain. During the thermodynamic equilibrium, cylindrical micelles will be transformed into hexagonal arrangement. In the second step, which is carried out in the autoclave,

the polymerization of the silicates occurs. In the third step, the template is separated from the skeleton by decanting in water or ethanol or calcining at about 400 ° C. The preparation of structurally templated mesoporous silicate and aluminosilicate molecular sieves is currently considered to be the most actual synthesis of porous materials [9].

## 5 WAYS OF USING NATURAL ZEOLITES IN PRACTICE

Application of synthetic zeolites in industrial practice is limited by their high cost. Therefore, great attention is paid to natural zeolites, clinoptilolite in particular, which is selective to some metals cations. Natural zeolites due to their specific physical and chemical properties are used as raw materials in various industries, in environmental protection and agriculture. From the point of view of their practical application, the deposits of clinoptilolite, morденite, chabazite and erionite are of great interest.

Application possibilities of natural zeolites result from their specific physical and chemical properties, namely ion exchange, sorption, derived properties of the molecular sieve, the possibility of dehydration and hydration as well as the structure of the silicate and the micron size crystals of a very active surface area.

Synthetic zeolites are used when the arrangement of the crystallographic structure of certain zeolites and high purity is required. Examples are catalytic, sorptive and separation purposes in certain sectors of the petrochemical industry and in organic synthesis [26].

Natural zeolites are widely used because of their low price especially in the sectors of industry and agriculture that require high consumption of zeolites.

These areas are crop production, drying and purification of industrial gases, cleaning and treatment of contaminated water, plastic fillers, carriers of different types of fertilizers. It is used not only to release nutrients necessary for plants but also to bind heavy metals and radioactive elements contained in the soil to zeolite structure. They are also suitable for neutralization of acid soils. The relatively high capacity of ion exchange and adsorption properties are required for effective carriers of herbicides and pesticides. Clinoptilolite is successfully used in Japan as a suitable carrier of benzylfosforothione which is used to prevent rice straw breaking. The ion exchange on clinoptilolite is profitable for the disposal of water metal residual pollution [4, 22, 26].

Geometry influences the replacement of metal cations in zeolite pores. This geometry in a three-dimensional lattice of zeolite either delimits or modifies ion diffusion. With the ion exchange process, the efficiency of ions exchange in a formal oxidation state one with relatively less favourable ion radius is more favourable than with the ions with higher oxidation number. Clinoptilolite possesses considerable exchange capacity and selectivity for potassium ions and ammonium which are active ingredients of mineral fertilizers. Therefore, to enrich the soil, potassium ammonium form of clinoptilolite is used.

To neutralize acid soils, considerable affinity of clinoptilolite against protons is used. Neutralizing effect of clinoptilolite retention is explained by passing a proton exchange of the cation to form a hydroxyl group not participating in the exchange. The results show that zeolite from Nižný Hrabovec after its addition to a suspension of NPK fertilizers artificially enriched by relatively high amounts of these ions was effective and washing out of zeolite substrate at different pH was close to zero [1, 2, 26,29].

Natural zeolite was used successfully in the industrial agglomeration Otrokovice when eliminating ammonia in the final stage of wastewater purification. The advantage of clinoptilolite is its regeneration ability resulting from washing with NaCl when saturated with ammonia or metal. Wastewater treatment plant in Truckee (California, USA) uses natural clinoptilolite to remove ammonium ions [22].

Thermally-activated material withdraws water from liquid medium. Therefore it is successfully used to remove water from the cold liquid media. The hydration of activated zeolite releases heat which is consumed in the process the dehydration. The heat released is about 10.5 kJ / 100 g of zeolite tuffs.

After the thermal activation, natural clinoptilolite zeolite has relatively high adsorption capacity for the following gases: NH<sub>3</sub>, CO<sub>2</sub>, H<sub>2</sub>S, SO<sub>2</sub>. Thermally activated zeolite tuffs from the deposit Nižný Hrabovec trap around six grams of CO<sub>2</sub> / 100g. Under normal conditions, it has a sorption capacity of 6.38 g of CO<sub>2</sub> / 100 g [11,15]. Rock in its natural state does not have CO<sub>2</sub> high sorption capacity. When temperature of activation is increasing gradually, the sorption capacity increases up to the activation temperature of 400° C [13, 15].

### **5.1 The use of zeolites in agriculture**

Natural zeolites are widely used as active carriers of agrochemicals such as pesticides, herbicides, fertilizers, growth promoters for increasing fertility and biological activity of soils, reclamation, improving productivity of acid and devastated soils as well as nitrogen balance particularly with light and sandy soils. Zeolites can be also used to neutralize acid soils. By adding zeolite to acid soils, neutralization effect is manifested by a similar liming. Zeolites are also useful for drying and storage of grain. It was found that 1% of zeolite in the soil profile increases the amount of nitrogen content of 20 to 30%, especially in light sandy soils. This reduces the amount of nitrates in flooded soil profile by an average of 33%. Zeolite has an impact on the accumulation of nitrate in vegetables. By adding zeolite to acid soils its neutralizing action, which is connected to proton ion exchange adsorption, is obvious. Neutralizing

effect of zeolite is explained by the transition of a proton from the cation exchange of the position to the oxygen matrix creating the hydroxyl groups not participating in the exchange [1, 2, 26]. Zeolite is a reservoir of soil moisture which is useful especially in sandy soils with low water capacity. The high selectivity of natural zeolites to the cations of heavy metals decreases the accumulation of these cations in plants. Various trace elements such as Se, Mo and Cd are bio-concentrators in crops, therefore, the access to the environment is controlled. These elements because of their mobility get very quickly into the food chain.

In industrial and suburban areas, trace elements are mostly of anthropogenic origin. In addition, these trace elements are naturally concentrated in soil, for example during weathering. Anthropogenic activity produces the highest concentrations of Cd, Pb, Zn and Hg. Elements such as V, Be, Tl are largely released from fossil fuels such as coal, fuel oils, etc. The metals penetrate into the soil from urban sewage, vehicles, pesticides, combustion plants, etc. The experimental results show the suitability of zeolites from the deposit in Nižný Hrabovec for the sorption of ions of lead, cadmium, chromium and mercury. Adding zeolite to a suspension of NPK fertilizer eliminates the concentration of these ions [27].

Generally, application of various types of fertilizers is based on zeolites. Natural zeolites are used as carriers for different types of fertilizers. Nutrients are released gradually not only in the first growing season but also in the second year. Water adsorbed in the pores of zeolite is an effective reservoir of soil moisture. Using zeolites in vegetables cultivating results in up to 50% reduction of nitrates. Zeolites absorb unpleasant litter odor improving hygiene and working environment in poultry farms. Zeolite is also used as an additive material to liquid multicomponent of nitrate-phosphate fertilizers to accelerate the sedimentation suspendability of impurities. After a series of experiments at CHEMKO Strážske, zeolite granular NPK fertilizer ZEOMIX, which contains the main nutrients as nitrogen, phosphorus, potassium, as well as some other nutrients, including sulfur, boron and molybdenum, was developed. This fertilizer has a beneficial effect on the production of crops because of the gradual release of its nutrients. This fertilizer does not increase nitrogen uptake by the plant resulting in crop production as well as it does not contain excessive values of nitrates.

The KlinoFert fertilizer - NPK containing nitrogen min. 6.0%, phosphate ( $P_2O_5$ ), 4.5% potassium ( $K_2O$ ), min. 7.5% sulfur ( $SO_4^{2-}$ ) min. 10% has been developed and produced in Zeocem. The advantage of this fertilizer lies in the fact that the nutrients in zeolite are closed and there is no leaching and the pollution of surface and groundwater [1, 2].

Insecticidal effect of micronized zeolite on pest in stored grain and seeds has been verified. Its efficient mechanism of action is particularly selectively toxic against ectopara-

sites and warehouse pests. Chemically, this method of pest control does not bring risks. Zeolites are particularly used as ion exchangers for ammonium in livestock production in ruminants. Ammonium ions are exchanged into zeolite structure which acts as a reservoir of ammonia protecting animals from poisoning. By gradual release of ammonia, continuous protein synthesis in the digestive tract is supported. It was shown that zeolite is a good medium for buffering a good acid metabolic disorder.

## 5.2 Water treatment

Zeolites from Nižný Hrabovec are suitable for potable water and removing ammonia from municipal and industrial wastewater. Zeolites have demonstrated the possibility of ammonium ions removing from water by selective ion exchange using clinoptilolite. Industrial agglomeration Otrokovice has used successfully natural zeolites in the final stage of purification of wastewater from ammonia. In the process of treatment, clinoptilolite is used to remove ammonium ions. The advantageous properties, such as low temperature climatic conditions, resistance to toxic industrial waste, the ability of multiple simultaneous removal of toxic metals and ammonia ions resulted in a compilation of several water treatment and sewage treatment technology using zeolites. Clinoptilolite is perspective for treatment of wastewater from urban and agricultural sewage systems. In USA and Japan, clinoptilolite is used in cleaning stations to protect drinking water sources. After the regeneration with dilute sulfuric acid, ammonium sulphate useful as a fertilizer is obtained [22].

Due to the adverse environmental impact of phosphate in wastewater, a need of its replacement in detergents has arisen. Research conducted in this field resulted in reimbursement of phosphates (40-60%) by A-type zeolites [22]. Chemically modified zeolite into modified form of  $\text{Na}^+$  has been successfully tested in detergent powders based on  $\text{Al}_2\text{O}_3$  as a partial substitute for sodium tripolyphosphate. In order to use zeolites in this field, such properties as high ion exchange capacity, good ion exchange kinetics at low temperatures, requiring the particle size below 50 microns with a high percentage of particles below 10 microns and the iron content of 100 ppm are critical.

After conversion of zeolite to monoionic form, water uptake of anionic components such as arsenic and chromium, which occur in the anion form as chromates and arsenates, is possible.

The use of natural zeolites to remove ammonia and ammonium from the water is known [66]. Filters based on natural zeolites are used for water purification in tanks and

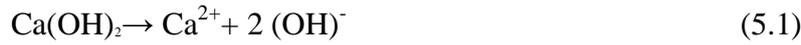
aquaria. Natural clinoptilolite zeolite is also used in water purification and removal of ammonia, trace elements of water, residual and turbidity coagulants. It can be used instead of silica sand for mechanical treatment of water in combination with other water supply materials such as coagulation multilayer filter cartridge. Clinoptilolite from several locations around the world has demonstrated the ability to capture radioactive elements. In this respect, natural zeolites are also used for cleaning of low-level liquid waste from nuclear power plants, especially for detection of radioactive strontium and radioactive cesium [27]. High affinity of zeolites is characterized mainly towards cesium. In Japan, a system of air separation zeolite sorbent has been introduced. It is the production of oxygen enriched air. In this respect, zeolites from Nižný Hrabovec were tested achieving 70% oxygen in the air [22].

Among the new alternatives to remove nutrients from the water, physicochemical processes using natural zeolite clinoptilolite are introduced.  $\text{NH}_4^+$  - forms are also used in products in which it is necessary to eliminate the presence and harmful effects of formaldehyde because formaldehyde reacts with  $\text{NH}_4^+$  resulting in harmless hexamethylenetetramine. This method is applied, for example, in timber industry, which use adhesives and hardeners based on formaldehyde, as well as in environmental protection [20].

The detoxification of human body is carried out by preparations containing liquid colloidal zeolite in the form of a mixture of crystals of pure natural clinoptilolite zeolite with a particle size below 5 microns in saline. The selected clinoptilolite microcrystals are free from undesirable impurities. They are acceptable exchangeable cations of calcium, magnesium, sodium and potassium. This preparation gives natural buffering and remineralisation effects and can penetrate into cell membranes. It reduces the content of heavy metals and the pH in the intestinal tract. The principle comprises reducing detoxification of free radicals [9].

### **5.3 Use of zeolites in construction industry**

In construction industry, zeolites can be widely applied as well. Their pozzolanic activity can be used as a binder for building material. Pozzolanic activity of the pozzolanic material is the ability to react in an aqueous medium at normal temperature with calcium hydroxide to form the bound hydration products. The amount of calcium hydroxide and its kinetics influence the result of the reaction. Calcium hydroxide is an alkaline substance and a strong electrolyte which completely dissociates in water to ions:



At 25° C, a saturated solution of a pH 12.45 indicates high concentration of hydroxide ions which causes the cleavage of bonds silicates, aluminosilicate to form ions:



The resultant silicate and aluminate ions react with  $\text{Ca}^{2+}$  cation and raise the hydrated calcium silicates and hydrated calcium aluminates, for which, however, a higher concentration of  $\text{Ca}^{2+}$  is needed as compared with the silicate ions dissolved more slowly. As the pozzolans can select materials which are silicate or aluminosilicate in nature, they show no binding capacity but can react at ordinary temperatures in an aqueous medium with calcium hydroxide to form compounds of the so-called CSH gel to solidify and harden. They are stable in the air and under water. These materials are resistant to water and acid environment of  $\text{pH} > 4$ , they have better mechanical properties, corrosion resistance, and generally increase the durability of concrete [30, 31].

#### 5.4 Gas separation using the modified zeolites

Some natural zeolites may be applied in the role of molecular sieves and can replace synthetic materials. The effective channel diameter is one of the important parameters for the use in this area. It enables to select the type of zeolite for the distribution of two or more substances of different effective diameter molecules. In this regard, zeolites with a large effective diameter of the cavities are applicable. Among naturally occurring zeolites, faujasite and clinoptilolite are the most appropriate.

The separating ability of the zeolites can be influenced by:

- a) changing the size and shape of the holes within the crystal;
- b) adsorption selectivity due to different interaction energies between adsorbed molecules.

In most cases, separation of zeolites is based on a combination of screen and affinity effects. One of the important parameters for the use of network effects is the effective channel diameter. It enables to select the type of the zeolite for the distribution of two or more substances.

Zeolites with a large effective diameter cavity are the most applicable. In this regard, faujasite crystallizing within cubic system has an optimal structure.

### 5.5 Reduction of harmful emissions

Zeolites are characterized by specific properties which result from their particular structure. This particular structure makes them suitable for use in environmental protection in the area of air cleaning. The sorption of nitrogenous components of the exhaust gas of diesel engines into natural clinoptilolite zeolite was compared with the sorption on synthetic zeolites Na-X and Na-P<sub>1</sub> [67]. From this point of view, natural zeolites are mostly used in Japan and in the United States.

Previous research showed that natural zeolites have high sorption at low concentration of adsorbed substances. Clinoptilolite zeolite from the deposit in Nižný Hrabovec is suitable for adsorption of SO<sub>2</sub>, mercaptan, NO, CO<sub>2</sub> and other gases [8]. It has been found that the sorption capacity decreases with increasing concentration of hydrogen sulfide and methylmercaptan [8].

In 1993, the Japanese firm Mazda announced zeolite catalyst that reduces NO<sub>x</sub> [32]. In several works, results of nitrogen oxides sorption have been published. The literature review shows that NO<sub>x</sub> molecules in zeolite exhibit a characteristic reactivity. It is expected that nitric oxide undergoes a chemical reaction after it is adsorbed inside the pores [33].



While N<sub>2</sub>O is easily desorbed, N<sub>2</sub>O<sub>3</sub> is retained in the pores and partly decomposes into NO and NO<sub>2</sub>.



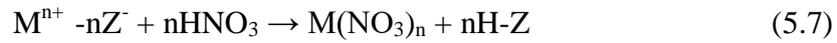
Previous studies have emphasized that in the presence of water vapor, only two-thirds of NO<sub>2</sub> can be adsorbed, the remaining one-third is converted to NO.

The presence of water vapor causes the nitric acid formation inside the porous.



