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NATURAL ZEOLITES AS ION EXCHANGERS IN ENVIRONMENTAL PROTECTION

This paper presents a short review of zeolite history. The explanation of crystal structures of zeolites, their primary, secondary and tertiary building units are illustrated as well. Description of topology, chemistry and of ion-exchange properties is focused predominantly on clinoptilolite species. Chapters 4, 5 and 6 deal with the principles of adsorption and ion-exchange processes involving zeolites. Finally, case studies of ammonium removal from drinking water with increased ammonium concentration by means of laboratory model are presented. The laboratory results are succeeded in field installation of the loading capacity of 900 dm³/h for tannery wastewaters at Waste Water Reclamation Facility in Moravia (former Czechoslovakia).

1. HISTORICAL REVIEW

Since 1756 when the Swedish mineralogist Cronstedt first recognized a new mineral species in the copper mine Svappari and called it *zeolite* more than 200 years have passed. Actually, this newly discovered mineral found in the vugs and cavities of basalt rocks was stilbite.

The word *zeolite* has Greek roots and means *boiling stones* (*zein* = to boil and *lithos* = stone) derived from a visible loss of water observed when the natural zeolite was heated in the „mineralogist's” blowpipe.

It is believed that zeolitic tuffs were used by Romans and Indians as early as about 2000 B.C. for constructing houses, roads, sewage channels, aqueducts, temples and pyramids. According to one of the life theory hypotheses zeolites may catalyse the reactions of ammonia with carbon oxides giving aminoacids and thus generating initial protein precursors for development of first living organism on Earth.

Indeed volcanic tuffs from Pozzuoli region (*tuffo Napolitano*) have been known as easily sculptured and shaped and except for an ancient Rome society they have been used worldwide for constructing many front parts of government buildings also in modern times.

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The early qualitative observations of natural zeolites were extended in the 1940's by the pioneering work of Barrer and his school in England as well as by Union Carbide Corporation laboratories in the United States. The studies of zeolites have been systematically conducted in order to promote their use as industrial minerals.

Characteristic properties of natural zeolites as molecular sieves that adsorb small-size gaseous molecules and reject larger ones were recognized in the 1930's for natural chabazite species. Based upon Barrer's earlier synthesis experiments, Milton of the Linde Division of Union Carbide Corporation in Tonawanda, New York, undertook an experimental program aimed at making chabazite suitable for air-separation applications. Although his early attempts to produce chabazite failed, he did prepare an entirely new zeolite structure not found in nature, but of better adsorption properties compared to chabazite. This was Linde's Type A zeolite, today one of the mainstays of the worldwide molecular sieve business.

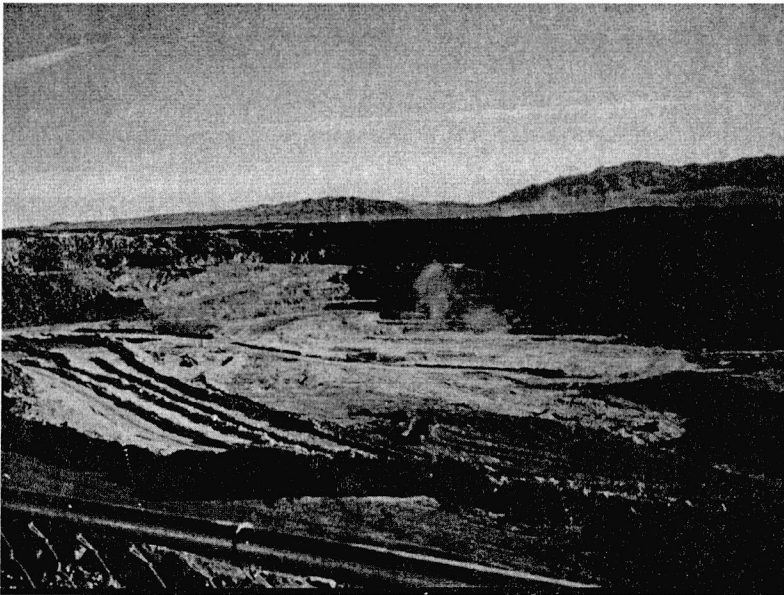
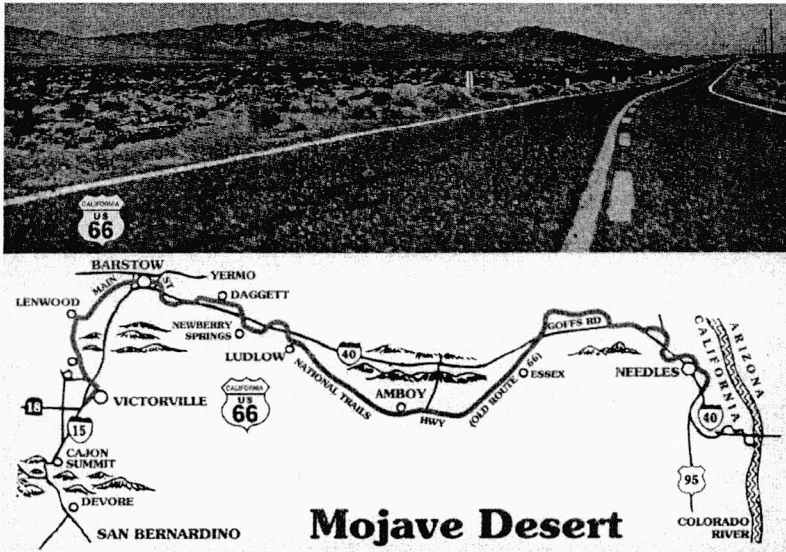
Development of environmental applications of natural zeolites was preceded by development of the permutites, i.e. synthetic amorphous aluminosilicate produced by the above company, especially for water softening. However, the permutites are soluble at extreme values of pH, which is their serious disadvantage.

Although the process of ion exchange was discovered in 1850, it was not applied as an industrial separation process until 1905, when Gans demonstrated it could be a unit process for both water softening and removal of iron and manganese ions (SHERMAN [1]). Extensive development of new organic ion exchangers, e.g. sulfonated and aminated copolymers of styrene and divinylbenzene, after the Second World War, with superior stability and ease of regeneration enabled a rapid expansion of industrial applications of the ion-exchange processes.

A greater stability of some natural zeolites vs. organic resin ion exchangers under certain conditions and their high selectivity towards particular ions have combined to allow the development of new environmental applications of zeolites. This has not generally involved the displacement of other exchangers by zeolites in existing applications, but rather the development of entirely new processes for which the existing ion exchangers were not well suited. In the 1950's, Union Carbide Corporation and some oil companies, especially Shell Development Company in the USA, Canada and Mexico, began to use the natural zeolites (erionite, chabazite and mordenite) as cheap supplements of molecular sieves for purification and desiccation of gases.

