REVIEW

Some Possibilities of Catalytic and Noncatalytic Utilization of Zeolites

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Some possibilities of catalytic and noncatalytic utilization of zeolites are introduced. Zeolites are very important materials with very broad applications not only in refineries as catalysts, in sorption and separation processes, but also in agriculture, new building materials, and environmental engineering. Some significant directions of zeolites utilizations are presented but the importance of these interesting materials is much greater. This paper summarizes the knowledge on zeolites use in chemical and petrochemical industry, agriculture, building industry, and environmental engineering.

1. INTRODUCTION

Zeolites are crystalline aluminosilicates with composition represented by the empirical formula

$$M_x D_y [Al_{x+2y} Si_{n-(x+2y)} O_{2n}] m H_2O$$
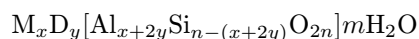
where x is the number of monovalent cations, y is the number of bivalent cations, n is cation valence, and m is the number of water molecules in the zeolite formula.

The history of zeolites was started by the discovery of the first zeolite mineral stilbit in 1756 by Cronsted. The huge progress in the knowledge of structure, synthesis, modification, characterization, and very broad usage of unique characteristics of zeolites and zeolite-like materials was reached in the period of about 250 years from the discovery of the first zeolitic material and especially in the period of the last 50—60 years. The development started from aluminosilicate zeolites to new zeolites and zeolite-like materials as aluminophosphates, metallosilicates, and metallophosphates and from microporous to mesoporous molecular sieves. Today, mainly synthetic zeolites are used widely in petroleum refining and chemical process industries as selective adsorbents, catalysts, and ion exchangers. But the importance of zeolites and zeolite-like materials is greater.

The present paper shows some possibilities of catalytic and noncatalytic utilization of zeolites.

2. BASIC CHARACTERISTICS OF ZEOLITES

Three-dimensional framework of zeolites consists of AlO_4 and SiO_4 tetrahedra linked to each other by the sharing of oxygen ions.
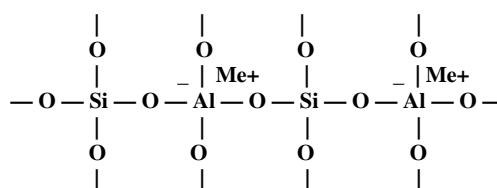
Each AlO_4 tetrahedron in the framework bears a negative charge which is balanced by an extra frame-

work cation. The cations can be ion-exchanged with the next usage of such modified zeolites in catalysis (H-forms and Me-forms of zeolites), in detergents (replacement of polyphosphates) and in the next very different areas of utilization (agriculture, waste-water purification, special building materials).

Different connection of SiO_4 and AlO_4 tetrahedra leads to the formation of three-dimensional framework with pores and voids of molecular dimension. Dimensions, shape, and linkage of zeolite pores and voids are characteristic of zeolite materials. The pores and interconnected voids are occupied with cations and water molecules. Cations can be changed by ion exchange and water can be removed reversibly by application of heat.

The basic types of zeolite structures consist of internal pore system with interconnected cage-like voids or system of uniform one-, two- or three-dimensional channels.

By pore size or diameter of pores zeolites include [1]:

– small-pore zeolites (eight-ring pores) with free diameter of pores 0.3—0.45 nm (*e.g.* zeolite A),

– medium-pore zeolites (ten-ring pores) with free pore diameter 0.45—0.6 nm (*e.g.* zeolite ZSM-5),

– large-pore zeolites (twelve-ring pores) with free pore diameter 0.6—0.8 nm (*e.g.* Y, Beta and Mordenite zeolites),

– extra-large-pore zeolites (fourteen-ring pores) with free pore diameter 0.8—1.0 nm (*e.g.* UTD-1).

Mesoporous materials have pores with diameter of some nanometers.

Structure commission of IZA registered in 2000 approximately 130 molecular sieve structures but only about 15 of them have commercial interest till now:

– from natural zeolites mordenite, chabazite, erionite, and clinoptilolite,

– from synthetic zeolites A, X, Y, mordenite, L, ZSM-5, Beta, ferrierite, MCM-22, SAPO-34, SAPO-11.