## WAYS OF USING NATURAL ZEOLITES IN PRACTICE

With the  $M^{n+}$  cations, the reaction takes place according to the following equation:

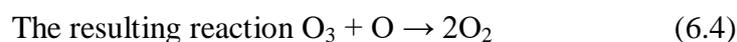


After the thermal activation, natural clinoptilolite zeolite has of a relatively high adsorption capacity for some gases such as  $NH_3$ ,  $CO_2$ ,  $H_2S$ ,  $SO_2$ ,  $NO_x$ . Thermally activated zeolite tuffs from the deposit in Nižný Hrabovec trapp around 6 grams of  $CO_2$  / 100g in static conditions. Under normal conditions, it gives a sorption capacity of 6.38 g of  $CO_2$  / 100 g [11]. Rock in its natural state does not have  $CO_2$  high sorption capacity. The sorption capacity increases up with the increasing temperature to the activation temperature of 400° C.

## 6 EFFECT OF INTERNAL COMBUSTION ENGINES ON ENVIRONMENT

Internal combustion engines are the source of harmful emissions which contribute significantly to overall air pollution (about 50% of total contribution). Vehicle exhaust emissions contain large amounts of organic and inorganic components. Exhaust gases have a large share of inorganic substances, mainly carbon monoxide, nitrogen oxides, and carbon dioxide. Exhaust gases contain considerable amount of organic components -polycyclic aromatic hydrocarbons and aliphatic hydrocarbons such as aldehydes and ketones which act on a living organism directly or indirectly via the food chain [33].

Carbon monoxide accounts for 4-8%, in some cases up to 36% of the flue gas [33]. Of the quantity contained in the urban atmosphere, approximately 2/3 of the cases contain CO. It is dangerous poison as it is not detected by the sense organs. Its toxicity lies in the fact that it is primarily bound to hemoglobin to form carboxyhemoglobin. It prevents the formation of oxyhemoglobin, consequently no transfer of oxygen and suffocation occurs. It is dangerous, especially in poorly ventilated areas such as tunnels. Oxides of nitrogen, specially nitrogen monoxide NO, nitrogen dioxide NO<sub>2</sub> are collectively denominated as NO<sub>x</sub>. They are developed at high temperatures. NO is oxidized into NO<sub>2</sub> in contact with air. NO<sub>x</sub> poisoning is a dangerous long-term latent period. It shows the signs of poisoning, headache, low blood pressure methemoglobinemia after 5-70 hours. Chronic poisoning results in an increase in red blood cells and increased tooth decay [33]. The combustion gases released by supersonic aircrafts are brought in the stratosphere, where N<sub>2</sub>O is treated with atomicoxygen to produce NO which reacts with ozone and is involved in the disruption of ozone in the atmosphere [34].



NO<sub>x</sub> formation depends on the fuel composition as well as the type of combustion plant, determining a combustion temperature and flue gas residence time in the zone of high temperature, the excess combustion air etc. The flame temperature and the oxygen concentration in the waste gas have a decisive influence on the formation of nitrogen oxides. The quantity of the oxide increases the residence time of flue gas in the high temperature zone.

More than 90% of nitrogen oxides are emitted in the form of nitrogen oxide NO which is oxidized in the atmosphere to nitrogen dioxide NO<sub>2</sub>. This fact negatively affects health of living organisms causing respiratory tract irritation. NO<sub>2</sub> emissions that destroy the ozone layer are also called greenhouse gases. They are responsible for global warming and climate change. Road transport accounts for 51% of the world's emissions of nitrogen oxides. By influence of proliferation of NO<sub>2</sub> in the air, undesirable increase of tropospheric ozone concentration occurs. The source of ozone includes the following reactions taking place in the troposphere [35]:



Ozone formation

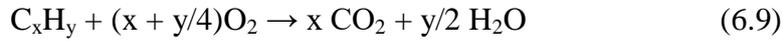


M is a neutral collision particle that does not take part in the actual reaction balancing the energy balance of the reaction conditions. Ozone is a gas that adversely affects human health, especially the respiratory and nervous system. Therefore, an excessive amount of ozone in the ground surface of atmosphere i.e. troposphere is as harmful as its deficiency in the stratosphere.

Hydrocarbons are part of the exhaust gases of internal combustion engines. From the point of view of their toxicity, benzene and benzo-(a)-pyrene are the most significant. The two substances were proven for their carcinogenic properties. Both of them are part of solid particles contained in the exhaust gas. Their presence has also been found in automobile interiors. Aldehydes, which are mainly included in the exhaust gas of diesel internal combustion engines, are dangerous poisons regarding their nephrotoxic and hepatotoxic effect [33].

Carbon particles are problematic especially with diesel engines tracking the ecological parameters of diesel engines. Problem of reducing carbon monoxide, hydrocarbons and nitrogen oxides is solved by a three-way catalyst with petrol engines. The term "three-way" refers to the ability of the catalyst to convert three kinds of pollutants to less harmful substances. It is the oxidation of carbon monoxide into carbon dioxide and water by using platinum and reduction of nitrogen oxides to nitrogen by means of rhodium.

Oxidation and reduction reaction occurs at a temperature of 300 °C as it is expressed in the following equations [32]:



The oxidation of CO to CO<sub>2</sub> is an exothermic reaction releasing heat which accelerates the onset of activity of the catalyst to the operating temperature. Carbon monoxide and unburnt hydrocarbons are nitrogen oxides reducing agent and using the catalyst are reduced to nitrogen. Oxygen derived from nitrogen oxides promotes oxidation of CO and hydrocarbons. The reduction of nitrogen oxides to nitrogen takes place with the best effect when oxygen is absent. The oxidation of carbon monoxide and hydrocarbons takes place with the best efficiency in excess oxygen condition in the exhaust gas. To achieve the best efficiency of reduction of all the three compounds, the composition of the exhaust gas must correspond to the stoichiometric composition of the mixture. The three-way catalytic converter is applicable only in petrol engines after the working temperature reaches 300°C. Using weak fuel-air mixture with an excess of oxygen prevents the reduction of nitrogen oxides in diesel engines. Engines with direct injection utilize lean-burn fuel and air as well. The exhaust gas, however, in this regime can not reach sufficient temperature for catalytic reaction course of a typical controlled three-way catalyst. One of the solutions was the introduction of the NO<sub>x</sub> catalyst, also called storage catalytic converter [36], the introduction of the catalytic particulate filter, liquid platinum catalyst and selective catalytic reduction.

In 2014, Euro 6 emission standards were introduced in Europe. The standards tightened limits especially with diesel engines. New solutions will be needed to maintain the new limits for the combustion processes and techniques for after-treatment of diesel engines exhaust gases.

The limits of emissions in category N1 are shown in Table 14 [37].

**Table 14**  
**Review of EURO standards**

Standard	Year	CO [g·km <sup>-1</sup> ]		NO <sub>x</sub> [g·km <sup>-1</sup> ]		CH+ NO <sub>x</sub> [g·km <sup>-1</sup> ]		CH [g.km <sup>-1</sup> ]	DPF [g.km <sup>-1</sup> ]
		gasoline	diesel	gasoline	diesel	gasoline	diesel	gasoline	diesel
EURO 1	1992	3.160	3.160	-	-	1.130	1.130		
EURO 2	1996	2.200	1.000	-	-	0.500	0.700		0.080
EURO 3	2000	2.300	0.640	0.150	0.500	-	0.560	0.200	0.050
EURO 4	2005	1.000	0.500	0.080	0.250	-	0.300	0.100	0.025
EURO 5	2009	1.000	0.500	0.060	0.180	-	0.230	0.100	0.005
EURO 6	2014	1.000	0.500	0.060	0.080	-	0.170	0.100	0.005

Reduction in road transport emissions is an important factor to improve air quality in urban areas because of the growing number of cars with diesel engines. In many areas, the EU limit values for NO<sub>x</sub> are exceeded, especially in densely populated zones near major roads. Euro 5 regulation sets tighter emission limits for particulate matter and NO<sub>x</sub> for new cars and light trucks sold in the EU market (i.e. 80% reduction of emission limits for diesel cars emissions).

After the introduction of Euro 6, 24% reduction in total NO<sub>x</sub> emissions from light diesel vehicles should have been achieved by toughening Euro 5 limits to Euro 6 limits. The introduction of Euro 6 will not have a significant impact on CO<sub>2</sub> emissions. Currently, the change-over to the Euro 6 limits is available:

- catalytic reduction using aqueous urea solution AdBlue;
- catalytic reduction using aqueous urea solution AdBlue + Denoxtronic-Exhaust gas recirculation.

Research teams in Germany, Japan and the USA are looking into the possibility of using synthetic or even natural zeolites for cleaning exhaust gases produced by combustion engines. Many inventions have been patented in this area.

More stringent requirements for exhaust emissions such as the American standard US 2010 or European EURO 6 emission standard are driving demand for advanced catalytic converters to clean exhaust gases. One of the key technologies used in vehicles with diesel engines is the so-called selective catalytic reduction catalyst (SCR) which uses advanced technology of corporation BASF on the base of zeolite type copper chabasite. Development of chabasite zeolite catalyst is considered to be a significant milestone to clean diesel engines.

## *EFFECT OF INTERNAL COMBUSTION ENGINES ON ENVIRONMENT*

Specialized zeolites such as copper chabazite are produced under pressure with the help of organic matters. It is possible to produce specific structures with a very high level of activity which are active at low temperatures. The active catalysts of zeolite are ions of copper which are located within the crystals. Copper chabazite zeolite achieves extraordinary catalytic activity at very low exhaust temperature and maintains its performance and stability even at high temperatures. The exhaust system of diesel engines emits significantly less nitrogen oxide.

## 7 OPERATION PRINCIPLES OF SORPTION AND CATALYTIC DEVICES

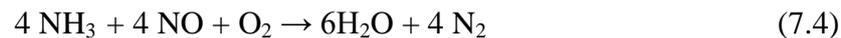
To reduce nitrogen oxide concentration, natural and synthetic zeolites can be used in combination with a conventional catalyst. Their application has been presented in several patents.

One of the inventions to solve the problem of pollutants disposal during cold start is a US patented invention [23]. The proposed device consists of two catalytic and one adsorption zone. The first catalytic zone comprises a three-way catalyst. The adsorption zone comprises natural adsorbent material, which is natural zeolite such as faujasite, mordenite, and chabazite. These can be replaced by synthetic zeolite beta zeolite or ZSM-5. The role of the adsorption zone is to capture hydrocarbons resulting from combustion during cold start while the three-way catalyst comes into optimum working temperature. The gas stream first passes through the first catalytic zone wherein the catalyst converts only part of hydrocarbons. The gas flows from the first catalytic zone. Then it flows through the adsorption zone, wherein the hydrocarbons are temporarily adsorbed during the period of cold start unless the three-way catalyst disposed in the second catalytic zone enters into the working temperature. After the entry into the operating temperature of the catalyst, the hydrocarbons are desorbed and then they are converted into carbon dioxide and water. In this catalytic device, beta zeolites are used successfully, particularly those in which the silicon to aluminum ratio ranges from 25/1 to 300/1. The preferred beta zeolites are modified by ion exchange as H / Beta zeolite and Fe / Beta zeolite. The acidity of zeolite is adjusted with inorganic acids. Sulfuric acid, nitric acid, hydrochloric acid, phosphoric acid, in a concentration of  $0.02 \text{ mol dm}^{-3}$  to  $12 \text{ mol dm}^{-3}$  (mainly  $0.1 \text{ mol} \cdot \text{dm}^{-3}$  to  $10 \text{ mol} \cdot \text{dm}^{-3}$ ) are used. The washing takes place within temperature range from  $10^\circ\text{C}$  to  $100^\circ\text{C}$  depending on the type of the used acid during a time interval of 0.5 to 3 hours. The acidity of zeolite is enhanced to increase shelf life of hydrocarbons adsorbed in zeolite. During the treatment process, carboxylic acids such as trifluoroacetic acid, glutaric acid, adipic acid, fumaric acid, phthalic acid are used. Preference is given to dicarboxylic acids. After its chemical treatment, zeolite is treated by passing steam at a temperature from  $350^\circ\text{C}$  to  $900^\circ\text{C}$  (usually  $550^\circ\text{C}$  to  $750^\circ\text{C}$ ) at atmospheric pressure from 0.5 to 48 hours.

After precipitation, adsorbent zeolite material is applied to a monolithic carrier in the form of thin coating. Ceramics and stainless steel are the most suitable materials for the carrier. Coating is prepared by calcining at a temperature of  $450^\circ\text{C}$ . The mass of the adsorbent

coating is prepared by mixing H-ZSM-5 zeolite (Si/Al = 50/1), silica of (28% Si), and deionized water. The mixture was milled to obtain 90% of the particles smaller than 8 microns and calcined at 450°C for one hour. After application of the coating, the monolith was dried at 110°C. In the latter case, the ammonium form of zeolite Beta (Si/Al ratio of 35/1) was used. Zeolite that weights 650 g was mixed with 315g of silicon. The mixture has been grounded for seven hours followed by addition of deionized water.

For diesel internal combustion engines, utilizing weak air-fuel mixture with an excess of oxygen cannot result in reduction of nitrogen oxides by means of classical three-way catalyst. Therefore, research teams around the world drew attention to this area. The apparatus for nitrogen oxides reduction, where in the carrier is highsilical zeolite such as mordenite with bound platinum and copper cations, has been developed in Japanese TOYOTA. The device synthesizes NO<sub>x</sub> from ammonia which is oxidized in the presence of oxygen to nitrogen. This can be expressed by the following equations [38]:



The carrier is ZSM-5 zeolite-bound platinum and copper (1% Pt and 2.4% Cu). The ratio of SiO<sub>2</sub> / Al<sub>2</sub>O<sub>3</sub> is equal to 40/1.

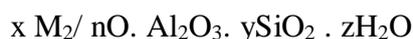
However, this method does not provide satisfactory results when applied to the purification of exhaust gases of mobile objects. The catalyst developed at the Japanese company TOYOTA, which reduces the concentration of carbon monoxide, hydrocarbons and nitrogen oxides by adsorption and catalysis in an excess of oxygen, is more effective. In this case, synthetic zeolites ZSM-5, ZSM-11, ZSM-12 and ZSM-20 are used. Among natural zeolites, ferrierite is the most appropriate [39].

Based on ion exchange in their structure, copper cations are incorporated. Such a catalyst effectively reduces nitrogen oxides onto the nitrogen in an excess of oxygen after their adsorption. It has a satisfactory reduction in capacity at a temperature interval from 200°C to

## OPERATION PRINCIPLES OF SORPTION AND CATALYTIC DEVICES

500°C. The catalyst will have the highest efficiency when subjected to a high temperature for a long time. At a temperature of 600 °C, the cations of copper begin to move and agglomerate, thereby causing a distortion of the catalyst structure and a decrease of catalytic activity.

The composition of zeolite used in this patent is expressible by the following formula:



where: M is cation,

n = oxidize number

x = 0.8 - 2

y = 2

To achieve catalytic activity of zeolite, copper can be substituted by cobalt. Aqueous solutions of copper and cobalt salts such as cobalt sulfate, cobalt chloride, cobalt nitrate, copper sulphate are used for washing. The catalyst was prepared by the following procedure: 20 g of  $NH_4^+$  ion exchanged in ZSM-5 with Si/Al ratio equals 40, was mixed with 80g of an aqueous solution of cobalt acetate tetrahydrate and dried for 16 hours at 80°C. The mixture was filtered and immersed in an aqueous solution of  $La^{2+}$  and  $Ba^{2+}$  cations. Then the mixture was dried at 110°C for 10 hours. It was subsequently calcined at 500°C for three hours. Then, 500g of zeolite powder, 700g of a gel containing  $SiO_2$  and 100g of pure water were mixed, while the pH was adjusted with ammonium hydroxide within the range of 10 to 11. The resulting mixture was applied to cordierite carrier.

The literature review shows that there exist several basic metal catalysts for effective  $NO_x$  reduction. Studies have suggested that in the absence of the  $NO_x$  inhibitors such as  $H_2O$ ,  $CO_2$  and  $SO_2$  in diesel exhaust, the addition of first row-transition metals to zeolite-supported catalysts results in a significantly improved reduction rate of  $NO_x$  [65].