New diagnostic methods, mostly X-ray powder diffraction, contributed to discovering dozens of bedded rocks of volcanic origin that appeared to consist of unuseful clay or low-grade bentonites actually containing near-monomineral assemblages of micrometer-size zeolite crystals. The largest known deposit of clinoptilolite in the United States was found in the Mojave Desert near Hector, California, within a deposit of bentonite called Hectorite because of its proximity to Hector. Similar to Hector clinoptilolite quality, with almost monoionic varieties and over 90%-zeolite

mineral contents, the other high-grade clinoptilolite ores were opened out in Castle Creek (Idaho), Buckhorn (New Mexico) and Fish Creek Mountains (Nevada). Clinoptilolite has been reported in 66 locations of the country, whereas the U.S. deposits were predominantly in the sodium form.



Photographs of the Hector deposit in California (the USA)

Nowadays over 1000 occurrences of zeolite minerals have been reported predominantly from sedimentary rocks of volcanic origin in more than 40 countries of the world, e.g. the USA, Mexico, Cuba, Chile, Argentina, South Korea, Japan, China, New Zealand, South Africa, Tanzania, Kenya, Iran, Israel, Bulgaria, Romania, Hungary, Slovakia, Slovenia, Ukraine, Croatia, Georgia, Turkey, Italy and the others. Most of mines are designed to exploit clinoptilolite or mordenite, although chabazite and phillipsite are also mined. Mining a zeolitic deposit is relatively simple compared to mining most of other minerals. Zeolite-bearing formations are generally at or close to the surface and require the removal of only small amounts of overburden to expose the ore. Currently, there are known about 45 structural types of natural zeolites and over 600 synthesized species have been prepared so far.

Most zeolites in sedimentary rocks are formed from volcanic ash or other pyroclastics in the reaction of the amorphous aluminosilicate glass with the water pervading pores. The other originate by the alteration of pre-existing feldspars, feldspathoids, biogenic silica or poorly crystalline clay minerals. The factors controlling a zeolite or a clay mineral formation are till now insufficiently understood; however, temperature, pressure, reaction time, alkalinity and dissolved salts in pore solutions seem to be important.

Although zeolites have attractive ion-exchange properties, they did not find any commercial use as ion exchangers until the early 1960's. This was largely due to their inaccessibility and lack of knowledge of their properties. AMES et al. [2] were the first to apply them in processing of high-level alkaline wastes produced during the PUREX processing of spent nuclear fuel. Their high stability in ionizing radiation and in aqueous solutions at elevated temperature and at elevated pH levels together with their excellent selectivities caused that certain zeolites proved to be uniquely suitable for the recovery and concentration of Cs (137) and Sr (90) radioisotopes for long-term storage.

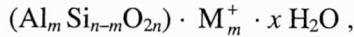
Later environmental use of clinoptilolite by Ames and Mercer was due to its excellent ammonium ion selectivity and in the early 1970's led to the development of the ammonium removal from municipal wastewater. These authors together with the Plant Engineering Service CH₂M-Hill proposed a tertiary treatment unit for Battelle Northwest/South Tahoe Public Utility District to protect the quality of water in the Truckee river in California. The regional facilities using naturally occurring clinoptilolite for ammonium removal in tertiary sewage treatment began to apply a full-scale operational cycle in the early 1980's and has been under uninterrupted operation since that time as the only industrial plant of such a type in the world.

Better knowledge of the natural zeolite properties together with ever-growing demand for selective, stable ion exchangers in pollution abatement, water treatment, energy production, agriculture, aquaculture, animal nutrition, metal processing, biomedical applications and others allowed us to expect an exciting practical development of these unique materials.

Nevertheless, a rapid escalation of the prices of raw materials will place natural zeolites even in future in an improving price-performance position compared to synthesized materials. Because of chemical and mineralogical variability of natural zeolites, ion-exchange and selectivity properties of the zeolites from various deposits have not been generalized, but become a scope of wide national research all over the world.

2. CRYSTAL STRUCTURE OF ZEOLITES

Zeolites are crystalline, hydrated aluminosilicates of alkali and earth alkaline cations that consist of infinitely extending three-dimensional networks of AlO_4^{5-} and SiO_4^{4-} tetrahedrons, linked in such a way as to share all oxygen atoms. Zeolites may be represented by the following empirical formula:



where M^+ are exchangeable cations and x is the number of crystalline water molecules.

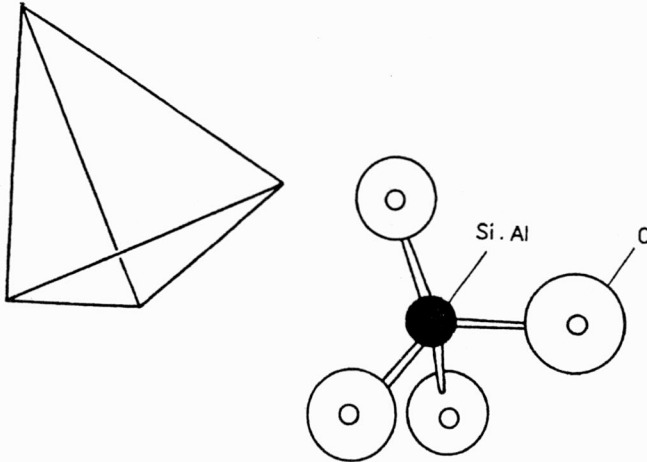


Fig. 1. Representations of SiO_4^{4-} and AlO_4^{5-} tetrahedron

Generally, the zeolite frameworks are much open and contain channels and cavities where cations and water molecules are located. The cations are quite mobile and can usually be exchanged to a varying degree for other cations. The aluminosilicate framework structure characterized by a reversible ion exchange as well as by dehydration-rehydration ability is negatively charged and balanced for electroneutrality by exchangeable cations.

The intracrystalline voids make up from 20 to 50% of the total crystal volume of most zeolites. The diameters of the open pores or pores leading into the voids range from 0.3 to 1.0 nm. The internal structure of these frameworks is decidedly hydrophilic and exhibits a strong affinity to water molecules. Owing to a large internal surface of zeolites (several hundreds of square meters per gram) and considerably lower costs than those of their synthetic equivalents, especially naturally occurring specimens, i.e. clinoptilolite, mordenite, erionite, phillipsite, chabazite, analcime, ferrierite and laumontite, they arouse a tremendous interest of a broad scientific community all over the world.