3. CATALYTIC UTILIZATION OF ZEOLITES

From the catalytic viewpoint the following factors can be utilized in catalysis:

– acidity of zeolites (for some reactions also basicity),

– redox properties (zeolites contain suitable metals),

– multifunctional character of specially prepared modified forms of zeolites,

– shape selectivity of zeolites.

Very broad areas of catalytic utilization of zeolites are acid-catalyzed reactions in petroleum refining processes, petrochemistry, and organic technology. Proton-donor Brönsted acid sites are generated by isomorphous substitution of tetravalent silicon by trivalent cations and mainly by aluminium. Lewis electron-

acceptor sites are formed by thermal treatment of silicon-rich H-forms of zeolites, *e.g.* ZSM-5 by dehydroxylation of Si—OH—M groups (M is trivalent cation) [2]. The largest utilization of acidic properties of zeolites is in petroleum refining processes and petrochemistry.

The acidity together with shape selectivity of zeolites can be prospective in many applications in the processes of fine chemicals and intermediates synthesis. Zeolites can perspectively replace unsuitable acid catalysts, *e.g.* $AlCl_3$, H_2SO_4, which leads to environmentally problematic waste, corrosion and to many other technical problems. Zeolite catalysts can be separated from the reaction mixture and regenerated.

From the viewpoint of shape selectivity and suppression of undesired secondary reactions is required suitable pore structure, high concentration of acid sites in the pores of zeolites, and the lowest concentration of acid sites on the outer surface. The outer surface of zeolites can be deactivated by different methods, *e.g.* by silanation, or impregnation with some metals.

Redox properties of zeolites which contain transition metals are very important. These active zeolitic forms can be prepared by direct synthesis or ion exchange, or by impregnation of zeolites with solution of suitable form of metal (*e.g.* Pd, Pt). Redox properties of zeolites can be used independently or together with acidic properties, *e.g.* H-forms of zeolites (isomerization activity), metal forms (hydrogenation activity) and moreover, shape selectivity of zeolites can be utilized.

Shape selectivity is a very important property of zeolites. It is connected with dimensions and shape of microporous system and with dimensions and shape of reactants, transition state, and products. There is known: *reactant selectivity, transition state selectivity, product selectivity*, and recently has been proposed *structure-directed transition state selectivity* [2].

Shape selectivity is used for obtaining organic intermediates which cannot be prepared selectively with classical catalysts. The utilization of the latter leads to equilibrium mixture of isomers.

3.1. Zeolites in Petroleum Refining

The first catalytic utilization of zeolites in petroleum refining industry is dated 40 years ago (zeolite X as cracking catalyst was introduced by MOBIL Company). This zeolite was replaced later by zeolite Y, which was utilized also as isomerization catalyst. Y zeolite has the most important utilization till now (95 % of the world market of zeolites in catalysis) mainly in refining processes (fluid catalytic cracking, hydrocracking).

In the 70's of the last century were started some processes of aromatic hydrocarbon transformations over natural and later over synthetic mordenites (dis-

proportionation and transalkylation of alkylaromatics and mainly transformation of toluene and isomerization of C_8 aromatics). MOBIL Company introduced new and very important synthetic zeolites (ZSM-5 and Beta) at the end of the 60's. These zeolites reached very broad utilization in refining and petrochemical processes. ZSM-5 has unique structure and dimensions of pores suitable for aromatic hydrocarbons transformations and this zeolite reached the great industrial importance. Zeolite Beta becomes very important synthetic zeolite also with the utilization in alkylation of aromatic hydrocarbons. From the other zeolites which play roles at different transformations of hydrocarbons are important: L, ferrierite, MCM-22, and molecular sieves SAPO-11 and SAPO-34 [3].