It is known that diesel engine exhaust gases contain gaseous pollutants such as carbon monoxide hydrocarbons and nitrogen oxides as well as solid particles in the form of carbon black. These include hydrocarbons in solid form. The soluble fraction of hydrocarbons is in gaseous or aerosol form depending on the temperature of the exhaust gas. In the USA, the oxidation catalyst for diesel engines for adsorption and oxidation of hydrocarbons and carbon monoxide to trap of solid particles was patented. Zeolites and zeolites enriched with metal elements were used in this patent. This catalyst comprises a particulate filter, the wall of

which is applied in dispersed form in the pores of the zeolite containing platinum. Used zeolites are of acidic cleavage characteristics facilitating long-chain hydrocarbons and aromatic hydrocarbons, faujasite, pentasil, mordenite. Natural zeolites such as faujasite, pentasil, mordenite are applicable in terms of this patent [24]. These zeolites must contain exchange cations and catalytic transitory metal ions. The literature review shows that the catalysts commonly used in exhaust systems of internal combustion engines are ineffective at a temperature lower than the working temperature. To capture harmful ingredients such as hydrocarbons and carbon monoxide, zeolites can be used as the adsorbent of hydrocarbons and carbon monoxide before reaching the working temperature of the catalyst.

Hydrocarbons are adsorbed using zeolite unless the exhaust gas temperature is below 200°C. When the exhaust system temperature rises above 200°C, hydrocarbons are desorbed and subsequently subjected to oxidation due to oxidizing components.

US patent is based on platinum metals usage. Zeolite is treated by neutralization and thermal or hydrothermic dealumination or chemical dealumination. Zeolite is treated with sulfuric acid or nitric acid at room temperature. The product is dried and annealed at a temperature of 1000°C. The carrier is an inert material such as cordierite or stainless steel. Other patents, [40] and [41] deal with the use of acidic zeolites for cracking of aromatic and aliphatic hydrocarbons with a long chain which is part of the exhaust gas of internal combustion engines. In the patent [42], acidic zeolite is combined with noble metals with catalytic properties. US Patent [42] deals with the catalytic device for diesel engines. According to the patent, zeolite is treated by dealumination before metal cations incorporation. The device comprises a carrier on which zeolite layer is deposited. The carrier is made of an inert material. The device is also used with the components of catalytic action, for example, platinum metals. Hydrocarbons produced by diesel engines are adsorbed by zeolite before heating the exhaust gases. Once heated to approximately 175°C - 200°C, hydrocarbons are desorbed followed by oxidation to carbon dioxide and water. The possibility of using basic or neutral zeolites for cracking of hydrocarbons is not known. These zeolites do not allow cracking of aromatic and aliphatic hydrocarbons as is the case with acidic zeolites.

The content of the American patent [43] is a method used for purifying exhaust gases. The apparatus consists of an adsorbent, which is natural or synthetic zeolite, and of the two catalysts. This is reduction of hydrocarbons and oxides of nitrogen. The catalyst mixed with the adsorbent consists of a monolith carrier, a ceramic material such as cordierite, mullite, etc. Catalyst consists of ceramic monolithic carrier or metal made of heat-resistant steel (e.g. Fe-Cr-Al alloy) and a shell containing a metallic material applied by powder metallurgy. Mono-

lithic carrier supports a cellular density from 0.9 to 233 pores·cm<sup>-2</sup>. The adsorbent-catalyst comprises one of the elements of the group of noble metal. These may be elements such as Pt, Pd and Rh that are important in the process of conversion of pollutants such as CO, NO<sub>x</sub> and hydrocarbons. Noble metals are used in the form of oxides or with the carrier of heat resistant oxides such as Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>. Rhodium is effective in the reduction of nitrogen oxides and therefore it is used in a redox catalyst and in the catalyst-adsorption device. Similarly, palladium, which promotes oxidation of CO and hydrocarbons, is used. Natural or synthetic zeolite is used as an adsorbent. The adsorbent should have a temperature resistance up to 500° C. Synthetic or modified natural zeolites satisfy this requirement.

Zeolite with the molar ratio Si/Al is equal to 40 or greater than 40 is preferred in view of heat resistance and hydrophobicity. Examples of such zeolites are ZSM-5, USY, zeolite beta. A combination of two or more samples of zeolites can be used as well. ZSM-5 has relatively small pores (about 0.55 nm) which are advantageous for adsorption of small molecules (propene) but disadvantageous for adsorption of large molecules such as toluene or xylene. Therefore, coating of mixture of ZSM-5 and USY on the carrier has been preferred. Zeolite ZSM-5 is placed against the carrier which can adsorb hydrocarbons at a relatively high temperature of 150°C. Zeolite beta is preferred because of the fact that it includes a dual pore size (0,55 nm and 0,70 nm) thus absorbing small and large molecules relatively well. Although zeolite itself can be used as the adsorbent, it is useful when combined with noble metals such as platinum, palladium and rhodium.

The presence of noble metal in zeolite structure enables its recovery without reducing adsorption ability. Palladium is preferred because it can effectively regenerate zeolite as well as it is affordable. Noble metal is incorporated into the zeolite structure by ion exchange. The thermal stability of zeolite is maintained. Zeolite enriched with noble metal is not only capable of regeneration but also is catalytically active. However, there is no sufficient catalyst durability. Zeolite surface containing heat resistant oxide and a noble metal has been preferred. Such an adsorbent-catalyst containing catalyst component has sufficient durability and sufficient cleaning power even during the cold start and steady state operation. It is also desirable for zeolite to contain at least one ion-selective element such as Cu, Ag, Au because the presence of ions can increase the adsorption capacity of zeolite. Ion content must account for 20% because if it is too low, it insufficiently increases its adsorption capacity. More preferred ion content is at least 40%. It is appropriate to use combinations of ions: Groups of elements with ions of Mg, Ca, Sr, Ba, Y, La, Ti, Ce, Mn, Fe, Cr, Ni and Zn, or at least the ions of Mg, Ca, Fe and Cr as their presence improves the heat resistance of zeolite. The device consists of

a carrier in which the first layer consists of zeolite such as ZSM-5, USY, beta-zeolite containing a noble metal. The second layer consists of the components of the oxides of  $\text{Al}_2\text{O}_3$ ,  $\text{CeO}_2$  or a mixture of the two oxides and noble metals.

According to the patent, acidic zeolite H-Beta was prepared as follows: 150g of ammonium nitrate were dissolved in 800 ml of water and adjusted to pH 3 [23]. Firstly, 200g of beta zeolite was added to this solution. The mixture has been mixed for 2 hours at 70° C and consequently filtered and washed with the deionized water. Then the material was dried during the night at 100°C. The prepared substrate was coated on the carrier. Then the catalyst has been dried at 100°C and calcined at 550°C for two hours to form an acid H-Beta material. During the test, the catalyst reduces the content of hydrocarbons by 80%. Na-Beta zeolite was prepared by ion exchange treatment with sodium nitrite using the following procedure: 150 g of sodium nitrate were dissolved in 600 ml of water. Having added 100g of zeolite beta, the mixture has been stirred for two hours at 70°C. This mixture was subsequently filtered and washed with one liter of deionized water. It was dried at 100° C. The slurry was coated on the carrier. Coated carrier have been dried at 100°C and calcined at 550° C for two hours.

Preparation of Mg-beta zeolite: 100g of magnesium nitrate were dissolved in 300 ml of water. After addition of 100g of beta zeolite, the mixture has been stirred for 2 hours at 70°C. After filtration and washing with one liter of water, mixture is applied in a thin layer on the catalyst carrier. The catalyst was then dried at 100°C and calcined for 2 hours at 220°C. The monolithic carrier is prepared from inert material such as cordierite, mullite, alumina, alumina-magnesia silicon, stainless steel. The inert carrier is coated with catalyst layer.

Ceramic monolith carrier (cordierite, mullite) or heat resistant metal such as stainless steel with density from 0.9 to 233 pores per  $\text{cm}^2$  is used. The lighter carrier has been preferred. The catalyst comprises at least one element from the group of noble metals (Pt, Pd, Rh) which successfully convert carbon monoxide, hydrocarbons and nitrogen oxides emitted from internal combustion engines. Noble metals are usually supported by heat-resistant oxides such as  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$  and  $\text{ZrO}_2$ .  $\text{Al}_2\text{O}_3$  with a specific surface of  $100\text{m}^2\cdot\text{g}^{-1}$  with dispersed noble metals has been preferred when used in combination with other noble metals such as Rh and Pt (Pd). These metals are used as heat-resistant oxides which are deposited on a monolith carrier in the form of thin film (shell). The catalyst component should include elements from the group of alkali and alkaline earth metals and actinides. The most common are the following elements: Li, Cs, Mg, Ca, Sr, Ba, Y, Ti, Zr, Hf, La, Ce, Pr, Nd, Th.

## 8 THE THEORETICAL BASIS OF ADSORPTION AS A MAJOR PROPERTY OF ZEOLITES

One of the basic physical characteristics of the adsorbent is equilibrium adsorption capacity. The equilibrium adsorption capacity can be expressed for one particular state (pressure temperature and relative humidity). Adsorption isotherm or over several adsorption isotherms are complex characteristics for the adsorbent and the adsorbate in the certain interval of adsorbate pressures. Adsorption is defined as a concentration of substances on the surface or in the volume of micro pores of solid. It is divided into physical and chemical adsorption. Physical adsorption is caused by similar forces, Van der Waals intermolecular forces acting between a solid surface and adsorbate molecules. These forces are not directional in nature and are relatively non-specific [35]. In contrast to physical adsorption, chemisorptions resulting from binding forces which are comparable to the forces that give rise to chemical compounds.

Physical adsorption can be distinguished from chemical sorption on the basis of infrared spectra of adsorbed molecules. From a thermodynamic point of view, adsorption is associated with the reduction of free enthalpy. This is exothermic process associated with the loss of one degree of freedom. It follows from the equation (8.1) [6, 8].

$$\Delta H = \Delta G + T \Delta S \quad (8.1)$$

Physical and chemical adsorption can be distinguished on the basis of adsorption heat. The quantity of gas adsorbed depends on partial gas pressure, temperature, the nature of gas and the nature of the micropores of the adsorbent. Amount of adsorbed gas is a function of partial pressure of adsorbate and a temperature at equilibrium for the system.

$$A = f(p, T) \quad (8.2)$$

The first quantitative theory of gas adsorption was published by Irving Langmuir who based his model of adsorption on the following assumptions:

1. During equilibrium, at optional gas temperature and pressure, a number of active centers  $Q$  is occupied by adsorbed molecules. The  $1 - Q$  remains free.
2. Each adsorption center can be captured by a single molecule adsorbed.
3. Adsorption heat is the same for all centers and does not depend on the degree of coverage  $Q$ .
4. The molecules adsorbed on different centers show no interaction.

## THE THEORETICAL BASIS OF ADSORPTION AS A MAJOR PROPERTIES OF ZEOLITES

Based on kinetic analysis of condensation and evaporation of gas molecules on the surface of the adsorbent, Langmuir adsorption isotherm equation was derived:

$$Q = k_a p / k_d + k_a p = bp / 1 + bp \quad (8.3)$$

where  $b$  is the ratio of the rate constants  $k_a/k_d$ .

For the degree of filling, the Langmuir adsorption isotherm is valid:

$$a \cdot \theta = b_0 e^{-\Delta H/RT} / 1 + b_0 e^{-\Delta H/RT} P \quad (8.4)$$

The Langmuir equation is often used in the form where adsorbed quantities are given in volume.

If  $V_m$  is the volume of gas required to form a monolayer and  $V$  is the volume of gas adsorbed at a pressure  $p$ , then

$$V = V_m bP / 1 + bP \quad (8.5)$$

The coordinates of  $P/V$  and  $P$ , the Langmuir equation of the straight line shows

$$P/V = 1/V_m b + P/V_m \quad (8.6)$$

The Langmuir adsorption isotherm was derived based on a model assuming full equality of all adsorption centers regarding heterogeneity of real surfaces. The Freundlich adsorption isotherm is more preferable in most cases:

$$a = k p^{1/m} \quad (8.7)$$

where  $k$  and  $m$  is the constant, the constant  $m$  is changed with the temperature and their values are greater than 1.

Constant  $k$  is dependent on the nature of the adsorbent. Adsorbed substance and its value with increasing temperature decreases. After logarithmization of the expression, constants can be determined graphically:

$$\lg a = \lg k + m \lg p \quad (8.8)$$

$m$  determines the value of the slope of the line, and the value of  $k$  of the portion which cuts off the straight line on the y-axis. The value  $k$  is defined for the adsorptive partial pressure of the adsorptive 1 Pa.

$$\text{If in the equation } a = W_0/V^+ \exp[-(RT/E \cdot \ln p_0/p)^n] \quad (8.9)$$

Describing adsorption by Dubinin theory of volume of micropores filling;

If  $n=1$ , then we can write the equation in the following form:

$$a = a_0 \exp(-RT/E \ln p_0/p) \quad (8.10)$$

If  $m = RT/E$  and  $\lg k = \lg a_0 - RT/E \cdot \lg p_0$ , after logarithmic shape of the Freundlich equation is compliant with logarithmic shape of the adsorption isotherm by the Dubinin theory of volume filling of micropores [8].

Among other factors, the course of isotherms depends on the strength of interaction between the molecules, which are found in the pores. If force of interaction between two molecules increases, isotherm has a steeper curve. Barrer dealt in details with sorption equilibrium of zeolites. According to Barrer results, the degree of saturation decreases in the host component with an increase in temperature. With the increase in temperature, the volume of the host molecules increases [6].

## **9 CLINOPTILOLITE TESTING TO REDUCE TOXIC COMPONENTS OF COMBUSTION ENGINES EXHAUST GASES**

The possibility of using natural clinoptilolite zeolite from the deposit in Nižný Hrabovec to reduce harmful exhaust components has been the subject of research at the Faculty of Manufacturing Technologies of the Technical University in Košice. Experiments were focused on the review of the appropriateness of the use of natural clinoptilolite zeolite for the purposes of reducing the content of toxic substances contained in exhaust gases of internal combustion engines using sorption, ion exchange and catalytic properties.

The measurements have been directed towards the use of zeolite as a sorbent and catalyst for reducing the content of nitric oxide and hydrocarbons contained in the exhaust gas of internal combustion engines. The impact of chemical treatment including incorporation of zeolite selected metallic elements on the sorption and catalytic properties has been also under investigation. The experimental measurements used granular samples with grain size from 2.5 mm to 5.0 mm as well as grain size from 5.0 mm to 8.0 mm.

A necessary condition for the use of natural zeolite is heat treatment due to the presence of water molecules in zeolite micropores. In collaboration with the technical inspection station ZPA CONTROL in Prešov, approximate repeated measurements performed with the modular analyzer MGA1200 recorded decrease of carbon monoxide and hydrocarbons in ten minutes. This gave rise to further study of the issue. Measuring of nitric oxides was performed using various samples.

In addition to changes in the concentration of  $\text{NO}_x$  in the exhaust gas, kinetic sorption course was studied. For the experimental measurements, sorption - catalytic device, consisting of a steel body filled with zeolite, has been designed and manufactured (Fig.3).