Zeolite structures contain several types of building units. The simplest is the primary building unit, a tetrahedron of 4 oxygen ions surrounding a central metal ion, either Si^{4+} or Al^{3+} (figure 1). Primary building units are connected in three dimensions such that all oxygen ions are shared by two tetrahedrons. Zeolite structures also contain secondary building units (SBUs) consisting of simple and double rings of tetrahedrons, such as single 4-, 6- and 8-rings and double 4-, 6- and 8-rings. In addition, the structures contain larger symmetrical polyhedrons such as the truncated octahedron or sodalite, cancrinite or 26-hedron (α -cage of the zeolite A). SBUs and common polyhedrons found in zeolite structures are shown in figures 2, 3, 4 (MEIER and OLSON [3]).

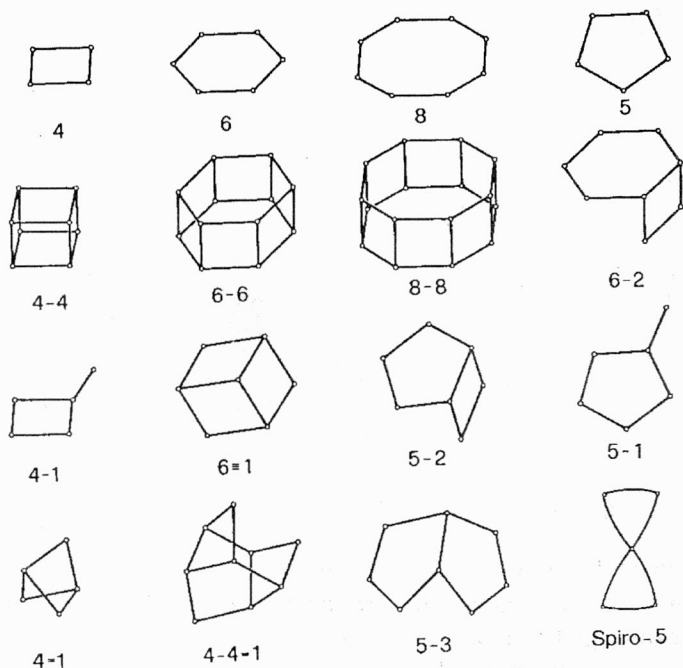


Fig. 2. Secondary building units

All zeolite structures can be viewed as the secondary building units and polyhedrons being packed in space. Heulandite, clinoptilolite, ferrierite and mordenite are the zeolites containing 5-ring tetrahedron. Clinoptilolite and heulandite have the same framework topology which consists of cross-linked sheets of complex tetrahedral units containing 4- and 5-member ring and 8- and 10-member ring pores (figure 5).

The structures illustrate the range of zeolites types. The pore systems vary from the most open, three-dimensional channels in zeolites A, X and Y to the two-dimensional channel system of clinoptilolite and mordenite.

Clinoptilolite, most frequently used in industry, consists of 4-4-1 SBU and has a special configuration of tetrahedrons in 4- and 5-rings arranged in sheets. The layers are open 10-ring and 8-ring channels parallel to the *c*-axis, with approximate free dimensions of $7.6 \times 3.0 \text{ \AA}$ and $4.6 \times 3.3 \text{ \AA}$, respectively (figure 6).

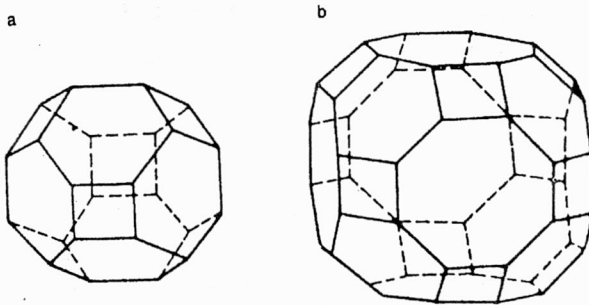


Fig. 3. Sodalite (a) and cancrinite (b) units

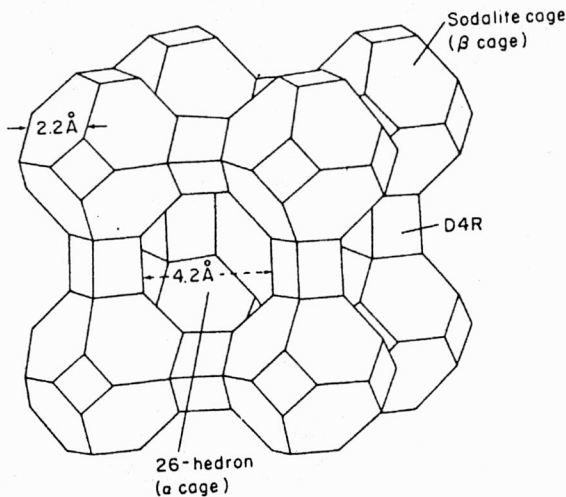


Fig. 4. The polyhedral units representing the structure of zeolite A

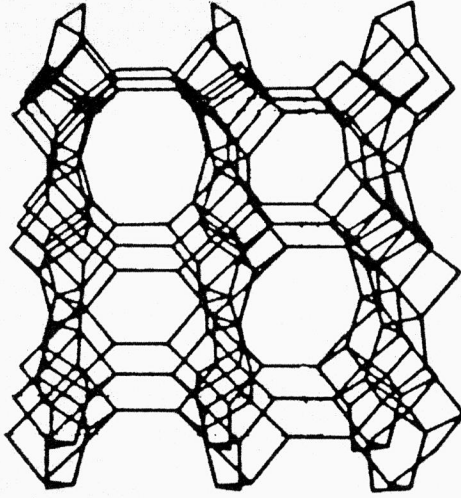


Fig. 5. Skeletal drawing of the heulandite and clinoptilolite structures

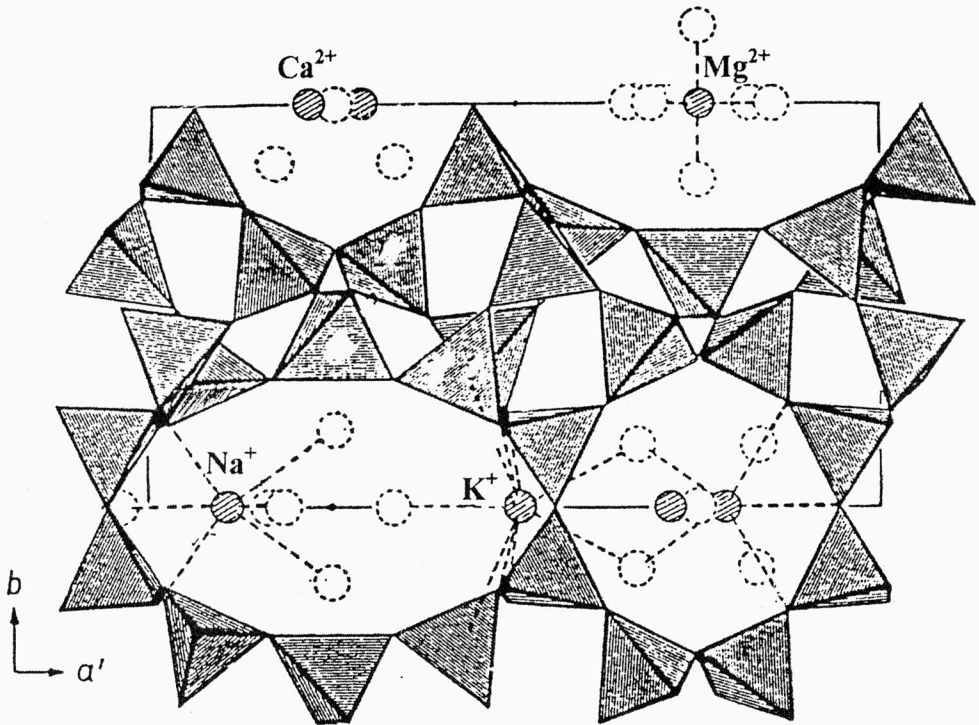


Fig. 6. Possible distribution of exchangeable cations in the clinoptilolite structure