Zeolites are used in refining industry in these main processes:

– Catalytic cracking
– Fluid Catalytic Cracking (FCC)   Y, ZSM-5
– Deep Catalytic Cracking (DCC)   ZSM-5
– Shape-selective cracking   ZSM-5
– Hydrocracking   Y, ZSM-5
– Catalytic dewaxing   ZSM-5
– Isomerization of C_4 olefins   Ferrierite
– Hydroisomerization of low   Pt/Mordenite
  paraffins
– Isomerization of xylenes   ZSM-5, Mordenite
– Aromatization of C_3/C_4 ZSM-5
– Methanol to Gasoline process   ZSM-5
  (MTG)
– Methanol to Olefin process   ZSM-5
  (MTO)

3.2. Zeolites as Catalysts in Organic Technology and Petrochemistry

There is a broad potential of utilization of catalytic properties of zeolites in many processes of organic technology. A unique pore system of zeolites can be used and a very broad range of acidity (also basicity), hydrophilicity or hydrophobicity, modification with metals, shape selectivity, and other properties. There is tendency to replace environmentally unacceptable catalysts and procedures in industrial organic synthesis and especially at the production of fine chemicals intermediates. But zeolites as environmentally accepted catalysts are only one group of heterogeneous catalysts and their application must be aimed at the utilization of their shape selectivity. It is not effective to use them in each case and particularly at the possibility to use cheaper catalysts.

Some potential advantages of zeolite catalysts in organic reactions:

– the utilization of shape selectivity and preparation of such isomers, which are not possible to synthesize with classical catalysts (*e.g.* with $AlCl_3$),

– the simultaneous utilization of shape selectivity

and the other properties of zeolites as acidity and redox properties,

– many zeolites can be used at the higher reaction temperature due to their thermal stability, *e.g.* in some refining and petrochemical processes. Zeolite catalysts can be reactivated by controlled oxidation of coke.

Some limitations of zeolites utilization as catalysts in organic synthesis:

– the most of zeolites have diameters of pores in the interval 0.3—0.8 nm and it is not possible to use them for bulkier organic molecules (some intermediates of fine chemicals). As a solution for some cases could be the utilization of mesoporous materials with pore diameters of nanometer size,

– some very reactive functional groups of organic compounds can very quickly deactivate zeolite catalysts by coking but they can be reactivated,

– as some limitation factor can be considered the higher price of zeolites but due to relatively very high price of produced special organic chemicals it is usually not decisive.

In comparison with the utilization of zeolites in refining processes, their use in the synthesis of organic intermediates and fine chemicals is in a relatively early state of development. But in the last years the catalytic usage of zeolites in organic chemistry and technology is searched for many organic reactions.

Some examples of catalytic utilization of zeolites in realized and developed organic processes are shown in the next paragraph.

3.2.1. Electrophilic Substitution of Arenes

Aromatic Alkylation

Alkylations of aromatic hydrocarbons are utilized for production of valuable organic intermediates (mono- and dialkylated aromatic hydrocarbons) [2, 4—6]. The most important are ethylbenzene and isopropylbenzene which are produced in large amounts. The zeolite-based processes are dominating for production of these organic intermediates now. Shape-selective zeolite catalysts are used for production of another alkylaromatics as 1,4-diisopropylbenzene, 3- and 4-isopropyltoluenes (*meta*- and *para*-cymenes), 4-ethyltoluene, C_{10-14} linear alkylbenzenes and *para*-dialkylnaphthalenes and biphenyls. Some of alkylation processes are catalyzed up-to-now by mineral acids, *e.g.* HF or with Lewis acids as $AlCl_3$. These catalysts are toxic, corrosive and lead to waste waters. Moreover, by utilization of these classical catalysts it is not possible to prepare linear *para*-dialkylaromatics because equilibrium mixtures of isomers can be reached only. Required linear alkyl- and dialkylaromatics are possible to obtain only on shape-selective zeolite catalysts.

Ethylbenzene

The conventional catalysts for production of ethyl-

benzene are $AlCl_3$ and BF_3/alumina. Applying of ZSM-5 zeolite (Mobil-Badger Company) as alkylation catalyst in this process was breakthrough in ethylbenzene manufacturing. Excellent selectivity of 99 % at benzene conversion of 20 % can be reached [6]. Zeolites with comparable very high selectivity are Y, Beta, and MCM-22.

Isopropylbenzene (Cumene)

The classical catalyst for the production of cumene is solid phosphoric acid (SPA). The new processes use zeolite catalysts based on Y, Beta, and MCM-22 zeolites with obtaining very high selectivity (98—99 %) [2, 6].