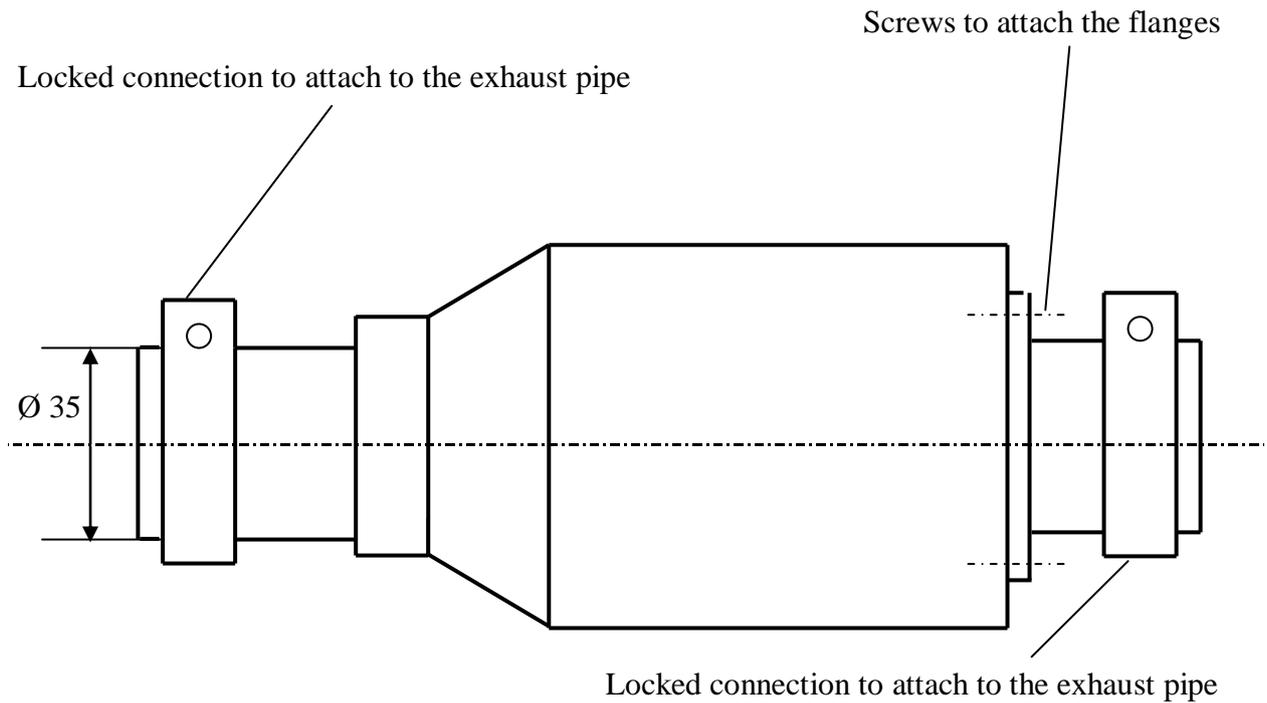
The samples of clinoptilolite zeolite in natural granular form as well as chemically modified samples were used.

*CLINOPTILOLITE TESTING TO REDUCE TOXIC COMPONENTS  
OF COMBUSTION ENGINES EXHAUST GASES*



**Figure 3: Sorption – catalytic device**

*CLINOPTILOLITE TESTING TO REDUCE TOXIC COMPONENTS  
OF COMBUSTION ENGINES EXHAUST GASES*



**Figure 4: Scheme of sorption – catalytic device**



**Figure 5: Clinoptilolite zeolite with grain size from 2,5 to 5 mm**

### **9.1 Samples treatment**

The chemical adjustment of the samples was based on the ion exchange originally contained cations for ammonium cations. Initial treatment of the samples of clinoptilolite zeolite consists in multiplicity decantation with distilled water and subsequent drying at 270 °C. Chemical treatment of zeolite samples lied in washing granular zeolite by 0.5 molar ammo-

*CLINOPTILOLITE TESTING TO REDUCE TOXIC COMPONENTS  
OF COMBUSTION ENGINES EXHAUST GASES*

nium chloride. Zeolite samples were washed during 24 hours and then dried at 270 °C. The samples were used for measurements as well as preparation of cobalt modification of zeolite. The use of a salt solution of different cations can be obtained by the catalytic properties of zeolite. In this case, zeolite catalyst converts the content of nitrogen oxides into nitrogen.

To increase the sorption capacity of clinoptilolite samples, modification of natural clinoptilolite was performed by washing of 1 molar solution of ammonium chloride. The ammonium form was prepared by replacing the cations originally contained in zeolite in ammonium ions using ammonium salt solution of the suitably chosen conditions. The samples, which were decanted with distilled water and thermally activated, were then washed with ammonium chloride solution at a concentration of  $1 \text{ mol}\cdot\text{dm}^{-3}$  for 24 hours with occasional stirring.

Other measurements were focused on the temporal change of concentration of the exhaust gas components. Sample treatment with hydrochloric acid at  $0.5 \text{ mol}\cdot\text{dm}^{-3}$  was performed by dealumination. The prepared sample was monitored regarding the change of content of nitrogen oxides in the exhaust gas in precise time intervals. Ammonium modification was used to prepare copper and cobalt modifications. Cobalt modification was prepared by washing with 0,5 M solution of cobalt chloride for five hours at room temperature. After adjusting by cobalt chloride, the original zeolite green color has changed to blue. This effect was probably due to the formation of the ammonia complex of  $[\text{Co}(\text{NH}_3)_4]^{2+}$ . This form of zeolite has been used for sorption of nitric oxide and PAH. Similarly, the copper sulfate treatment took its course. Having its first deamonization, the sample has been washed with 0,5 M solution of copper sulfate for 24 hours at room temperature. After drying, the sample was ready for measurement.

## 10 REDUCTION OF TOXIC EXHAUST COMPONENTS FOR INTERNAL COMBUSTION ENGINES

Nitrogen oxides, carbon monoxide and various hydrocarbon compounds are considered to be toxic exhaust gas components. Carbon dioxide contributes to global climate change.

Our experimental measurements are aimed at reducing the content of nitrogen oxides and polycyclic aromatic hydrocarbons. Measurements of CO and CO<sub>2</sub> reduction using zeolite were indicative only.

The first samples regarding indicative measurements were prepared from natural zeolite with a particle size 2.5 mm to 5.0 mm and 5.0 mm to 8.0 mm. Heat-treated samples of the same grain size were treated at 250°C.

**Table 15:**  
**Results of the determination of hydrocarbons and carbon monoxide after heat treatment of natural zeolite with grain size from 5,0 to 8,0 mm**

<b>ŠKODA FAVORIT 136L</b>	<b>Intervals [min]</b>	<b>Gas temperature at the filter output [°C]</b>	<b>ppm</b>	<b>CO [%]</b>	<b>CO<sub>2</sub> [%]</b>	<b>CxHy [ppm]</b>
<b>Without filter</b>	6	40	911	1.02	13.55	333
<b>Cold filter</b>	12	30	899	0.77	11.87	298
<b>Heated filter</b>	18	50	954	0.53	9.93	211
<b>Heated filter</b>	24	50	968	0.88	9.44	227

Having installed the filter, a decrease of all monitored components was observed. After 24 minutes, however, there was a slight increase in hydrocarbon and carbon monoxide content in exhaust gases. Decrease of carbon dioxide content is interesting due to the fact that it belongs to greenhouse gases. Original value of 13.55% has declined to 9.38% with CO<sub>2</sub> levels. However, after 24 minutes the level started to rise. In order to improve sorption and catalytic properties of zeolite samples, they have to be chemically modified.

*REDUCTION OF TOXIC EXHAUST COMPONENTS FOR INTERNAL  
COMBUSTION ENGINES*

**10.1 Reduction of nitrogen oxides in exhaust gases using the filter-sorption device with differently modified samples**

To study the sorption of nitrogen oxides or their intended catalytic conversion, natural and chemically modified zeolites were used in the following experiments. In the process of measuring nitrogen oxides in exhaust gases, we have proceeded from unmodified zeolite samples to samples that were thermally and chemically treated. Before the exhaust device was used at the output, the content of nitrogen oxides was recorded at regular time intervals. Similarly, the nitrogen oxides have been recorded after using the device at the output. All content measurement of nitrogen oxides were performed using the same vehicle without catalyst at an engine speed of 800 ppm. From the measured values, the average efficiency of the device has been calculated.

The first three measurements were performed using the samples in their natural form. After indicative measurements, heat and chemically treated samples were modified by ammonium chloride, hydrochloric acid, cobalt chloride and copper sulphate. Measurements of nitrogen oxides using the modified samples were performed at the same conditions.

From the measured values we have calculated the efficiency of the device according to the following equation (10.1).

$$\text{The efficiency (\%)} = [(C_1 - C_2) / C_1] \times 100 \quad (10.1)$$

where  $C_1$  is the concentration of NO<sub>x</sub> in exhaust gases at the filter input and  $C_2$  is the concentration of NO<sub>x</sub> in exhaust gases at the filter output.

Using untreated zeolite, the efficiency values of the adsorption of the filter-force device was within the range of 19% - 25%. The highest efficiency was achieved in 150 seconds. Then the efficiency curve obtained a falling character. Values were averaged from the calculated performance. The calculated average value of the effectiveness of filtering-sorption device using unmodified zeolite accounted for 20.7%. Table 16 shows the results of measuring nitrogen oxides using the natural sample.

*REDUCTION OF TOXIC EXHAUST COMPONENTS FOR INTERNAL  
COMBUSTION ENGINES*

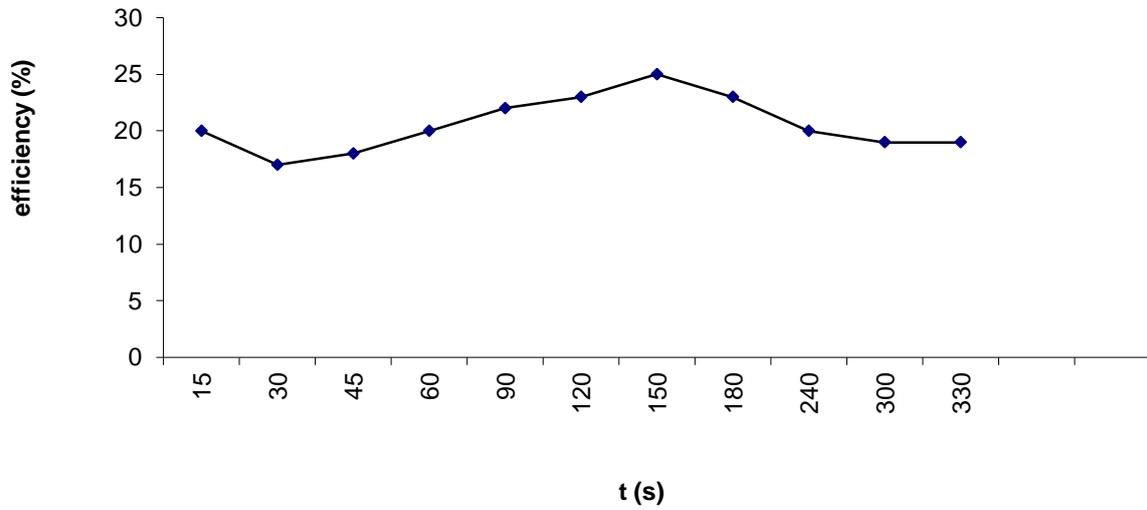
**Table 16:**  
**The results of measurement of NO<sub>x</sub> in exhaust gases using natural untreated zeolite sample with grain size 5-8 mm**

Time t [s]	NO <sub>x</sub> concentration at input filter [mg · m <sup>-3</sup> ]	NO <sub>x</sub> concentration at output filter [mg · m <sup>-3</sup> ]
0	0	0
15	6.7	5,36
30	18.76	16
45	33.5	24,12
60	45.6	36,18
90	65.6	50,9
120	80.4	61.64
150	91.12	68.34
180	96.48	73.7
210	96.48	75
240	96.48	76.3
270	96.48	77.7
300	96.48	77.7
330	96.48	77.7

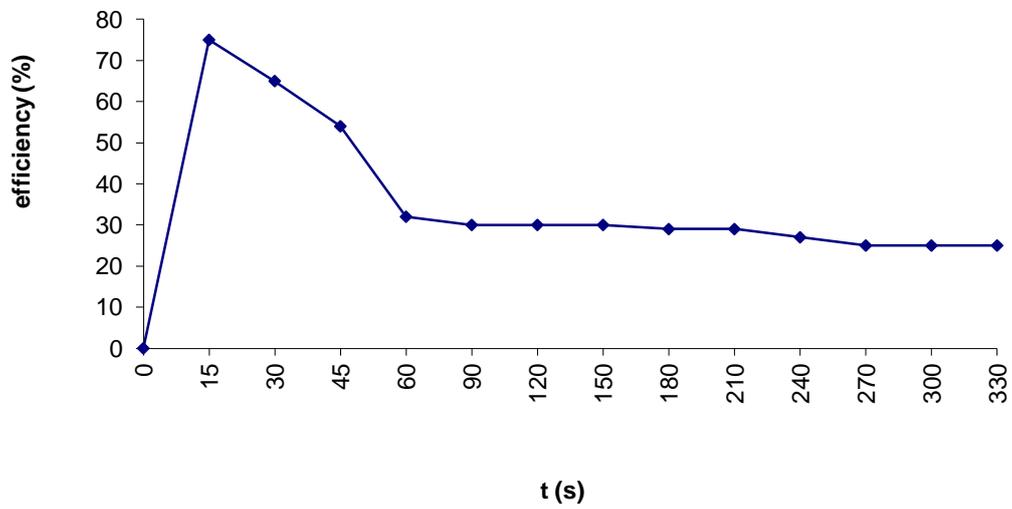
Figure 6 shows the change in the filter efficiency during the period of time.

In order to remove the molecules of water contained in the sorbent, ducts thermal activation at 270 ° C was performed. The average efficiency of filtering-sorption device using heat-treated zeolite accounted for 31%. Efficiency curve changes are shown in Figure7 [71].

*REDUCTION OF TOXIC EXHAUST COMPONENTS FOR INTERNAL  
COMBUSTION ENGINES*



**Figure 6: Changes of the efficiency of the sorption - filtering device while using unmodified zeolite [71]**



**Figure 7: Changes of the efficiency of the sorption - filtering device while using thermally activated zeolite**

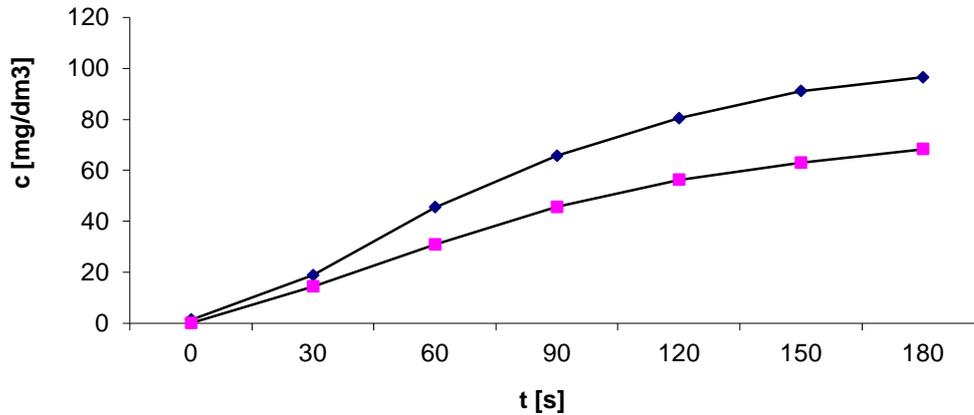
*REDUCTION OF TOXIC EXHAUST COMPONENTS FOR INTERNAL  
COMBUSTION ENGINES*

**Table17:**  
**Results of measurements of NO<sub>x</sub> after heat-treatment of zeolite  
(5.0 to 8.0 mm)**

Time [s]	NO <sub>x</sub> concentration at output [mgm <sup>-3</sup> ]	NO <sub>x</sub> concentration at input [mgm <sup>-3</sup> ]
0	0	1.34
15	1.34	5.36
30	14.36	18.76
45	18.76	33.5
60	30.82	45.5
90	45.56	65.66
120	56.28	80.4
150	62.98	91.12
180	68.34	96.48
210	69.68	96.48
240	76.38	96.48
270	72.36	96.48
300	72.36	96.48
330	72.36	96.48

Figure 8 [71] is compared to the curve of changing the content of nitrogen oxides in exhaust gases without using filtering-sorption device as well as using the device.