3. CHEMISTRY OF CLINOPTILOLITE

Both Si/Al ratios and cation contents determine the properties of most zeolites, but precedents for this subject usually favour differentiation on the basis of framework composition rather than the readily variable exchangeable cations. The Si/Al ratios of natural zeolites vary from low of about 2.7 for heulandite to high of about 5.3 for clinoptilolite. Calcium, sodium and potassium (magnesium) are the major cations, with high calcium concentration generally prevailing at a lower Si/Al ratio (heulandite) and high potassium concentration at a higher Si/Al ratio (clinoptilolite).

Clinoptilolite is the only economically important variety in terms of both stability and availability. Calcium and sodium cations in this zeolite structure are close to 8- and 10-ring sites in the main channels, particularly in the region of high Al^{3+} substitution in the tetrahedral bridging positions between the dense sheets. Potassium is located almost in the center of the 8-membered ring of the secondary channels coordinated by 6 framework oxygen atoms and three water molecules. Magnesium is octahedrally coordinated by 6 water molecules. It is located at the site of the single 8-ring tetrahedron, in the main channels characterized as poorly mobile (KOYAMA and TAKEUCHI [4]).

The potassium form of zeolites belonging to this group shows high thermal stability. Calcium heulandite with low Si/Al ratio tends to degrade at a temperature of 500–550 °C, but potassium-exchanged heulandite and various potassium and hydrogen clinoptilolites are stable up to 800 °C (SHEPARD and STARKEY [5]).

Clinoptilolite in terms of the molecular sieve has rigid, strong framework resistant to high temperature, oxidation/reduction, ionizing radiation and is not prone, as are many organic resin ion exchangers, to physical attrition due to osmotic shock. The ion-exchange properties of clinoptilolite are more constant and predictable over wide ranges of temperature, ionic strength, etc., than those of other ion exchangers. Similarly, zeolite ion exchangers should not tend to adsorb organic molecules or ions and become fouled as readily as other ion exchangers.

Zeolites synthesized at elevated pH level, e.g. pH of 12–13, and at a temperature in the range of 100–300 °C and are quite stable under conditions only slightly less severe than those applied during their synthesis. Although some zeolites are stable at lower and high pH levels, the most natural zeolites should not be used at $pH < \sim 4$ and over $pH > \sim 9$. Slow hydrolysis of framework aluminium leading to gradual loss of ion exchange properties and collapse of the crystal structure proceeds in mineral acids. The degradation reactions occur more readily in the zeolites with low SiO_2/Al_2O_3 molar ratios and are more rapid at elevated temperature. Strongly alkaline environments ($pH > 11$ –12) cause silicon dissolution and gradual degradation of the zeolite crystal structure, even in the case of clinoptilolite.

The rate of silicon removal is much more rapid than that of aluminium, i.e. the zeolite dissolves incongruently, which results in the formation of a solid product of a lower SiO_2/Al_2O_3 molar ratio compared to its initial form.

4. ADSORPTION AND ION EXCHANGE AT NATURAL ZEOLITES

Adsorption is a process in which adsorbate is extracted from one phase (solution) and concentrated at the surface of a second phase (adsorbent). Adsorption from solution upon a solid surface, properly termed a *surface phenomenon*, occurs as the result of one of two characteristic properties of a given solvent–solute–solid system or their combination.

Three principal types of adsorption are distinguished, i.e. the surface phenomenon may be predominantly one of electrostatic attraction of the solute (adsorbate) to the adsorbent, physical adsorption of the van der Waals attraction or adsorption of a chemical nature. The first type of adsorption falls within the ion exchange and is often referred to as exchange adsorption. Exchange adsorption is the case of ionic solute–zeolite interaction.

For two potential ionic adsorbates, the ion charge is the factor that determines exchange adsorption. In a system, e.g. containing a monovalent and trivalent ions under the conditions defined, a kinetic energy necessary to hold them in solution is the same for each of them, but a trivalent ion is attracted much more strongly towards a site of opposite charge on the surface of adsorbent.

In the case of ions of equal charges, their molecular size (hydrated radius) determines the order of preference for adsorption, the smaller ion being able to accomplish closer approach to the adsorption site and thus being favoured. Generally, ion exchange processes at natural zeolites are replaced by electrostatic adsorption characterized above.

Moreover, if such adsorbates as halogenides or arsenates are exchanged for silver ions in clinoptilolite, this phenomenon is referred to as chemisorption. Precipitates of silver arsenate or silver halogenide on the surface of clinoptilolite are formed.

Generally, reversible ion exchange on the surface of natural zeolites is a function of the specific surface area of these minerals, specific zeolite topology, the charge of the zeolite framework associated with framework geometry, $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio, the heteroenergetic nature of the cation sites available for occupation inside the framework, crystals irregularities, the size of both anhydrous and hydrated cations and cation charge, temperature and concentration of the cation species in solution, structural characteristics of each zeolite, and so on.

In contrast to silica gel and activated carbon adsorbents, the zeolite crystal structure is unique because of a uniform pore distribution, which limits the filling of zeolite micropores volume on the basis of the relative sizes of adsorbates and their states of solvation inside and outside the zeolite, the difference in energies required to lose solvent molecules by intracrystalline migration and other very specific factors of adsorption characteristic of zeolites only.

5. ADSORPTION EQUILIBRIA AND ADSORPTION ISOTHERM

Adsorption of the solutes from solution and their concentration at the surface of the solid in such time that the concentration of the solute remaining in solution is in a dynamic

equilibrium with that at the surface is defined as distribution coefficient. The amount of solute adsorbed per unit weight of a solid adsorbent q_e as a function of the concentration of solute in solution at the equilibrium C and at a constant temperature is termed an adsorption isotherm. This functional expression of the variation in adsorption with concentration of adsorbate in solution has exponential character typical of natural zeolites (the Langmuir, Freundlich model of adsorption isotherm valid for single-layer adsorption).