4-Ethyltoluene

This compound is a precursor of *para*-methylstyrene (comonomer). 4-Ethyltoluene is produced by alkylation of toluene with ethylene over Mg, B, Mn, P – modified H-ZSM-5 zeolite with selectivity up to 98 % [2].

Isopropyltoluenes (Cymenes)

3- and 4-isopropyltoluenes (*meta-* and *para*-cymenes) are produced by isopropylation of toluene [2, 4]. These isopropyltoluenes are intermediates for production of *meta-* and *para*-cresol. *Meta*-cymene is more stable than *para*-isomer and it is possible to reach this isomer by isomerization of cymenes mixture. The basic catalytic system for isopropylation of toluene is $AlCl_3$—HCl, or phosphoric acid on support. The most prospective catalyst for this reaction is Beta zeolite.

Linear Alkylbenzenes

Alkylbenzenes with longer linear alkyls (C_{10-14}) are important precursors for anionic surfactants. The conventional catalysts for alkylation of benzene with olefins are HF and fluorided silica—alumina. The zeolite catalysts can be used for this reaction. The best results were reached over Y and Beta zeolites [4].

2,6-Dialkylated Naphthalenes and 4,4′-Dialkylated Biphenyls

Linear dialkylnaphthalenes and biphenyls are precursors for preparation of polyesters of dicarboxylic acids with utilization for preparation of special polymer materials. These *para*-dialkyl bicyclic aromatics can be prepared with high *para*-selectivity (near 70 % for 2,6-dialkylnaphthalene and 85 % for 4,4′-dialkylbiphenyls) by alkylation of naphthalene or biphenyl with lower olefins or alcohols over shape-selective zeolite catalysts. The best results were obtained by utilization of dealuminated mordenites [7—9].

Acylation of Aromatic Hydrocarbons

The present acylation processes are based mostly on metal chloride catalysts ($AlCl_3$, $FeCl_3$, $TiCl_4$). It is known that these catalysts lead to environmental, corrosion, and next technical problems. Zeolite catalysts are more suitable and acylation can be carried out with anhydrides of acids without previous problems. Acylation of aromatic hydrocarbons can be carried out over Beta zeolites at the mild reaction conditions with high selectivity to desired products [6, 10, 11]. Some acylated aromatics are intermediates for pharmaceuticals and fragrances.

3.2.2. Isomerizations and Rearrangements

Zeolites are used as catalysts of many different isomerization reactions as a replacement of non-regenerated catalysts [6, 12—15]. Isomerization of dialkylaromatics (xylenes) is a very important industrial process. Isomerization of butenes is extensively investigated. Isobutylene is very desirable olefin for preparation of antioxidants and octane boosters (MTBE, ETBE). This olefin can be obtained by skeletal isomerization of butenes over zeolite catalysts (ferrierite is attractive catalyst for this application).

The Beckmann rearrangement is the very important industrial process to produce ε-caprolactam which is intermediate for polyamide. The usage of oleum (fuming sulfuric acid) for Beckmann rearrangement is classical procedure with many technical and environmental problems. In order to eliminate problems with fuming sulfuric acid the more suitable catalysts have been studied from the beginning of the 60's. Many zeolite catalysts for this process have been developed from this time. As the most suitable zeolites are B-MFI (BASF Company) with selectivity to ε-caprolactam 95 % at conversion 94 % and silicalite (SUMITOMO Company) with nearly equal results [14, 15].

3.2.3. Nucleophilic Substitution and Addition

There are known many nucleophilic substitution reactions catalyzed by zeolites (*e.g.* amination, hydration, esterification, etherification) with industrial importance.

Methyl- and Dimethylamines

Lower aliphatic amines have utilization as organic intermediates (for agrochemicals, additives to rubber, pharmaceuticals).

The mixture of methyl- and dimethylamines can be produced by reaction of methanol with ammonia over special modified mordenites with poisoning of the outer surface (the formation of trimethylamine is decreased) [6, 16].

tert-Butylamine

BASF developed a new process of direct amination of isobutylene over MFI-type zeolite with selectivity

99 %. *tert*-Butylamine is an important intermediate product for fine chemicals [14].