*REDUCTION OF TOXIC EXHAUST COMPONENTS FOR INTERNAL  
COMBUSTION ENGINES*



**Figure 8: Time change of NO<sub>x</sub> in exhaust gases using the sorption-filtering device and without using filtering-sorption device**

Filter efficiency was evaluated according to the equation 10.1. To improve the sorption properties of zeolite sample it has been chemically treated with ammonium chloride. Following from previous laboratory experiments it was stated that ammonium hydroxide is not appropriate for the modification of natural zeolite. Regarding the previous statement, for the sample amonization solution of ammonium chloride at a concentration of 1 mol.dm<sup>-3</sup> was used. Chemical treatment was preceded by decantation and dried at 270°C. Measurements have been performed under the same conditions as in the previous case when the engine speed was 800 ppm. The results of measurements of NO<sub>x</sub> after treatment of zeolite with grain size 5-8 mm are presented in the table 18 [45,71].

*REDUCTION OF TOXIC EXHAUST COMPONENTS FOR INTERNAL  
COMBUSTION ENGINES*

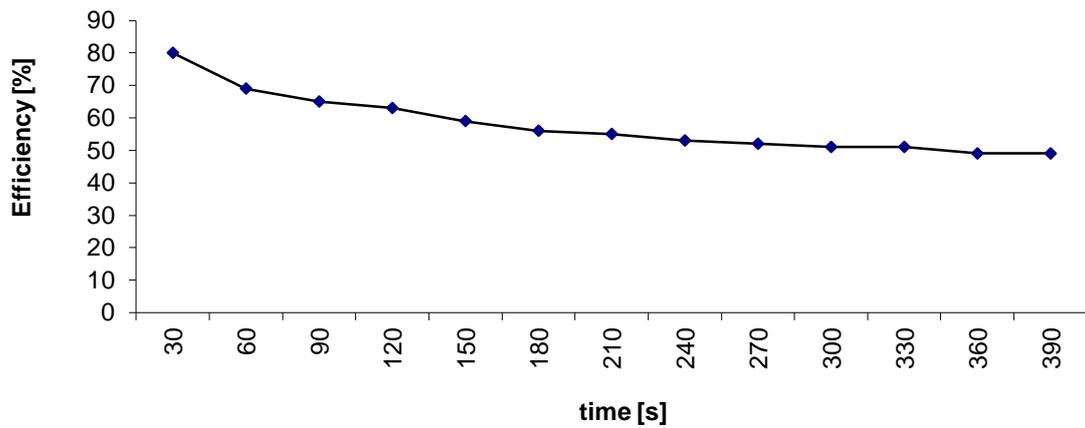
**Table 18:**  
**Measured results after treatment with ammonium chloride**

<b>Time (s)</b>	<b>NO<sub>x</sub> concentration at filter output [mgm<sup>-3</sup>]</b>	<b>NO<sub>x</sub> concentration at filter input [mgm<sup>-3</sup>]</b>
0	0	0
15	0	9.366
30	4.01	20.07
45	10.7	33.45
60	14.7	48.16
90	25.4	73.59
120	34.7	94.99
150	42.8	105.7
180	46.8	108.3
210	49.5	112.3
240	52.18	112.3
270	53.52	112.3
300	54.858	112.3
330	54.858	112.3
360	56.196	112.3
390	56.196	112.3
420	56.196	112.3

The average efficiency of the filter after chemical treatment with ammonium chloride has risen to 59 %.

The graph in Figure 9 [71] shows the time dependence of the efficiency of the sorption-filtration device using chemically treated sample with ammonium chloride.

*REDUCTION OF TOXIC EXHAUST COMPONENTS FOR INTERNAL  
COMBUSTION ENGINES*



**Figure 9: Changes of the effectiveness of sorption - filtering device in relation to time**

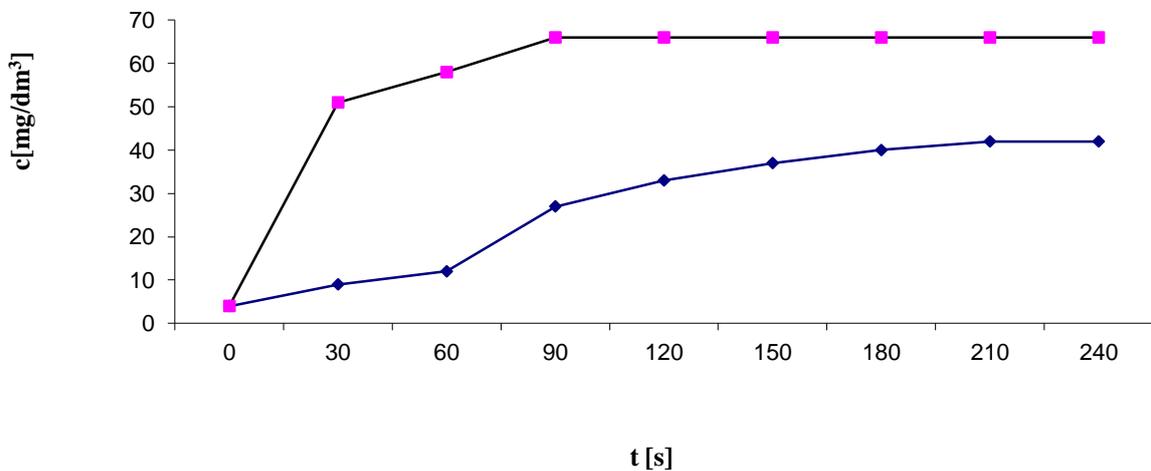
Table 19 [45,71] compares differently treated samples. The highest efficiency was observed when the sample treated with ammonium chloride was used in the sorption - filtering device.

**Table 19:  
Changes of the effectiveness of sorption - filtering device using natural,  
heat and chemically treated samples at the time period**

Time [s]	Filter efficiency with natural sample [%]	Filter efficiency heat-treated sample [%]	Filter efficiency chemically treated sample (NH <sub>4</sub> Cl) [%]
30	20	75	80
60	18	54	69
90	20	32	65
120	22	32	63
150	23	30	59
180	25	29	56
210	23	29	55
240	20	27	53
270	19	25	52
300	19	25	51
330	19	25	51

*REDUCTION OF TOXIC EXHAUST COMPONENTS FOR INTERNAL  
COMBUSTION ENGINES*

Additional experiments related to sample preparation for the purpose of incorporation of cobalt and copper cations into the structure of natural zeolite were conducted. The aim was to modify clinoptilolite so that it can obtain sorption and catalytic properties. Ammonium modification is the starting point for treatment into copper and cobalt modification. Similar to the samples that were chemically unmodified as well as with modified ones, the change of concentration of nitrogen oxides in exhaust gases in the sorption-filtering device was observed. The measurements were performed at 25 °C. The variation in time of the NO<sub>x</sub> is expressed in the graph in Figure 10.



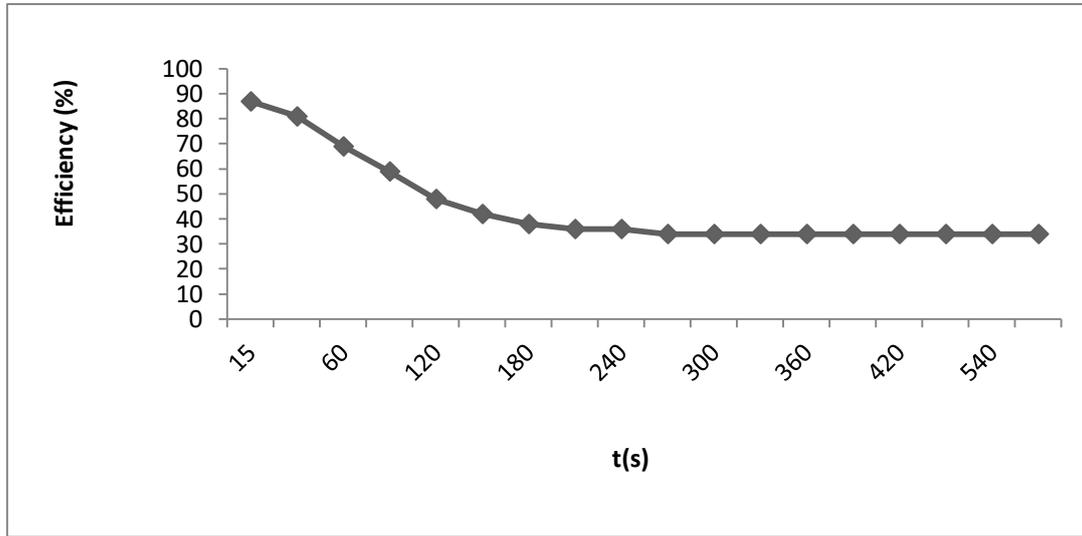
**Figure 10:** Time curve of the NO<sub>x</sub> in exhaust gases in the sorption-filtering device both at input and output using cobalt form of zeolite [44]

The values listed in Table 20 were measured by cobaltous modification [71]. Efficiency of the device has been improved and at the same time the period of time the device useful life has been prolonged after the treatment of the heat-treated sample. The average efficiency of the device in relation to nitrogen oxides accounted for 46,4%. Supreme efficiency in the filter was recorded during the first 15 seconds. Then its value decreased to 270 seconds. After five minutes, efficiency value has stabilized.

It can be considered that in this modification catalytic conversion of nitrogen oxides to nitrogen except adsorption has been realized by means of cobalt cations bound to zeolite structure.

*REDUCTION OF TOXIC EXHAUST COMPONENTS FOR INTERNAL  
COMBUSTION ENGINES*

A graph of time change efficiency is shown in Figure 11.



**Figure 11:** Graph of time change efficiency using cobalt modification of zeolite [45]

**Table 20:**  
**The results of measuring the change of NO<sub>x</sub>**  
**using zeolite after treatment with 0,5 M CoCl<sub>2</sub> [45]**

Time t [s]	NO <sub>x</sub> concentra- tion at input [mgm <sup>-3</sup> ]	NO <sub>x</sub> concentra- tion at output [mgm <sup>-3</sup> ]
0	4.01	4.01
15	44.15	5.35
30	50.84	9.36
45	52.18	12.04
60	57.53	17.39
75	65.56	22.74
90	65.56	26.76
105	65.56	30.77
120	65.56	33.45
135	65.56	36.12
150	65.56	37.46
165	65.56	38.80
180	65.56	40.14

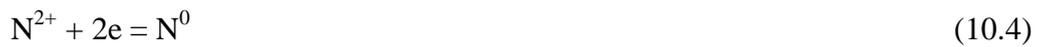
*REDUCTION OF TOXIC EXHAUST COMPONENTS FOR INTERNAL  
COMBUSTION ENGINES*

210	65.56	41.47
240	65.56	41.47
270	65.56	42.81
300	65.56	42.81
330	65.56	42.81
360	65.56	42.81
390	65.56	42.81
420	65.56	42.81
480	65.56	42.81
540	65.56	42.81
600	65.56	42.81

It can be assumed that in this case the influence of cobalt ions bound to zeolite structure resulted in transformation of nitrogen oxides into nitrogen and oxygen according to the following equation (10.2).



Ongoing partial oxidation-reduction reactions:



Previous study has shown that decomposition of  $\text{N}_2\text{O}$  is realized according to the equation (10.5) before its oxidation to  $\text{NO}$  in the presence of a catalyst [46].



*REDUCTION OF TOXIC EXHAUST COMPONENTS FOR INTERNAL  
COMBUSTION ENGINES*

**Table 21:**  
**Time-dependent efficiency of the sorption-filtering device  
using cobalt modification of zeolite**

Time [s]	Efficiency [%]
15	87
30	81
60	69
90	59
120	48
150	42
180	38
210	36
240	36
270	34
300	34
330	34
360	34
390	34
420	34
480	34
540	34
600	34
660	34

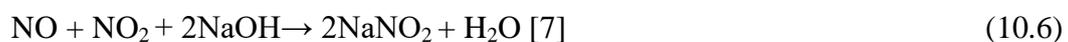
Table 21 shows the results of the effectiveness of the filter using natural zeolite without any treatment, heat-treated natural zeolite, chemically modified into ammonium form and chemically treated into cobalt modification [71]. Cobalt modification shows catalytic activity.

*REDUCTION OF TOXIC EXHAUST COMPONENTS FOR INTERNAL  
COMBUSTION ENGINES*

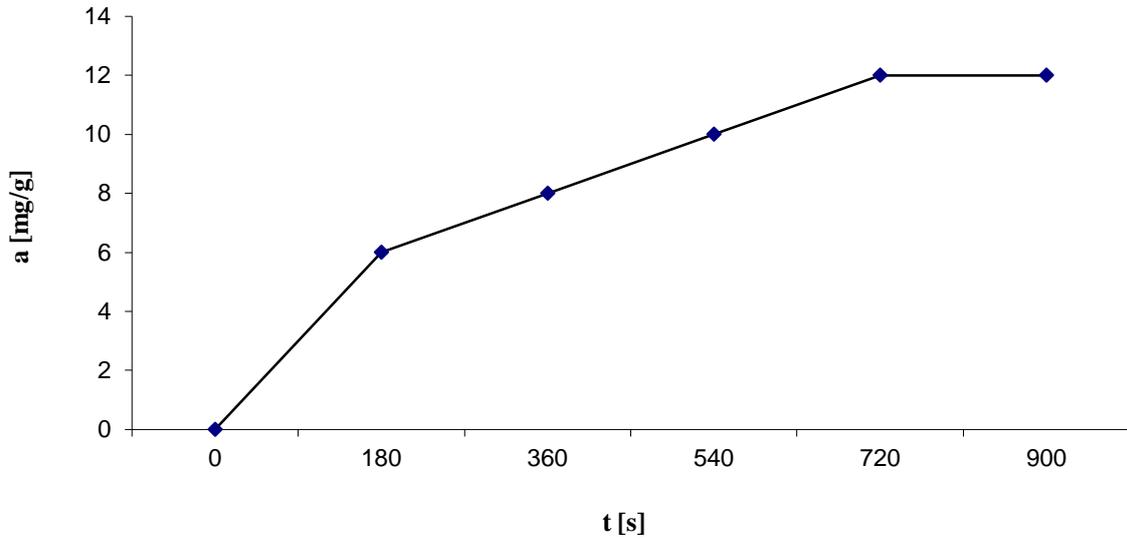
**Table 22:**  
**Time dependence of the effectiveness of NO adsorption from exhaust gases using various zeolite samples**

Time [sec]	Natural form	Heat - activated	NH <sub>4</sub> <sup>+</sup> - form	Co - modified
30	20	75	80	81
60	18	54	69	69
90	20	32	65	59
120	22	32	63	48
150	23	30	59	42
180	25	29	56	38
210	23	29	55	36
240	20	27	53	36
270	19	25	52	34
300	19	25	51	34
330	19	25	51	34
360	19	25	51	34
390	19	25	51	34

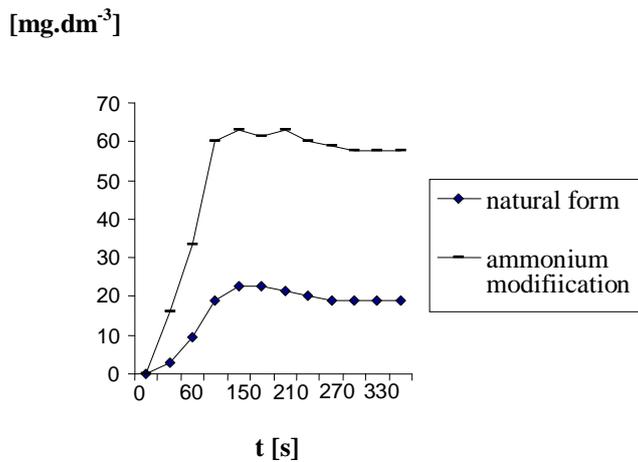
Kinetics of nitrogen oxides sorption process was monitored using thermally activated natural zeolite as well as modified zeolite. The experimental results were obtained by concentration of the sorbed substance for different times at a constant temperature of sorption. The sample was contaminated by exhaust gases. The samples were taken at specific time intervals. Nitrogen oxides have been extracted from the adsorbent by treatment with sodium hydroxide. Their content was quantitatively indirectly determined in the form of nitrite present in the eluent. The essence of this action is expressed by the chemical equation (9.2.6). Time dependence of the sorption of nitrogen oxides in zeolite was obtained indirectly on the basis of quantitative mass balance of nitrite in the eluate after elution of sodium hydroxide.