This model is based on the following assumptions: the maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface; the energy of adsorption is constant and there is no transmigration of adsorbate in the plane of the surface.

Basically, the empirical Freundlich equation of isotherm

$$q_e = K_F \cdot C^{1/n},$$

where K_F , n are constants, generally agrees quite well with the Langmuir equation of isotherm

$$q_e = q_m b \cdot C / (1 + bC),$$

where q_m , b are constants.

Unlike the Langmuir equation, the Freundlich model does not reduce to the expression of linear adsorption at very low concentrations, nor does it agree well with the Langmuir equation at very high concentrations, since n must reach some limit when the surface is fully covered.

It is the rate of adsorption from dilute aqueous solutions by solid adsorbents that is a highly significant factor taken into account when applying this process to water quality control. Generally it can be stated that in rapidly stirred, batch-type systems, the rate of uptake is controlled primarily by the rate of adsorbate transport from the exterior to the interior sites of the adsorbent particles and that "diffusion" in the pores of solid adsorbents or resins is the rate-controlling step in many adsorption and ion-exchange processes.

6. CATION SIEVE EFFECTS IN ZEOLITES. SELECTIVITY OF ZEOLITES

In zeolites, the sieve and partially sieve effects relating to various cations have been governed by one or more of three possible mechanisms: (1) the cation may be too large to enter smaller channels and cavities within the zeolite structure or in some zeolites the exchangeable cations are blocked up and cannot be replaced, (2) the distribution of charge on the zeolite surface may be unfavourable for the cation, (3) the size of the hydrated cation in aqueous solution may influence and retard its exchange, since the exchange of solvent molecules must occur for the cation that diffuses through apertures which are too small to accommodate the solvated cation (BRECK [6]).

In addition to some ion sieve effects, zeolites commonly exhibit high selectivity in ion exchange if ions easily enter the zeolite pores. Naturally occurring zeolites

show higher selectivity for some monovalent cations than for common divalent cations.

The decrease in the aluminium content of the zeolite also increases an average distance between the adjacent anionic sites in the zeolite framework. Therefore a single divalent cation tackles a greater difficulty in "satisfying" the fields of two adjacent anionic sites. As a result, the preference of the zeolite for divalent cations decreases, and that for univalent cations – increases.

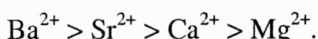
Often a zeolite favours the least hydrated ion, while the solution phase favours the most highly hydrated ion. In other words, water molecules in solution compete with the zeolite for attraction of the cations (SHERMAN [1]).

Large, totally hydrated ions are preferred in "weak" field zeolites, i.e. those with lower aluminium content, and thus lower framework charge density. However, even the relative selectivities of these zeolites for the cations in the series differ greatly.

The zeolite ion-exchange affinity sequence is often found to be in accord with the hydrated ionic radius, so this sequence is:



and for divalent ions:



Selectivity series of decreasing preference for the exchange of different cations for the clinoptilolite of Slovakian origin is shown below (HORVÁTHOVÁ-CHMIELEWSKÁ [7]):



Exchange of multivalent metal ions is complicated, because we have to maintain the pH levels in solution low enough to be beyond the solubility limits of the metals and high enough to minimize a proton exchange and hydrolysis of the zeolite (primarily it is realizable on more acid-resistant clinoptilolite and mordenite).

Ion exchange is principally a stoichiometric, reversible exchange of ions between a liquid and solid phases which produces no significant changes in the structure of the solid. In a binary system, the mass action equilibria could be expressed by the equilibrium constant:



$$K = \frac{\text{AZ} \cdot \text{B}}{\text{A} \cdot \text{BZ}},$$

where A, B are ions and Z zeolite.

Alternatively, the selectivity coefficient can be expressed in terms of dimensionless concentration:

$$K = \frac{q_{\max}}{C_0} = \frac{Y_A \cdot X_B}{X_A \cdot Y_B}.$$

These variables are expressed in terms of the total solution concentration C_0 (in mmol/dm^3) and the total exchange capacity q_{max} (in mmol/g), thus $X = C/C_0$ and $Y = q/q_{\text{max}}$. The preference of an ion exchange for one ion relative to another in binary systems is often expressed as the separation factor α .

If the equivalent fraction of ion A in the solid phase Y_A is plotted against the equivalent fraction of A in the solution X_A , three cases can be identified corresponding to $\alpha < 1$, $\alpha = 1$ and $\alpha > 1$. It is assumed that the isotherms of upward concavity $\alpha < 1$ represent the "unfavourableness" of the uptake of ion A; those which fall along the rising diagonal $\alpha = 1$ are termed "linear" and exhibit no preference for ion A or B; and the curves of downward concavity $\alpha > 1$ are referred to as "favourable" isotherms since the solid prefers the ion A to the ion B (figure 7).

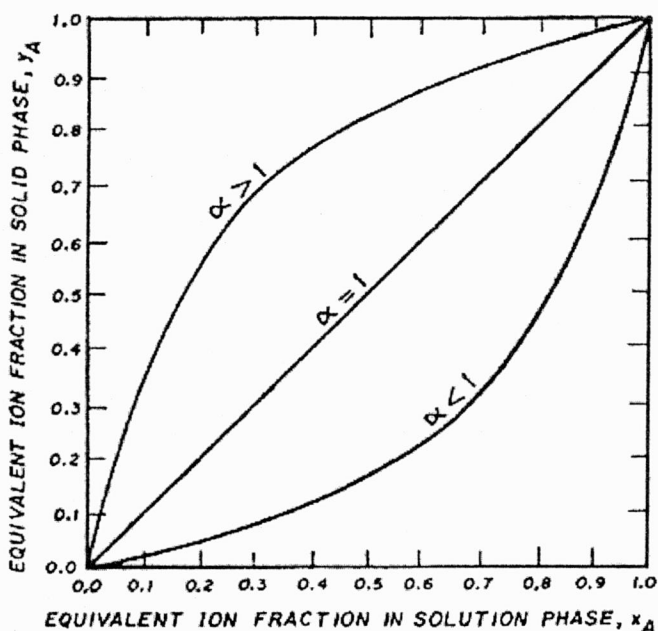


Fig. 7. Generalized ion-exchange isotherms

Ion exchange almost exclusively occurs in the systems in which a separation factor of the ion of concern is greater than unity during the service cycle.

7. ENGINEERING PRINCIPLES OF USE OF CLINOPTILOLITE FOR AMMONIUM REMOVAL BY SELECTIVE ION EXCHANGE

Increasingly stringent water quality standards implemented by the state regulatory authorities and increased public awareness have led to a re-evaluation of wastewater

treatment objectives. Nitrogen has not been removed from wastewater during its treatment due to high costs of treatment and a lack of adequate technology in process design and operation.