3.2.4. Selective Oxidation Reactions

Oxidations Catalyzed by Transition Metals Ion-Exchanged and Modified Zeolites

As an example can serve the Wacker process of ethylene oxidation to acetaldehyde with selectivity 90 % on CuPdY zeolite catalyst. It is possible to work in the gas-phase and there is not necessary pretentious separation of catalyst [17].

Direct oxidation of benzene to phenol by N_2O over ZSM-5 zeolite with the higher amount of extra framework aluminium (higher share of Lewis acid sites) can be a very prospective procedure of phenol manufacture. Selectivity to phenol is 99 % at conversion of benzene near 30 % [14].

Selective Oxidation Reactions Catalyzed by Zeolites with Transition Metals Built in the Framework

The typical zeolite is TS-1 (titanium silicalite-1) with MFI structure. This zeolite has broad usage in the oxidation reactions with the aqueous solutions of hydrogen peroxide (there is used also its shape selectivity) at the low temperatures.

The selectivity higher than 85 % can be reached at alkenes epoxidation with TS-1. The oxime of cyclohexanone is produced by ammoxidation of cyclohexanone over TS-1 with selectivity up to 95 % [18].

4. NONCATALYTIC UTILIZATION OF ZEOLITES

Natural zeolites in the amounts of 290 000 t/y are used all over the world in ion-exchange reactions and adsorption processes. The main share from produced synthetic zeolites (near 1.3 Mt/y) belongs to zeolite A. This zeolite has utilization in detergents (NaA) for softening of water (as a compensation of polyphosphates). Approximately 100 000 t/y of synthetic zeolites is used in adsorption processes (drying of gases, liquids) and in separation processes. The main zeolites with utilization in adsorption processes are zeolites A and X [1, 3, 6, 19].

4.1. Adsorption and Separation Processes

The unique pore structure of zeolites and large inner volume are the most important factors for many very different applications of them in catalysis and adsorption processes. The strictly defined and constant dimensions of pores have utilization in selective separation of molecules with different dimensions and shapes [1, 6].

In 1959 the Union Carbide Company introduced the process ISOSIV (CaA zeolite) for separation of linear and branched alkanes. It was the first big industrial process with the usage of "molecular-sieving effect" of zeolites.

Parex process uses the molecular-sieving effect for separation of *p*-xylene from the mixture of C_8 aromatics.

Tuning of effective diameters of pores can be reached by ion exchange of basic zeolites by different cations. It can be used in separation processes, *e.g.* at A and X zeolites for separation of gases, hydrocarbons and for drying of gases and liquids.

Hydrophobic character of zeolites with high content of silica (*e.g.* silicalite) can be used for selective separation of organic molecules from aqueous solutions. Zeolites with hydrophilic character with low content of silica (*e.g.* NaA and KA) are usable for drying of gases and liquids.

The chemical equilibrium of different organic reactions, *e.g.* esterification, transesterification, can be moved by sorption of small molecules (water, methanol) as reaction by-products on zeolites.

Sorption properties of zeolites are utilized in industrial processes, agriculture, and environmental engineering.

4.2. The Utilization of Zeolites in Detergents

Zeolite type LTA (NaA) is used in modern detergents to replace sodium tripolyphosphate with the aim to soften water. The higher concentration of polyphosphates in waters (rivers and lakes) leads to eutrophization of water.

The world consumption of zeolites to detergents is approximately 800 000 t/y of zeolite type A. This zeolite is more effective for exchange of calcium than magnesium. It can be combined with zeolite X which is better for removing of magnesium. Recent studies showed that P zeolite is more effective to detergents than zeolite A [19].

4.3. Cleaning of Waste Water

Zeolites and other materials with ion-exchange properties are used for removing of radioactive elements in the waters soiled by radioactive waste and mainly by ^{90}Sr and ^{137}Cs. Natural zeolites clinoptilolite and chabazite are used for this purpose. Synthetic zeolites A and X are effective for removing of ^{90}Sr and mordenite for ^{137}Cs. Zeolites were used for removing of radioactive nuclides from technological waters of crashed nuclear power stations. Zeolites can be used for concentration of radionuclides and their safe storage afterwards, *e.g.* in concrete blocks.