*REDUCTION OF TOXIC EXHAUST COMPONENTS FOR INTERNAL  
COMBUSTION ENGINES*



**Figure 12: Time-dependent uptake of nitrogen oxides using natural clinoptilolite**



**Figure 13: Kinetic curve of sorption using natural zeolite and its ammonium modification [45]**

Polycyclic aromatic hydrocarbons, which are characterized by carcinogenic and mutagenic properties, occur in exhaust gases produced by combustion engines. Benzo(a)pyrene is especially dangerous. Eluent analysis of thermally activated clinoptilolite zeolite and chemically modified zeolite samples after their contamination by exhaust gases was carried out regarding to pollutants sorption.

*REDUCTION OF TOXIC EXHAUST COMPONENTS FOR INTERNAL  
COMBUSTION ENGINES*

The experiments were conducted at the Faculty of Manufacturing Technologies in Košice in cooperation with the Institute of Analytical and Physical Chemistry of the Faculty of Natural Sciences of Pavol Jozef Šafárik and the Institute of Medical Chemistry, Biochemistry, Medical Pharmacology of the Medical Faculty of Pavol Jozef Šafárik University in Košice.

The samples were contaminated by exhaust gases from car Škoda favorit at an engine speed of 1500 ppm/min for 15 minutes. Eluate analysis was carried out by independent chromatographic methods, high performance liquid chromatography and gas chromatography. Analysis was focused at contaminated samples to confirm the presence of polycyclic aromatic hydrocarbons. To identify the recorded chromatographic peaks, sixteen of the most important standards according to the US Agency for Environmental Protection (EPA) for polycyclic aromatic hydrocarbons were used. These standarts are as follows: Naphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo (a) anthracene, chrysene, benzo (b) fluoranthene, benzo (k) fluoranthene, benzo (a) pyrene, indeno (c,d) pyrene, dibenzo (a,h) anthracene, benzo (g,h,i) perylene.

The presence of polycyclic aromatic hydrocarbons in the eluate as well as carcinogenic benzo(a)pyrene were observed. Results of liquid and gas chromatography have been published in the Proceeding of the 55th Congress of the chemical companies [47].

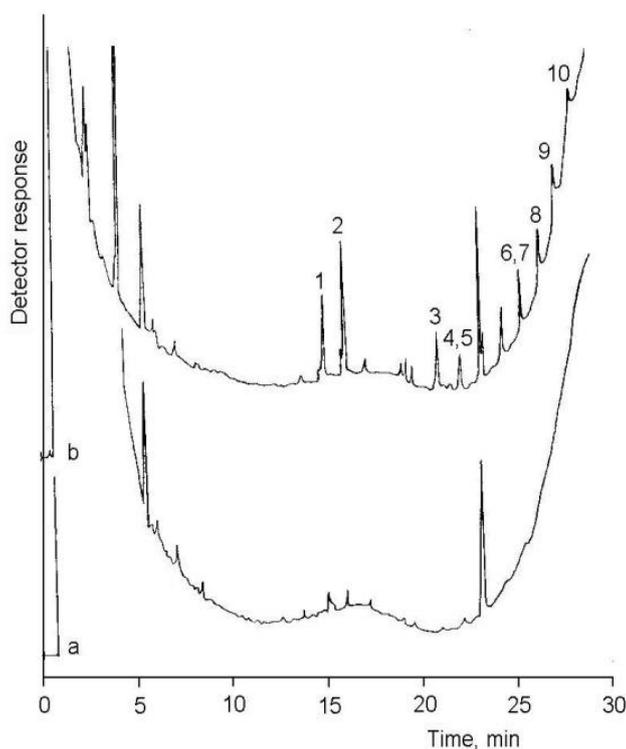
**Table 23:**  
**Content of polycyclic aromatic hydrocarbons determined by HPLC  
using the heat-activated sample**

Polycyclic aromatic hydrocarbons	Concentration [ppb]
Pyrene	310.43
Benzo(a)pyrene	0.37
Benzo(a)anthracene	31.4
Benzo(b)florantene	11.7
Fenantrene	2.5
Dibenzo(a,h)anthracene	2.09

Other experiments for reducing PAH content were carried out with modified zeolite samples. After chemically modified zeolites contamination by means of exhaust gas filtering-sorption equipment, chromatographic analysis focused on polycyclic aromatic hydrocarbons

*REDUCTION OF TOXIC EXHAUST COMPONENTS FOR INTERNAL  
COMBUSTION ENGINES*

in the corresponding extracts using gas chromatography method and fluorescence spectrometry, was performed once again. Based on the comparison of the obtained results it was found that in the extract of modified zeolites by ions of  $\text{Cu}^{+2}$  and  $\text{Co}^{+2}$  carcinogenic polyaromatics compared to natural zeolite and its ammonium form were not observed. It is assumed that this is due to the influence of catalytic reforming of copper and cobalt cations. The results obtained by GC were confirmed by fluorescence spectroscopy (Figure 14, 15, 16, 17 [71]).



**Figure 14: GC chromatogram of extract of noncontaminated (a) and contaminated natural clinoptilolite (b) [47]**

1 fluorene; 2 phenantrene; 3 pyrene; 4 benzantracene; 5 chryzene;  
6 benzo[b]fluorantene; 7 benzo[k]fluorantene; 8 benzo[a]phyrene;  
9 dibenzo[a,h]anthracene; 10 benzo[ghi]pherylene

REDUCTION OF TOXIC EXHAUST COMPONENTS FOR INTERNAL  
COMBUSTION ENGINES

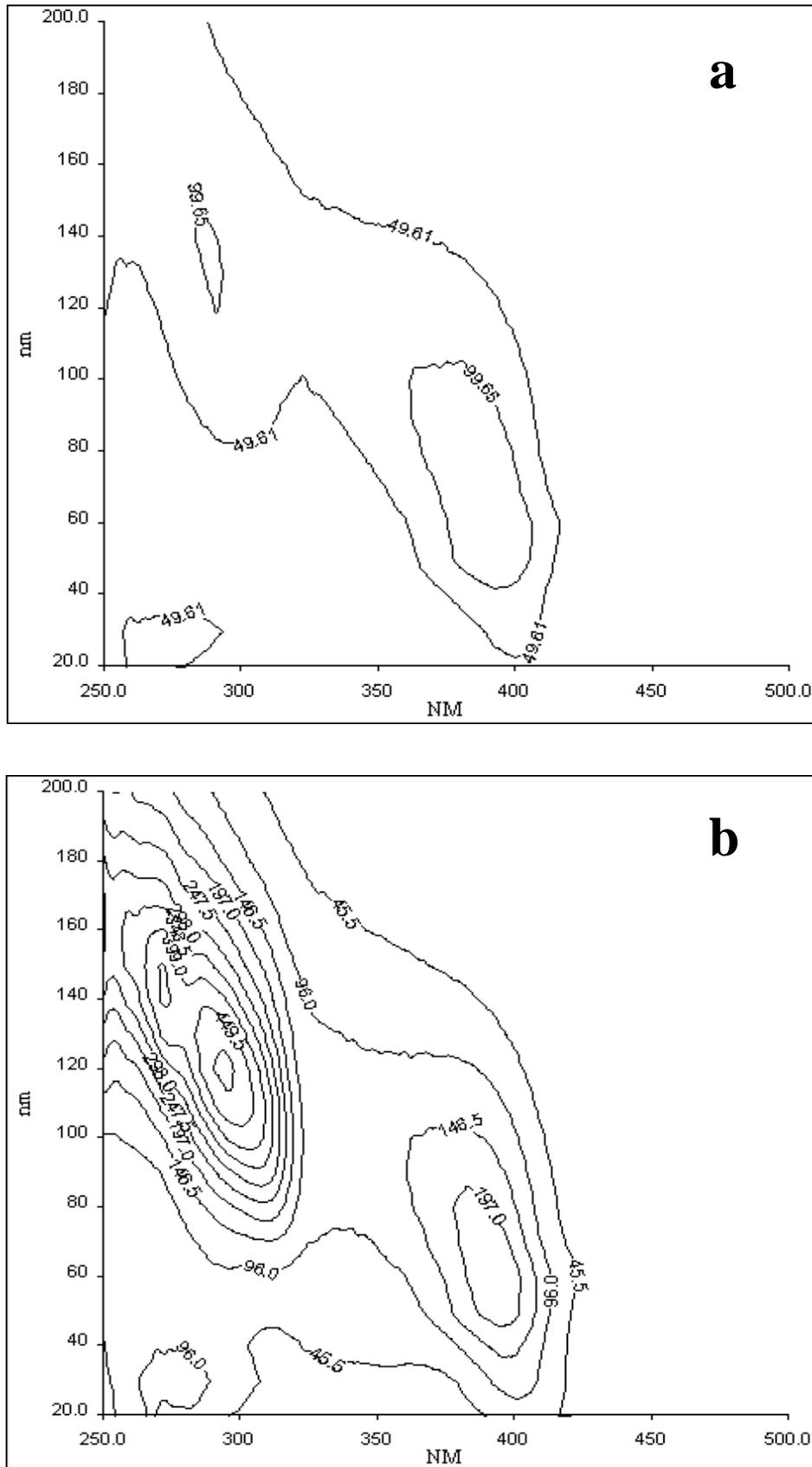
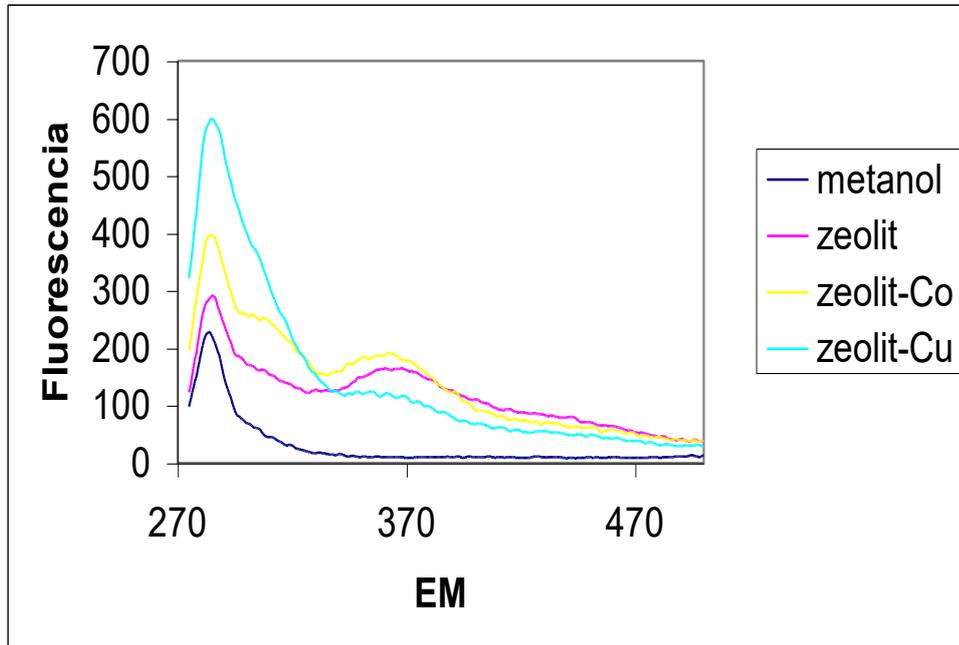


Figure 15: Contour maps of noncontaminated zeolite  $\text{NH}_4^+$  extract (a) and contaminated zeolite  $\text{NH}_4^+$  extract (b) [48]

*REDUCTION OF TOXIC EXHAUST COMPONENTS FOR INTERNAL  
COMBUSTION ENGINES*



**Figure 16: Emission spectra of zeolite extracts**

REDUCTION OF TOXIC EXHAUST COMPONENTS FOR INTERNAL  
COMBUSTION ENGINES

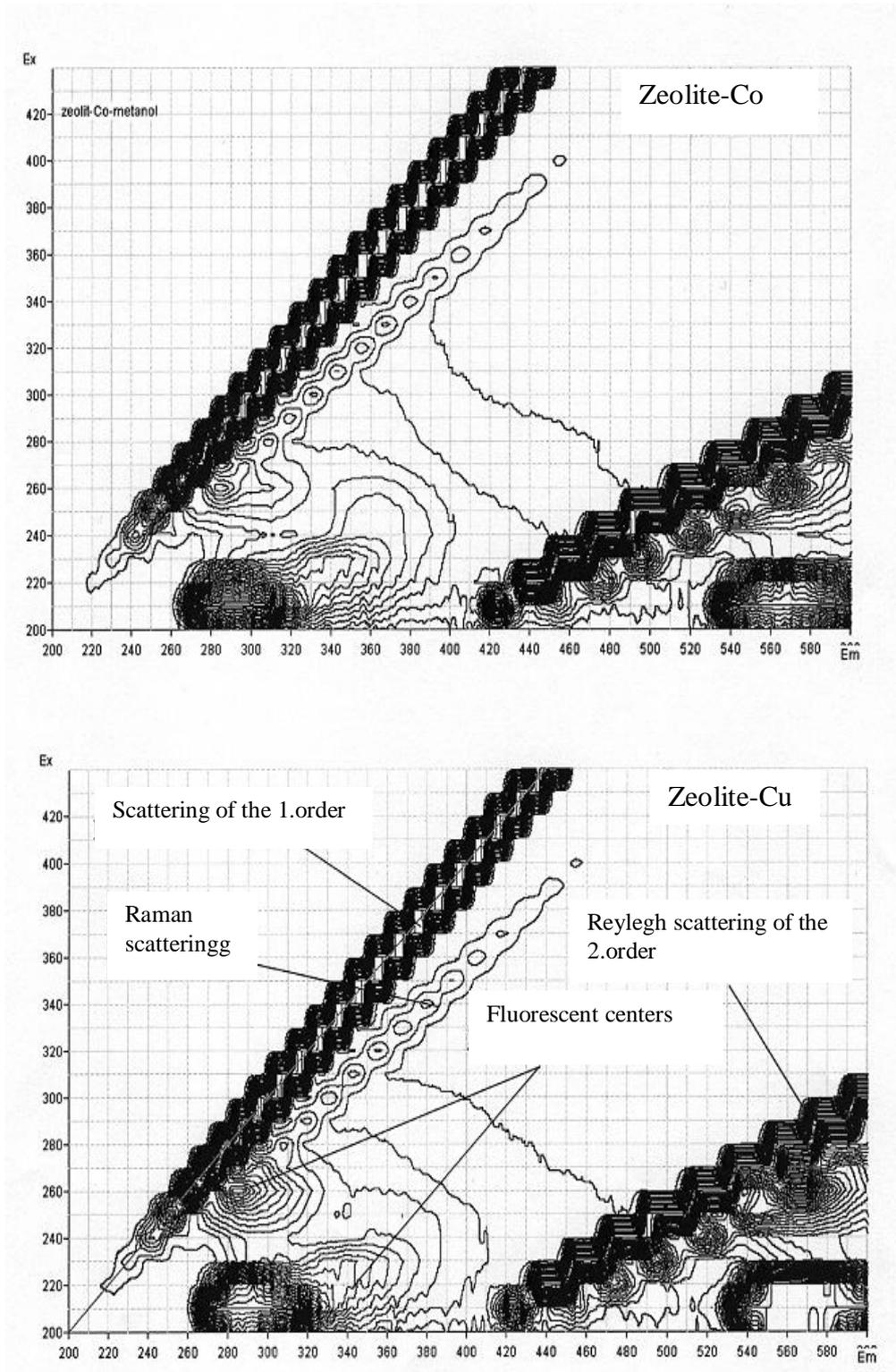
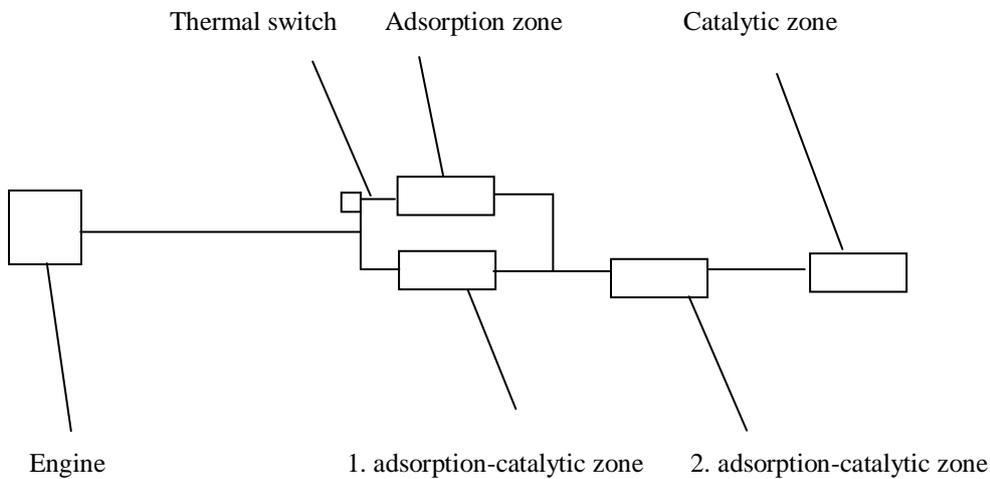