The use of conventional ion-exchange resins for removing nitrogenous material from wastewater has not been found attractive because such resins are expensive and not sufficiently selective. Moreover, we meet the difficulties with handling of regenerant effluents. Above limitations may be easily overcome by using a clinoptilolite, which is naturally abundant and appropriate for selective ammonium removal and enhanced control of nutrient-water pollution on the basis of its specific sorption characteristics.

Clinoptilolite is selective for ammonium and all other cations commonly found in municipal wastewaters such as calcium, magnesium and sodium, except for potassium. Although clinoptilolite prefers ammonium ions to other cations, it is not absolutely selective and other cations do compete for the available exchange capacity.

In an industrial treatment process, the water is usually passed downward through a clinoptilolite bed during a normal service cycle. When the concentration of effluent ammonium increases to critical level, the clinoptilolite is regenerated by passing 2–4 per cent sodium chloride solution through the exchange bed. While during a normal service cycle the effluent flows downwards, regeneration is carried out by passing the regenerant up through the clinoptilolite bed. After removing the ammonia from a spent regenerant, the latter may be reused, eliminating the difficult problem of brine disposal associated with a conventional use of exchange resins. Some of the regenerant recovery techniques make it possible to remove ammonia as nitrogen gas, which is discharged to the atmosphere, while others allow us to remove and recover the ammonia in solution form for a potential use as a fertilizer.

The general objective of many case studies dealing with exploitation of clinoptilolite for both drinking and wastewater treatments is mostly to define various operational parameters necessary to remove ammonia efficiently through clinoptilolite bed, to predict more accurately column performance and thus the costs of the process. Total exchange capacity, chemical and physical stability and major service cycle variables, i.e. pH, hydraulic loading rate, clinoptilolite mesh-size, wastewater composition, bed depth, one column vs. series column operation and the other, are commonly verified in a laboratory before pilot-measure operation.

The key to the applicability of the ion exchange involving clinoptilolite and regenerant recovery process is the method of handling the spent regenerant. Pilot tests of the overall ion exchange–regenerant recovery system may be useful, however, in evaluating physical and economical aspects of the proposed system design as applied to a specific wastewater (SVETICH [8]).

A pronounced exchange between NH_4^+ , Na^+ and K^+ ions and a slight increase in the concentration of NO_3^- component in effluent took place. They were probably due to slow nitrification as well as the increase in the number of psychrophil and mesophil bacteria in water samples after reaching the steady-state conditions. However, after alkaline regeneration and backwashing of clinoptilolite bed with the tap water this phenomenon disappeared. Moreover, water treated in the zeolite should be finally conditioned either by means of chlorine or chlorine oxide which usually ensures its satisfactory quality.

The zeolite ion-exchange pilot installation in the field laboratory of Water Research Institute with a hydraulic loading rate of 900 dm^3 per hour (12.8 BV/hour) made it possible to treat the tap water enriched with ammonium chloride to an initial ammonium concentration of $1 \text{ mg per } 1 \text{ dm}^3$ in two pressure steel columns operating in series. Each column was filled with 70 dm^3 (56 kg) of clinoptilolite having a grain size of 0.2–1.0 mm. Bottom of each column was filled with 14 dm^3 of sand. Columns were operated in down flow mode during the common service cycle and upflow mode in regeneration cycle. A solution of 2 per cent sodium chloride with $\text{pH} \sim 9$ was used for clinoptilolite regeneration. In pilot-scale, an HDPP tower of a total height of 6.5 m consisting of 6 modules of ground plan measures of $980 \times 650 \text{ mm}$ was used for ammonia stripping.

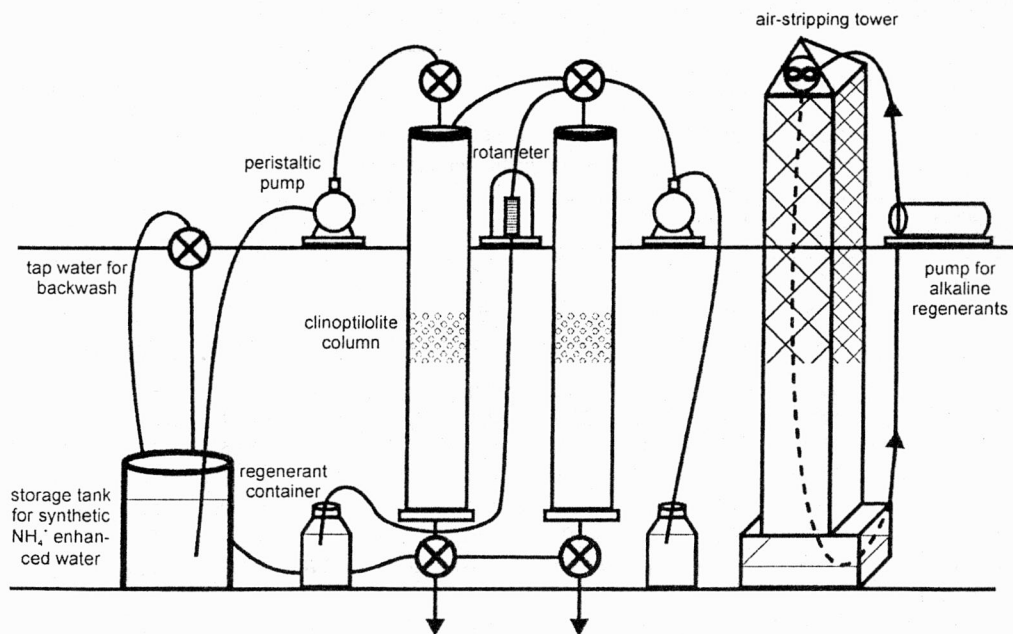


Fig. 8. Sketch of laboratory ion-exchange in clinoptilolite-regenerant recovery system

To strip ammonia out of the regenerant brines a large quantity of air had to be passed through the tower, therefore the tower was equipped with the installation of two lateral air blowers at the bottom. Countercurrent tower configuration by which the entire air flow entered the bottom, while the treated solution entered the top and moved downwards (through the vertical waves shaped laminated glass slats) to the bottom of the tower, resulted in the above tower design improvement (figure 9).