Zeolites can be used for removing of ammonia from waste waters. Very effective and selective for removing of NH_4^+ cations from waste water is clinoptilolite [19].

A new treatment process aimed at water and metal reuse was developed for the selective separation of

heavy metals (copper, nickel, and zinc) from waste water to reduce costs and mitigate the environmental impact of waste-water pollutants. Synthetic zeolite P was used as a bonding agent for heavy metals separation [20].

4.4. Agriculture

Ion-exchange and sorption properties of natural zeolites are utilized in agriculture, too. Zeolites improve physical and chemical properties of soils. It is typical for dry soils because zeolites improve water regime (storage and better usage of water).

Zeolites in the soils change sodium and potassium cations for NH_4^+ (at simultaneous fertilization with natural and artificial fertilizers). After the 2nd and 3rd year of zeolite action in the soil, zeolite is effective nitrogenous fertilizer. It was shown that very effective is combination of zeolite and natural fertilizer for improving of crop [21].

The application of zeolites to the soil contaminated with heavy metals or radionuclides can be effective to lower their input by vegetables [22].

Natural zeolites can be added as dietary additives to the food for animals and can be used in treating of animals [23, 24].

Clinoptilolite is very effective sorption material in digestive tract of sheep after intoxication by organophosphates (pesticides in agriculture) [25].

Natural zeolites are usable in partial liquidation of fast and liquid wastes from animal production in agriculture and can be utilized for removing of smell in stables [26, 27].

4.5. Utilization of Zeolites in Building Materials

Large utilization of natural zeolites in building materials has been started at the end of the 8th decade of the 20th century. The reason of this fact was the growing knowledge on their sorption and ion-exchange properties having in mind well-known pozzolanic character of zeolite material. As the result of blending ordinary Portland cement with certain amounts of zeolite, the binary composite cements were prepared. The main feature of such cements is the increased chemical resistance to environmental aggressiveness compared to that of commonly used ordinary Portland cement.

Pozzolanic zeolite actively enters the hydration of cement increasing the strength and chemical resistance of the blend. This is taking place due to changes in the microstructure of the formed hydrate phase, and consequently in the pore structure. The hydrated cement—zeolite blend is characterized by the decreased content of $Ca(OH)_2$ capable of reacting with aggressive solutions and decreased volume of hydration products of C_3A in comparison with those occurring in hydrated Portland cement. The reasons

for increased chemical resistance are: *1.* binding of CaO into chemically resistant and poorly leachable on Ca^{2+} ions CSH (calcium silicate hydrate) and CAH (calcium aluminate hydrate) gel, *2.* intensification of surface absorption of chemically unbound $Ca(OH)_2$, and *3.* the pronounced restriction of Ca^{2+} ion mobility in the hydrated cement matrix. The reduced C_3A content in cement—zeolite blend due to the substitution of certain content of cement by zeolite (15 to 50 mass %) eliminates formation of the voluminous reaction products due to less volume of C_3A capable of reacting with aggressive media such as chloride or sulfates. Both the mentioned effects markedly improve chemical resistance of Portland cement—zeolite blends in comparison with the resistance of commonly used ordinary Portland cement.

The above knowledge was firstly utilized when developing cement—bentonite suspensions modified by zeolite addition. Bentonite was partially or fully replaced by zeolite in the cement suspensions finding their application at the construction of slurry cut-off walls. These suspensions using natural zeolite from Nižný Hrabovec (Slovakia) are known under commercial trade name ZEOFIX®. The unique composition of the ZEOFIX® suspensions enables their application in highly aggressive environment where commonly used cement—bentonite suspensions fall down. ZEOFIX® is characterized by permanently low permeability kept on the level of 10^{-10} m s^{-1} in 5 % Na_2SO_4 solution, CO_2-saturated water ($\rho(CO_2) = 140$ mg dm^{-3}) of the solution and acid water with pH $\geq$ 4. The first application was done by the Zakládaní staveb a.s. Prague Company at the construction of slurry cut-off wall in 1992. From 1992 to date ZEOFIX® has become the important cement-based material used for an effective and reliable protection of life environment. Besides evident technical contributions, the application of ZEOFIX® made it possible: *1.* to reduce the width of sealing element from the suspension by 25 % compared to classical cement-clay barrier, *2.* to avoid using secondary protection by inserting geomembranes into fresh mixtures decreasing thus the costs necessary for the construction of slurry cut-off wall, and *3.* to reduce a volume of exploited soil necessary for liquidation [28, 29].