Figure 17: Excitation-emission matrix of modified zeolite extracts

*REDUCTION OF TOXIC EXHAUST COMPONENTS FOR INTERNAL  
COMBUSTION ENGINES*

The use of natural clinoptilolite zeolite to reduce hydrocarbon content can be recommended during the period of cold start firstly by means of dismissal of exhaust gases through a layer of chemically modified activated zeolite and after reaching the working temperature of the catalytic converter exhaust fumes must be redirected by temperature switch to the branch with the adsorption-catalytic equipment and conventional three-way catalyst. For this purpose we recommend to use a combination of heat-activated natural clinoptilolite for adsorption of hydrocarbons and nitric oxides with the cupric and cobaltous modification.

The purpose of this combination is the initial adsorption of hydrocarbons and nitric oxides followed by catalytic conversion after desorption from natural zeolite after heating above 300°C. After heating zeolite to 300°C, hydrocarbons sorbed during cold start are desorbed and subsequently passing the modified zeolite they can be converted catalytically into carbon dioxide and water. Similarly, after heating, nitric oxides are desorbed and subsequently passing the cobaltous modification of zeolite they are converted into nitrogen. Gases can be finally cleaned by a conventional three-way catalyst. The proposed scheme of adsorption-catalytic device is shown in Figure 18 [45,71].



**Figure 18: Proposed scheme of the sorption-catalytic device**

## 11 THE USE OF ZEOLITES IN WASTE WATER TREATMENT

Application possibilities of natural zeolites in water treatment and purification result from their specific physical and chemical properties such as selectivity of ion exchange, sorption properties as well as large active surface sorption and specific crystal structure. They can be used where they can replace the properties of synthetic cation exchangers but they cannot replace such properties as high purity and homogeneity of material. Clinoptilolite application as one of the industrially most used natural zeolite is based on research results on the removal of ammonium ions from water as well as radioactive and metallic elements.

In technologically advanced countries, problems with ammonia are solved by means of ion exchange using clinoptilolite. In Truckee, California, a fully automated deammonization stations that operate on the basis of using natural clinoptilolite zeolite, have been built. Waste water treatment plant with capacity of 26,000 m<sup>3</sup>/day consists of eleven steps including final technological water deammonization using zeolites. One column (filter) contains 40 tons of load and has a capacity of 270 m<sup>3</sup> · h<sup>-1</sup>. The average concentration of ammonia nitrogen at the filter output to the filter is 25 mg · l<sup>-1</sup> and at the output it is 2 mg · l<sup>-1</sup>. When sorption capacity of zeolite is depleted, it is regenerated with sodium chloride solution. Regenerative solutions with eluted ammonia stripped out with air and ammonia are washed with sulfuric acid in the absorption module. Obtained ammonium sulfate is used as raw material for fertilizers. Technology of ion exchange using clinoptilolite is compared with conventional biological nitrification-denitrification. Several advantages of ion exchange using clinoptilolite are as follows:

- it is not dependent on weather conditions;
- it requires less space;
- it transforms ammonia nitrogen into nitrogen undesirable residue;
- adsorbed ammonium ions can be re-used in agriculture as a fertilizer.

Although the capacity of natural zeolite is lower than that of synthetic cation exchangers, its selective features are significant. Moreover, natural zeolites are more affordable [9].

### **11.1 Copper cations removal using natural and synthetic sorbents**

Waste water containing heavy metals seriously pollutes the environment. Every day, different industries produce a large amount of waste water that is contaminated with non-ferrous metals, for example copper, cobalt and nickel. Various industrial operations such as mining and raw materials processing, rolling mills, metal finishing, using inorganic pesticides in agriculture are the sources of toxic metals in water. Heavy metals and their compounds pollute the environment with no hope of their breaking down naturally. Waste water treatment plants use mainly oxidation redox reactions, coagulation and sedimentation, sorption using activated carbon, ion exchange using ion exchangers to reduce the amount of heavy metals. One method of water treatment is the use of ion exchange. Ion exchangers are inorganic or organic polyelectrolytes practically insoluble in water and common solvents. In the process of water purification, synthetic organic ion exchangers having large capacity, a sufficient chemical and mechanical resistance, controllable adjusting of grain in production process are being used. The ability of introducing various functional groups into a fundamental structure enables the occurrence of ion exchangers to be selective for particular ions [55].

Among a large group of the so-called alternative processes, various natural rock-forming sorbents play an important role and are sufficiently effective as well as cost-efficient. They are useful as adsorbents and ion exchangers as well. Whereas the use of synthetic zeolites is quite expensive, we are looking for the possibility of using zeolites as natural sorbents and ion exchangers. Natural zeolites act as strongly polar sorbents [56]. The application possibilities of natural zeolites in waste water purification follow from their specific physico-chemical properties: Selective ion exchange and adsorption. When contacting zeolite with an aqueous solution there occurs a process called ion exchange sorption. Transition of ions from the solution to zeolite is determined by diffusion regularities while the total diffusion is divided into solution diffusion, liquid film at the interface and diffusion through zeolite [57]. Ion diffusion is influenced by geometry of the three-dimensional zeolite lattice. In the process of ion exchange, cations with an oxidation number one having smaller radius of hydrated ion and lower enthalpy, are more movable [57].

In this regard, attention is being paid to the use of natural zeolites. Their advantage is their high selectivity to some metal cations, relatively easy renewability and negligible price [1, 2]. Heavy metals do not frequently occur in nature in the form of elements. More often they are present as compounds which are capable of forming organometallic complexes which are very toxic. Heavy metal toxicity is related to solubility, through cell membranes, lipids,

proteins, and their ability of binding to protein which is associated with the accumulation in certain tissues. Copper, soluble salts of which are toxic, belongs to the group of toxic metals, maximum concentration of which is determined by the standards. Symptoms of acute poisoning such as gastric problems, lethargy, anemia and convulsions can occur [61].

**Table 24:**  
**Inorganic and organic forms of cooper in water [25]**

Inorganic form	Organic form
$\text{Cu}^{2+}$ , $[\text{CuCO}_3(\text{aq})]^0$ , $[\text{Cu}\{\text{CO}_3\}_2]^{2-}$ , $[\text{CuOH}]^+$ , $[\text{Cu}(\text{OH})_3]^-$	Organic complexes with amino acids, polypeptides and humic substances

Current European Union legislation states limit values for the content of copper and nickel cations in waste water. The limit values are given in Table 25.

**Table 25:**  
**Limit values of copper and nickel cations in drinking  
and waste water**

Cations	Concentration (waste water)	Concentration (drinking water)
$\text{Cu}^{+2}$	1 mg.dm <sup>-3</sup>	1 mg.dm <sup>-3</sup>
$\text{Ni}^{+2}$	1 mg.dm <sup>-3</sup>	0,02 mg.dm <sup>-3</sup>

We have experimentally compared copper cations sorption sorbents: Natural clinoptilolite zeolite and synthetic zeolites: Nalsite, potashite, calsite, y-site. During the experiments, fifty grams of each kind of zeolite have been used.

Table 26 shows physicochemical characteristics of the synthetic sorbents.

**Table 26: Physicochemical characteristics of synthetic zeolites [58]**

Characteristics	Potashite	Nalsite	Calsite	Y- site	Y – site/P
Type	3A	4A	5A	13Y	13Y
Effective pore diameter (10 <sup>-10</sup> )	3	4	5	9	9
Modul SiO <sub>2</sub> : Al <sub>2</sub> O <sub>3</sub>	1.9 – 2.1	1.9 - 2.1	1.9 -2.1	4.5 – 5.5	4.5 – 5.5
Prevailing cation (%)	K <sup>+</sup>	Na <sup>+</sup>	Ca <sup>2+</sup>	Na <sup>+</sup>	Na <sup>+</sup>
Equilibrium adsorption capacity for water at 25°C, (g/100g ads.),	17	19	18	23	23
Rate of exchange of prevailing cation (%)	50 – 70	90 - 100	70 -80	90 - 100	99 – 100

Rate of copper cations sorption and its effectiveness on the solid interfacial interface has been monitored. For this purpose, model samples with initial concentration of  $2.56 \text{ g.dm}^{-3}$  have been prepared. Changes in concentration of copper cations in the same time intervals were determined photometrically. Summary of changes in the concentration of copper cations using clinoptilolite, calsite and Y- site is given in Table 27 [71].

**Table 27:**  
**Copper cations concentration removal using sorbents**

Sorbent	Time (hours)	0	1	2	3	24	48	72
Clinoptilolite	Concentration	2,56	1,53	1,13	0,81	0,59	0,50	0,55
	[g.dm <sup>-3</sup> ]							
Calsite	Concentration	2,56	0,13	0,03	0,28	0,42		
	[g.dm <sup>-3</sup> ]							
Y-site	Concentration	2,56	0,34	0,27	0,18	0,56		
	[g.dm <sup>-3</sup> ]							

Based on changes in concentration of copper cations during accurate time intervals, kinetic curve of sorption at a constant temperature of  $23^{\circ}\text{C}$  was determined. Samples of sorbents were heat-treated at  $250^{\circ}\text{C}$ . Each of the sorbent samples was embedded by the same volume of sample model after cooling. Experiments to determine kinetics were carried out in volumetric flasks in which the suspension was stirred occasionally. In precise time intervals, samples of solution were collected. Amount of copper cations was determined by photometric method. Sorbed amount in given sorbents was determined from the differences of initial concentrations and concentrations determined at a given period of time.

Sorption kinetic changes of concentrations are listed in Table 28 [71].

**Table 28:**  
**Kinetics of sorption using sorbents**

Sorbent	Time [hour]	1	2	3	24	48
Clinoptilolite	Sorbed amount [g.dm <sup>-3</sup> ]	1.03	1.42	1.74	1.96	2.2
Calsite	Sorbed amount [g.dm <sup>-3</sup> ]	2.42	2.53	0		
Y - site	Sorbed amount [g.dm <sup>-3</sup> ]	2.22	2.29	2.39	0	

Measured results show that due to copper cations sorption, the fastest decrease of cations was observed on calsite where amount of cations was reduced to almost zero during the sec-

ond hour. The Y – site was in the second place. The slowest curve of sorption was observed in clinoptilolite and its sorption capacity was depleted during 48 hours. The following results were recorded after one hour of operation:

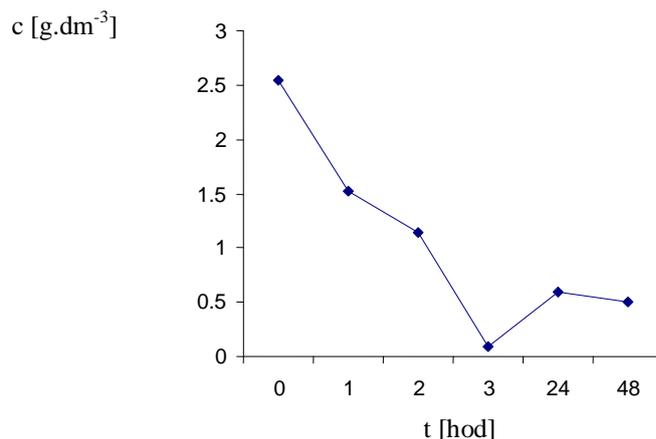
Calcite: 5% of the initial concentration.

Y-site: 13% of the initial concentration.

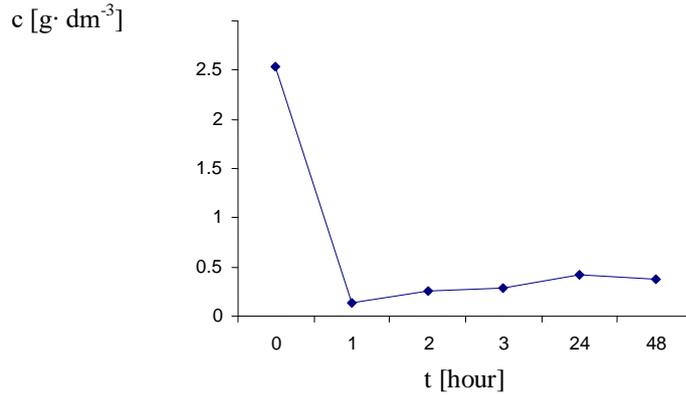
Clinoptilolite: 60% of initial concentration.

The highest efficiency was observed on calcite. Having applied calcite, decrease of copper cations to 5% of the original concentration occurred. Its total efficiency was 94% while absorption capacity was depleted during two hours. The total efficiency on the y-site was 92%. After one hour, concentration of copper cations was reduced to 13% of the initial concentration. After one hour, when using clinoptilolite, a decrease of copper cations accounted for 60% of the initial concentration and the total efficiency of the sorbent used 81%. Changes in concentrations of copper cations in the solution after their sorption on sorbents are shown graphically in Figures 19 – 21 [71].

During equilibrium, when comparing natural clinoptilolite with synthetic zeolites, a decrease of concentration of copper cation to approximately same value was observed with all the three sorbents. The sorption process was faster with synthetic zeolites. When comparing with the limit values using all the sorbents, a decrease of concentrations of copper cations under limit value was observed.



**Figure 19: Decrease of copper cations in the solution using clinoptilolite**



**Figure 20: Decrease of copper cations in the solution using calcite**

When sorbent is added to the solution of substance with the initial concentration of  $c_0$ , the concentration of the solute in the solution begins to decrease and the action time is asymptotically approaching to the equilibrium concentration of  $C_r$ . Equilibrium concentration value for aqueous solutions depends on the sorbent properties. Different values of equilibrium concentrations are obtained for different initial concentrations of the solute and various sorbent volumes. Kinetic course of copper cations sorption was monitored up to the equilibrium state of the system using model samples of aqueous copper cations solutions. Model samples contained copper cations with concentration of  $1,93 \text{ g}\cdot\text{dm}^{-3}$ ,  $2,56 \text{ g}\cdot\text{dm}^{-3}$ ,  $4,95 \text{ g}\cdot\text{dm}^{-3}$ ,  $6,72 \text{ g}\cdot\text{dm}^{-3}$ ,  $7,05 \text{ g}\cdot\text{dm}^{-3}$ . If we represent the experimentally obtained values  $C_r$ , in the graph, then the dependence  $a = f(c_r)$  expresses the desired adsorption isotherm. The measured and calculated data are shown in Table 29 [71].