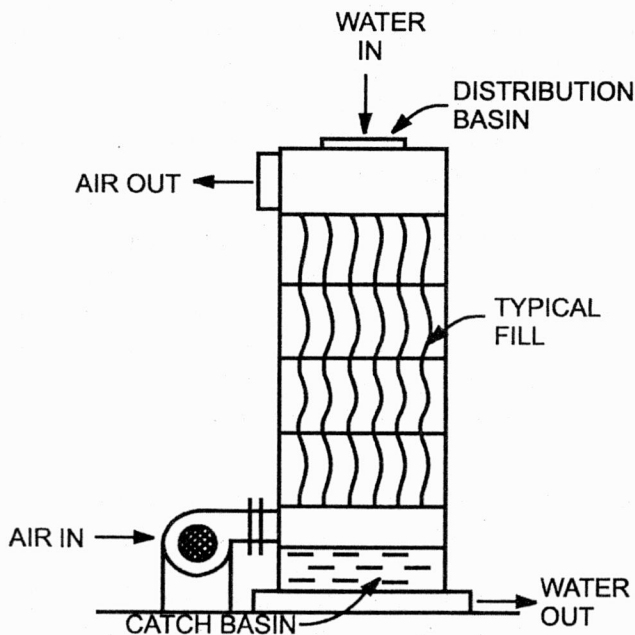


Fig. 9. Principle sketch of a pilot air-stripping tower

In a laboratory model of such a structure, we can treat during one service cycle a volume of 675 dm^3 and obtain an acceptable effluent concentration, i.e. 0.5 mg ammonium per 1 dm^3 , while in the pilot clinoptilolite column 85 cubic meter of water can be treated, which means that 4-day operation of clinoptilolite bed enables removal of 81 g ammonia from water. The comparison of zeolite capacity data in both synthetically prepared ammonium-enhanced tap waters testifies to a higher capacity in laboratory conditions, where the initial ammonium concentration is higher ($a_{\text{lab}} = 3 \text{ mg/g}$; $a_{\text{pilot}} = 1.5 \text{ mg/g}$).

In pilot operation, a single, separated clinoptilolite column was in service until the ammonium concentration in effluent reached 0.5 mg/dm^3 . Then the second column in series was connected. When the first column became exhausted its regeneration began by the disconnection of assemblage, while only the second column took part in operation. Accepting the rule that the more exhausted column was always at the influent

end backed up by the column having lower loading, the throughput of a number of bed volumes in service cycle increased by a half.

The exhausted pilot clinoptilolite bed was regenerated by means of 2 per cent sodium chloride of pH \sim 9, at flow rate of 900 dm³ per hour in upflow mode. 2-hour regeneration and the throughput of 25 regenerant bed volumes (BV) enabled a 85 per cent ammonia elution out of the clinoptilolite bed, which was enough to maintain a constant time schedule with the effluent quality required. A half-hour backwash of tap water at about 30 per cent bed expansion followed the regeneration cycle.

Elutriates produced during regeneration were air-stripped without mass closed loop operation, because discharging of such amount of stripped ammonia into the atmosphere has not polluted air significantly. Total volume of a regenerant (1800 dm³) in pilot facility was recycled in the tower for 150 minutes to decrease the initial ammonia concentration from 50 to less than 10 mg per dm³. In the first stripping cycle, 47 per cent of ammonia were removed, thus the second cycle had to be performed additionally. Elutriates were pumped to the top of the tower at the same loading rate as in the clinoptilolite column, however against the air blown from the bottom of the tower with the rate of 800 dm³ per second. For the recovery of 1 dm³ of elutriate 3.8 cubic meters of air were necessary. To maintain pH \sim 11 of elutriates during the stripping process and to compensate a loss of sodium ions in solutions, sodium hydroxide was regularly added (HORVÁTHOVÁ-CHMIELEWSKÁ [9]).

9. AMMONIUM REMOVAL FROM WASTEWATER BY ION EXCHANGE IN CLINOPTILOLITE

Similar installation was used for ammonia removal from mixed tannery wastewater and municipal sludge at Moravian Wastewater Reclamation Facility in Otrokovice (WWRFO). The pilot-plant based on the inland clinoptilolite ion exchange-regenerant recovery system operated with the capacity approaching 1 cubic meter per hour and consisted of three pressure steel columns, each with clinoptilolite bed volume of 70 dm³, four regenerant storage tanks of the volume of 0.75 cubic meter and one counter-current air stripping tower of a 0.6 m diameter and operating volume of 0.9 cubic meters filled with 32×50 mm PVC tubes.

Three-column operation (two beds under on-stream control, while the third bed being regenerated) as well as more complicated valving and piping than those for tap water treatment was required at this facility. In order to guarantee a sufficiently long (4 days) treatment of tap water with enhanced ammonium concentration, wastewater service cycle lasted only 15 hours. To provide the continuous plant operation in this case, the regenerative part of the overall ion exchange-regenerant recovery system should have been limited to the fractional three-volume elutriate method. According to this regeneration method only the elutriate volume was air-(steam) stripped. It exhibited the highest ammonia concentration and therefore could be used as a final polishing one in clinoptilolite bed regeneration cycle (figure 10).