The next step done in this field was the research and development of Portland—zeolite cements which are industrially made in the ZEOCEM a.s. Bystré Company [30, 31]. The research at the Slovak Academy of Sciences was aimed at the verification of the resistance of these cements to sulfate and acid attack [32, 33] with the following final results: Portland—zeolite cement with the fraction of cement to zeolite 85 to 15 mass % can replace a sulfate-resistant Portland cement at any application in the sulfate solution up to the concentration of 5 % Na_2SO_4 per 1 dm^3. Portland—zeolite cement with 35 mass % of zeolite in the blend has extremely increased sul-

fate resistance and evidently increased resistance to 0.5 % HCl solution when compared to ordinary Portland cement. The acid resistance is further improved by a substitution of siliceous sand by zeolite material, either sand or crushed fine gravel. Mechanical properties of Portland cement—zeolite blends are comparable with those of ordinary Portland cement.

This finding enables to use special composite cements with the increased resistance to chemical attack. Verification of the resistance of Portland—zeolite cement to Mg^{2+} and NH_4^+ ion-rich solutions continues in the present days.

Having in mind all this knowledge the ZEOCEM a.s. Bystré cement plant established the production of two cement blends in 2001: Portland pozzolan cement CEM II/B – P 32.5 R (in average with 30 mass % of zeolite) and pozzolan cement CEM IV/B 32.5 N (in average with 45 mass % of zeolite). Both cements are suitable for the manufacture of concrete with increased resistance to the sulfate, carbon dioxide, and acid waters; slurry cut-off walls exposed to aggressive environment, grouting mixtures and fill-in mortars for micropiles contacted with aggressive media.

Natural zeolite was also applied in the mineral filler ZEOBENT of geosynthetic clay liner (GCL) TATRABENT which is industrially made since 1997 by the TATRABENT Ltd. Kežmarok Company. The investigation of ZEOBENT filler consisting of a bentonite—zeolite mixture proved that zeolite markedly increases the sorption efficiency on heavy metals and oil products [34], and entrapping deleterious gases released from burning dump pile of the black-coal mine [35]. Next characteristics of the mentioned dump pile were increased radiation and metal content (Fe, Cu, Pb, Zn, Mo, As, Ti, Se, and Ge). The sealing efficiency of ZEOBENT filler was so high that surroundings of the dump pile were completely protected against underwater and air pollution. It is noteworthy to report that permeability to water ($k = 3.0 \times 10^{-11}$ m s^{-1}) is comparable with those of competitive GCLs from abroad. Bentonite—zeolite filler enhances special utility properties (sorption of heavy metals, oil products, gases, *etc.*) over application levels of competitive products having only bentonite filler.

CONCLUSION

Zeolites are important materials with very broad catalytic and noncatalytic applications in:

1. refineries, chemical and petrochemical industry as important catalysts,

2. sorption and separation processes and in detergents and cleaning of waste waters,

3. improving physical and chemical properties of soils and used as dietary additive to the feedstuff and sorption material in agriculture,

4. increasing chemical resistance of cement-based composites and sorption efficiency of the mineral filler

in geosynthetic clay liner in building industry and environmental engineering, respectively.

The utilization of zeolites as microporous materials is based on their unique pore structure consisting of pores with molecular dimensions. Today, mainly synthetic zeolites are used widely in petroleum refining and chemical processes as selective adsorbents, catalysts, and ion exchangers and natural zeolites are utilized mainly in many noncatalytic applications. In this paper are presented only some important directions of zeolites utilizations but the possibilities, the use of these interesting materials are much broader.

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