**Table 29:  
Values of the equilibrium concentration and sorbed quantity**

$c_r \text{ [g}\cdot\text{dm}^{-3}]$	$a \text{ [mg}\cdot\text{g}^{-1}]$
0.2	4.1
0.3	6.2
0.66	12.8
0.76	17.9
0.82	18.9

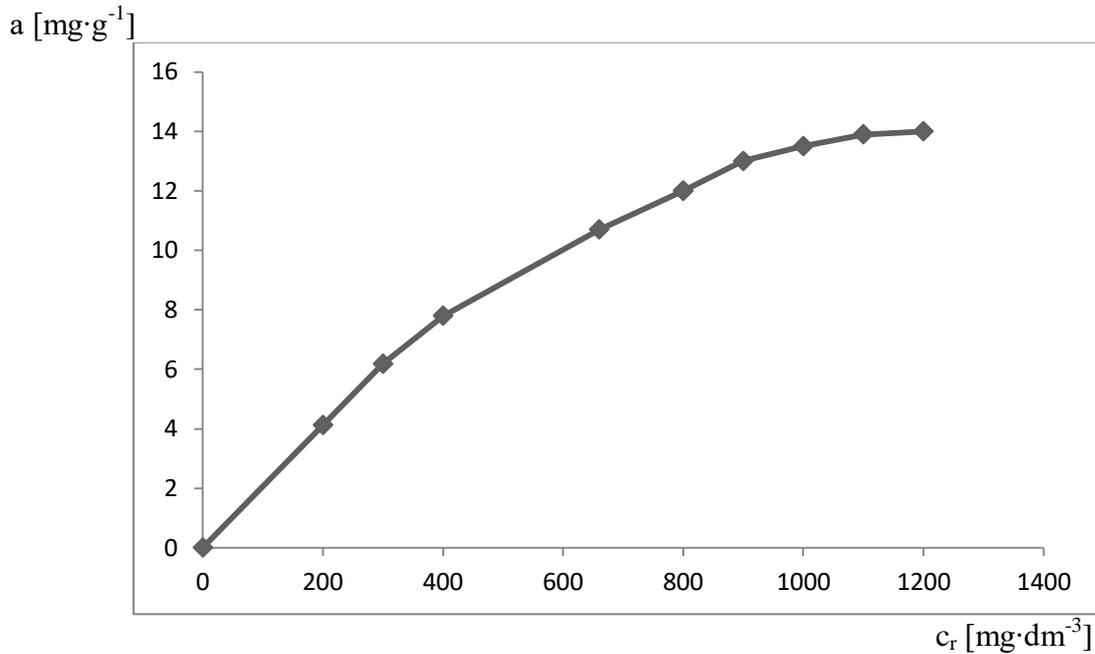


Figure 21: Sorption isotherm of copper cations sorption from the solutions

### 11.2 Removal of nickel cations from waste water using clinoptilolite zeolite

An important feature of zeolite minerals is their sorption and ion exchange ability. The aim of this work was to study the removal of nickel ions from solutions by sorption using zeolite. The experiments were aimed at removing nickel ions from model solutions. In order to conduct the experiments, we have used natural clinoptilolite zeolite from the deposit in Nižný Hrabovec in Slovakia. The method of static sorption has been used.

The process of sorption of chemical solution from the solid can be expressed as a result of the reversible reaction, sorption and desorption which reaches its final equilibrium between the concentrations of the substance in both phases. This process is well studied by determination of equilibrium concentration of ions using total sorbent as a function of the equilibrium concentration in solution at a stable temperature. To define the time needed to achieve a balance in the system, we have observed the dependence of adsorbed amount on contact time of adsorbent with adsorbate. Equilibrium concentration was determined at 22 °C.

Based on the initial and equilibrium concentrations, we have determined the amount of nickel cations adsorbed using sorbents. To perform calculations, the following equation has been used [62]:

$$a = \frac{c_0 - c_r}{m} \cdot V \quad (11.1)$$

where  $V$  is the volume of solution and  $m$  is the mass of adsorbent. Equilibrium concentration of nickel ions and ion concentration of the sorbents were used for calculation of the partition coefficients. Partition coefficient  $K_R$  [63] is a quantitative indicator of distribution of substances between the solid and liquid phase. It indicates the ratio between the concentration of the sorbent material  $C_s$  ( $\text{g} \cdot \text{g}^{-1}$ ), and the concentration of  $C_r$  in the solution ( $\text{g} \cdot \text{dm}^{-3}$ ) during equilibrium. It is a quantitative indicator of the distribution of substances between the solid and the liquid phase.

$$K_R = \frac{c_0 - c_r}{c_r} \cdot \frac{V}{m} \quad (11.2)$$

Clinoptilolite pore geometry allows free passage only for simple ions. As the hydrated metal cation is approximately the same as zeolite channel, its mobility in zeolite structure is not easy. From theoretical point of view, nickel ions are in the form of  $[\text{NiOH}]$  after ion exchange and hydration by water molecules. Exchanged  $\text{Na}^+$  and  $\text{NH}_4^+$  hydroxides of which are highly soluble in water are replaced by  $[\text{NiOH}]_2$ . Laboratory work was focused on the removal of nickel cations from the solution. Kinetic sorption of nickel cations using natural sorbent - clinoptilolite with grain size from 2,5 mm to 5 mm was observed. From the measured values, we have determined the partition coefficient and efficiency of sorbent.

The degree of purification of contaminated water was evaluated with parameter  $\eta$  sorption efficiency expressed as a percentage. Rate of sorption of nickel cations and their effectiveness was monitored at the interface of solid and solution.

For this purpose, the three model samples were prepared at the initial concentration of  $6,6 \text{ g} \cdot \text{dm}^{-3}$ ,  $2,1 \text{ g} \cdot \text{dm}^{-3}$ ,  $1,93 \text{ g} \cdot \text{dm}^{-3}$ . The change of concentration of nickel cations was determined photometrically. The influence of time of contact on the sorption of nickel cations was observed in time interval of 48 hours. To define the time required to reach equilibrium, dependency of adsorbed amount of contact time with the adsorbent adsorbate was studied.

For this experiment, 40 g of clinoptilolite zeolite which was embedded by nickel cations solution were used. Model samples with initial concentration of  $1,93 \text{ g dm}^{-3}$ ,  $2,091 \text{ g dm}^{-3}$  and  $6,6 \text{ g} \cdot \text{dm}^{-3}$  were used. Individual samples were taken in half-hour intervals until equilibrium for analytic determination of nickel cations. Based on the analytical determination, sorption curve was found in various sorbents. The determined values were used to calculate

sorbed amount, partition coefficients  $K_R$  (Table 28) and efficiency of sorbents. For all samples, the steady-state has occurred for three hours.

Sorption curve shows that size of initial concentration of nickel ions in the solution increases the amount of sorbent. The kinetics of reduction of nickel ions concentration was observed and efficiency of individual sorbents was calculated according to the following formula [63]:

$$E(\%) = \frac{C_1 - C_2}{C_1} \cdot 100 \quad (11.3)$$

The efficiency of clinoptilolite based on the amount of nickel ions ranged from 33,3% - 81,6% depends on initial concentration of nickel ions in solution.

**Table 28:**  
**Sorptional characteristics**

$C_0$ [g·dm <sup>-3</sup> ]	$C_r$ [g·dm <sup>-3</sup> ]	$K_R$
6.6	1.21	0.025
2.1	1.3	0.0028
1.93	0.93	0.001

As the cost of heavy metals removal from water using classic technologies is relatively high, we are looking for cheap but effective cleaning methods. Ion exchange and sorption are one of the possible ways. Frequently used active carbon is relatively cost expensive as compared to zeolite.

Natural zeolites are available natural materials. Experimental results indicate the potential use of clinoptilolite for reducing the content of copper cations in water. Currently, teams of researchers are working on preparing a new generation of environmental sorbents that prefer natural matrices including natural zeolites as carriers for functional groups to obtain usable sorbents for the purification of water because of occurrence of impurities in waters in the form of anions.

## 12 CONCLUSION

Following from literature review and the conducted experiments we suggest some possibilities of using zeolites in environmental protection. The aim of the experiments was to test the suitability of natural clinoptilolite zeolite from the deposit in Nižný Hrabovec for activation of reducing toxic exhaust components as well as to find a suitable modification for this purpose. It is obvious from the results of the measurements that ammonium and cobalt modification is the most suitable one to reduce the content of nitrogen oxides. While in the process of applying ammonium modification, increase sorption is achieved using cobalt modification, reduction of nitrogen oxides is achieved by catalytic effect of cobalt cations present in the structure of clinoptilolite. Zeolite enriched with heavy metal cations is not only capable of regeneration but it is also catalytically active. To increase the catalyst life, it is appropriate for zeolite to contain heat-resistant oxide except metal cations. This combined sorbent-catalyst equipment containing catalyst component should have sufficient durability and can have sufficient cleaning power even during cold start and steady state operation.

Based on these results we can conclude that natural clinoptilolite zeolite from the deposit in Nižný Hrabovec can reduce the content of polycyclic aromatic hydrocarbons and nitrogen oxides, which are substances that are found in exhausts of internal combustion engines. Based on the achieved results as well as affordability of natural zeolite it is possible to use it in automotive industry to reduce the content of hydrocarbons, which are part of the exhaust gases of internal combustion engines, in particular during the period of cold start, when the standard catalyst has no effect, and to reduce the content of nitrogen oxides by catalytic transformation. Zeolites can be also applied to clean air in workplaces where combustion engines are used in the working process. Natural zeolites are also used for water purification. Frequently used methods of metals removing from solutions such as precipitation processes are effective especially at higher concentrations. In such a way it is not always possible to achieve the limits set by law and therefore the use of zeolites appears to be a suitable method for purifying waste water after treatment, for example by precipitation. Natural zeolites are more cost-effective than synthetic ion exchangers. The efficiency of natural zeolites as sorbents and ion exchangers as well as its sorption capacity is influenced by modification. Currently, the world's annual production of natural zeolite is about 4 million tons. Due to its good availability and low cost of its extraction, natural zeolite is still profitable. Mining of

## *CONCLUSION*

natural zeolite has a great potential in the future. However, zeolites are insufficiently utilized for environmental protection.

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WITH A FOCUS ON THE AUTOMOTIVE INDUSTRY**

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## ***Authors:***

***Iveta Pandová***, RNDr., PhD.

Iveta Pandová obtained her university degree at the Faculty of Science of Pavol Jozef Šafárik University in Košice in 1989. PhD. degree was obtained at the Faculty of Mining, Ecology, Process Control and Geotechnology of the Technical University of Košice in 2005. She has 12 years of experience in company laboratories for manufacturing of medicine, infusion and inoculators. Since 1998, Iveta Pandová has been working as university teacher and researcher at the Faculty of Manufacturing Technologies of the Technical University of Košice with the seat in Prešov. She is the author (co-author) of the 7 monographs. 1 of the monographs was published in Springer. She is the author of the 5 university textbooks, 9 certificates, 11 patents and discoveries, several domestic and foreign original scientific papers in the scientific and professional journals, 7 original scientific papers in Current Contents Connect journals, in journals with ISI impact factors and publications included in the world renowned databases (Web of Science, Thomson Scientific Master Journal List (Web of Science – 13 publications, Scopus – 24 publications)) and in proceedings from domestic and foreign scientific conferences from the following areas: Research, development and manufacturing and verification of catalytic equipment based on zeolites, exploitation of zeolites, ecology, environment and ecotechnics and so on. Solver of several projects and grant projects.

***Anton Panda***, prof. Ing., PhD.

Professor Panda obtained his university degree at the Faculty of Mechanical Engineering of the Technical University of Košice in 1987. PhD. degree was obtained at the Faculty of Manufacturing Technologies of the Technical University of Košice in 2002. In 2008, he was appointed to the position of an associate professor in the study branch 5.2.51 Manufacturing Technologies at the Faculty of Manufacturing Technologies of the Technical University of Košice. In 2015, Professor Panda was appointed as a professor in the study branch 5.2.51 Manufacturing Technologies at the Faculty of Manufacturing Technologies of the Technical University of Košice.

Professor Panda has 29 years of experience in the engineering company supplying the products for automotive as well as agricultural industry (constructor of special machinery and equipment, systems analyst, head of the department for development and technical preparation of production, methodist of statistical methods, commercial and technical director, quality manager).

Nowadays, Professor Panda deals with expertise and design activities in the area of development, production and verification of rolling bearings. He works in the area of rolling bearings deposition for various domestic and foreign customers. Since 2008 (since 1994 external), Professor Panda has been working as a teacher and scientist at the Faculty of Manufacturing Technologies of the Technical University of Košice with the seat in Prešov. He is an expert coordinator (auditor) for quality management systems.

Professor Panda is the author (co-author) of 14 monographs (8 foreign, 6 domestic) – 2 monographs published in Springer. He is the author of 2 university textbooks (1 foreign, 1 domestic), 16 university lecture notes, 15 author's certificates, 16 patents and discoveries, 2 bearings catalogues, several domestic and foreign original scientific papers published in scientific and professional journals, 10 of them published in Current Contents Connect journals in Web of Science, in impacted journals and publications led in the world renowned databases (Web of Science, Thomson Scientific Master Journal List (Web of Science – 38 publications,

Scopus – 91 publications) and lot of his papers can be found in the proceedings from domestic and foreign scientific conferences in the following areas: automobile production, manufacturing technologies, experimental methods in manufacturing technologies, machining, development, manufacturing and verification of new products in accordance with the standards EN ISO 9001 and in accordance to the specific requirements of automobile manufacturers ISO/TS 16 949 (after IATF 16949), quality control, statistical methods and techniques of quality for the production of parts, capability of machine, capability of manufacturing processes, capability of gauges and measuring equipment, technical preparation of production, product audits, system audits of quality management system, analysis of potential errors and their effects on construction (FMEA-K) and on manufacturing process/technology (FMEA-V), statistical regulation of manufacturing processes SPC, process of approval of parts to the production PPAP, modern quality planning of product APQP, control plans and regulation, requirements the association of automobile manufacturers in Germany VDA 6.1, quality system requirements for suppliers of Ford, Chrysler, GM, specific requirements the using of EN ISO 9001:2015 in organizations ensuring the mass production in automotive industry IATF 16949:2016 (before ISO/TS 16949), method of Poka-Yoke, quality assurance before the mass production for suppliers of automobile manufacturers in Germany VDA 4.3, quality assurance of supplies for suppliers of automobile manufacturers in Germany VDA 2, product liability, method of Global 8D (8-step method for problem solving), etc.

Professor Panda has been the coordinator of several projects and grant projects for engineering companies at home and abroad, solver of research tasks. He is the author of directives, methodological guidelines, technical regulations and other technical documentation for domestic and foreign manufacturing companies. He has been the auditor of quality system management at Technical University in Košice for several years. He actively collaborates with the universities at home and abroad. He is recognized as an expert for the production of bearings in companies in Germany, Italy, China, Slovakia and Czech Republic.

In 2010, as the coordinator of research team and co-author of EFQM documentation, Professor Panda won the Award for Improvement of Performance at National Award of Slovak Republic competition for quality for the Technical University of Košice. In 2012, at the same competition he won the same award. As a result, Technical University of Košice obtained the highest score in this category. Since 2014 Professor Panda has been a member of Polish Academy of Sciences. Since 2014 he has been a member of ASME in the USA.