FLOW DIAGRAM OF pH = 9 REGENERATION SYSTEM USING AIR STRIPPING

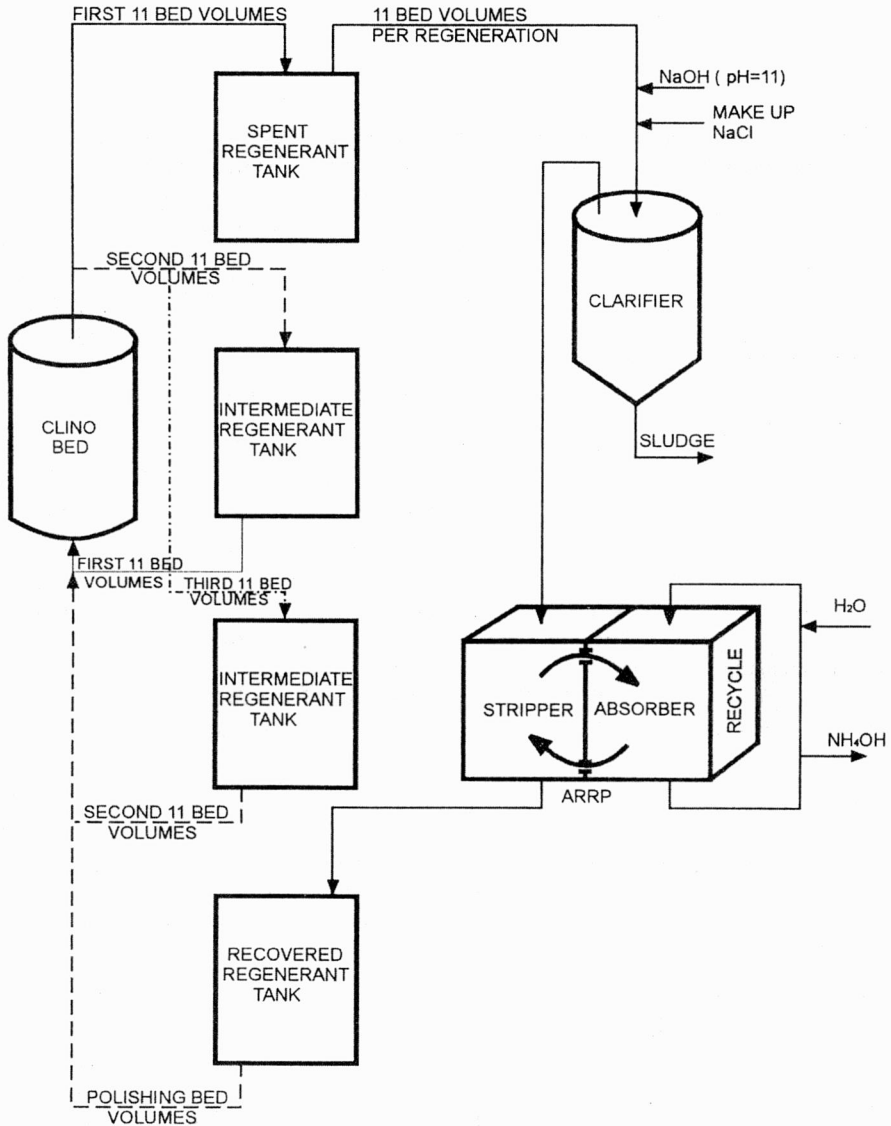


Fig. 10. Principle scheme of three-volume elutriate (fractional) regeneration and ammonia recovery system applied to mixed municipal sludge and tannery wastewater treatment at WWRFO

One of the most preferential benefits of the advanced treatment process, which is based on the selective ion exchange in clinoptilolite with the mass closed loop operation, was the recovery of the elutriates and the return of stripped ammonia to the tannery processing plant (HORVÁTHOVÁ [9]). Average wastewater quality of influents treated in WWRFO and the technological characteristics of the pilot plant structure are presented in tables 2 and 3.

Table 2

Average wastewater quality expressed by selected indexes of the mixed municipal sewage and tannery wastewaters treated in WWRFO and in pilot plant with clinoptilolite

Index (mg/dm ³)	Influent	Effluent mechanical treatment	Effluent mechanical and biological treatment	Influent to clinoptilolite column after experimental unit pretreatment
Dissolved substances	1997	1906	1317	1200
Inorganic solids	1500	1482	1117	1026
BOD ₅	488	310	55	17
COD	2044	827	199	108
NH ₄ ⁺	61	55	43	40
Cl ⁻	482	508	465	301
SO ₄ ²⁻	278	259	206	156
Cr ³⁺	12	7.2	2.8	2.4
Ca ²⁺	138	141	135	139
Mg ²⁺	46	21	16	17
Petroleum compounds	—	2.5	—	—
pH	9	8.9	7.2	7.4
Total hardness, mmol/dm ³	5.3	4.4	4.0	4.2

Table 3

Technological characteristics of pilot ion-exchange in clinoptilolite–regenerant recovery system installed at WWRFO

Specific bed volume loading (BV/hour)	12.8
Clinoptilolite volume in column, dm ³	70
Clinoptilolite grain-size, mm	0.3–1.0
Ion-exchange capacity of clinoptilolite in wastewater, mg/g	10.0
Service cycle operation, hour	20
BV	260
Regeneration cycle, hour	2.5
BV	32
Volume of wastewater treated for one service cycle, cubic meter	18
Volume of elutriate recovered by air stripping, cubic meter	0.75
Consumption of air by elutriate recovered at 20 °C, cubic meter per liter	20

One clinoptilolite bed was able to remove 550 g of ammonia from the wastewater during one operation cycle, i.e. about 13 kg over the entire treatment period, provided that it was regenerated 23 times over the period of pilot plant verification. A single clinoptilolite bed was operated until the ammonium content in treated water had reached 20 mg/dm^3 , then the second one was put in motion.

After regeneration of clinoptilolite column with 2 per cent sodium chloride ($\text{pH} \sim 9$) the column began to be rinsed with 0.02 N hydrochloric acid to reduce the residual alkalinity, because backwashing with tap water was rather time consuming. The mixed air and waste steam medium injected into the stripping tower brought about a rise in the temperature of its inside up to 45°C reducing thus considerably, i.e. to 2.5 hours, the cycle of the regenerant recovery.

The industrial locality has delivered up to 55 000 cubic meters of wastewater per day, therefore the ion exchange–regenerant recovery process was designed for the entire capacity of the WWRFO. The advanced wastewater treatment plant consisted of three series of clinoptilolite columns, each of five column sets, every one weighing about 30 tones, while the set of five columns operated simultaneously.

A large air stripping tower operating uninterruptedly with the same elutriate loading rate as in service cycle for clinoptilolite bed provided the necessary regenerant recovery using the countercurrent injection of mixed air and waste steam to the bottom of the tower.

10. BRIEF ECONOMY EVALUATION

Costs analysis of ion-exchange technology based on clinoptilolite with chemical regeneration and regenerant recovery by air stripping and on biological nitrification–denitrification for the model hydraulic loading rate of 6000 cubic meters per day was carried out.

In order to estimate the cost of ion-exchange technology using inland clinoptilolite, the method investigated was compared only with suspension nitrification–denitrification, externally enhanced by addition of organic carbon. Both technologies were set after mechanical treatment of wastewater and 2-hour activated sludge process.

Higher thermal energy demand for ammonia stripping was optimized and calculated based on the mass closed loop operation, i.e. ammonia absorption into diluted acid in foam absorber. Operation costs of biological variant were slightly lower than those of ion exchange in clinoptilolite, but the opposite investment costs for biological variant proved to be higher. The lower investment costs and the other benefits of final physicochemical treatment, i.e. saving of plant construction area, temperature and toxic metals resistance, high ammonium selectivity, favour clinoptilolite method. Nevertheless biological technologies being more conventional allow a complex degradation of water pollutants.

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WYMIANA JONOWA Z WYKORZYSTANIEM ZEOLITÓW NATURALNYCH
W OCHRONIE ŚRODOWISKA

W artykule przedstawiono krótki przegląd historii zeolitów, a także opisano ich krystaliczną budowę wraz z pierwszo-, drugo- i trzeciorzędowymi elementami strukturalnymi. Omówiono topologię, chemię i własności jonowymienne zwłaszcza klinoptylolitu. Rozdziały 4, 5 i 6 dotyczą mechanizmu adsorpcji i wymiany jonowej z wykorzystaniem zeolitów. W końcowej części artykułu przedstawiono możliwość usuwania azotu amonowego (przy podwyższonej jego zawartości) z wody pitnej w warunkach laboratoryjnych. Wyniki badań laboratoryjnych zostały potwierdzone w Stacji Odnowy Wody na Morawach korzystającej z instalacji oczyszczającej ścieki z garbarni pracującej przy obciążeniu 900 dm³/h.