$$\left(\frac{U_{E_A}}{E_A}\right)^2 = \left(\frac{U_{M_{A,f}}}{M_{A,f}}\right)^2 + \left(\frac{U_{TN}}{TN}\right)^2 . \quad \text{(A-6)}$$

The equation for the uncertainties in $\bar{E}_A$ calculated from the $B^{z_B+}$ data (Eqn. A-2) is the same as Equation (A-5), except the molarities are those for $B^{z_B+}$. The uncertainty equation for $E_A$ calculated from $B^{z_B+}$ data is slightly different from Equation (A-6), and is given by

$$\left(\frac{U_{E_A}}{E_A}\right)^2 = \left(\frac{z_B M_{B,f}}{TN - z_B M_{B,f}}\right)^2 \cdot \left[\left(\frac{U_{M_{B,f}}}{M_{B,f}}\right)^2 + \left(\frac{U_{TN}}{TN}\right)^2\right]. \quad \text{(A-7)}$$

Note that Equation (A-5) has terms with concentration differences in the denominator. Where the difference in initial and final concentration is small, the uncertainty in the calculated parameter can be large. Therefore, errors in $\bar{E}_A$ calculated from the $A^{z_A+}$ analysis become large as $\bar{E}_A$ approaches one. On the other hand, errors in $\bar{E}_A$ calculated from the $B^{z_B+}$ data become large as $\bar{E}_A$ approaches zero. These trends explain why it is important to analyze the solution concentrations of both cations participating in the exchange reaction when constructing ion-exchange isotherms. In this manner, the ion-exchange isotherm is well-constrained throughout the entire composition range

Uncertainties in the selectivity coefficient, $K_{v(A,B)}$, derived using $A^{z_A+}$ analytical data (Eqn. A-3) can be calculated from

$$\left(\frac{U_{K_v}}{K_v}\right)^2 = \left(\frac{z_A U_{\bar{X}_A}}{1 - \bar{X}_A} + \frac{z_B U_{\bar{X}_A}}{\bar{X}_A}\right)^2 + \left(\frac{z_A^2 U_{M_A}}{TN - z_A M_A} + \frac{z_B U_{M_A}}{M_A}\right)^2 + \left(\frac{z_A U_{\gamma_B}}{\gamma_B}\right)^2 + \left(\frac{z_B U_{\gamma_A}}{\gamma_A}\right)^2 . \quad \text{(A-8)}$$

The corresponding uncertainty equation for $K_{v(A,B)}$ calculated from the $B^{z_B+}$ data (Eqn. A-4) can be derived by interchanging coefficients A and B in Equation (A-8). Also,

$$U_{\ln K_{v(A,B)}} = \frac{U_{K_{v(A,B)}}}{K_{v(A,B)}} \quad \text{(A-9)}$$

and

$$\frac{U_{\bar{X}_A}}{\bar{X}_A} = \frac{(z_A - z_B)U_{\bar{E}_A}}{z_A + (z_B - z_A)\bar{E}_A} + \frac{U_{\bar{E}_A}}{\bar{E}_A} . \quad \text{(A-10)}$$

15

# Applications of Natural Zeolites in Water and Wastewater Treatment

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## INTRODUCTION

The world is faced with increasing demands for high-quality drinking water and for removal of contaminants from municipal, agricultural, and industrial wastewaters. Treatment is required to obtain drinking water from most natural resources as well as from wastewaters with varying amounts of impurities. These impurities may occur in a variety of forms including large particles such as microorganisms or suspended solids or as dissolved or colloidal inorganic and organic substances. This chapter provides an overview on the use of natural zeolites in removal of impurities from water or wastewater (Murphy et al. 1978, Tarasevich 1994, Kalló 1995).

Most technologies using natural zeolites for water purification are based on the unique cation-exchange behavior of zeolites through which dissolved cations can be removed from water by exchanging with cations on a zeolites exchange sites (see Pabalan and Bertetti, this volume). The most common cation in waters affecting human and animal health is $NH_4^+$. It can be removed by exchanging with biologically acceptable cations such as $Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$ or $H^+$ residing on the exchange sites of the zeolite. Fortunately, many natural zeolites (e.g. clinoptilolite, mordenite, phillipsite, chabazite) are selective for $NH_4^+$ (*vide infra*), meaning that they will exchange $NH_4^+$ even in the presence of larger amounts of competing cations. Clinoptilolite and mordenite are also selective for transition metals (e.g. $Cu^{2+}$, $Ag^+$, $Zn^{2+}$, $Cd^{2+}$, $Hg^{2+}$, $Pb^{2+}$, $Cr^{3+}$, $Mo^{2+}$, $Mn^{2+}$, $Co^{2+}$, $Ni^{2+}$), which are often present in industrial wastes and can be very toxic even in concentrations as low as several mg/L. As emphasized in discussions of radioactive waste treatments, both clinoptilolite and mordenite have very high selectivities for $Cs^+$ and $Sr^{2+}$ and can therefore be used to remove minute amounts of radioactive $^{137}Cs$ and $^{90}Sr$ from nuclear process wastewaters.

Organics are also often present in wastewaters in either dissolved or colloidal form as hydrocarbons, oxygen-containing compounds, halogenated derivatives, amines, humic acids, proteins, and lipids. Unfortunately, most organic molecules or particles are too large to penetrate into channels and cages to access the extraframework exchange sites of natural zeolites; thus their adsorption must take place on the surfaces of the zeolite-containing materials (e.g. external crystal surfaces of zeolites), which can have a surface area as large as several 10 $m^2/g$. The volumetrically most important natural zeolites on the surface of the Earth are of sedimentary origin, and zeolites in such deposits occur in clusters of crystals often having intercrystalline pore sizes of 10 to 1000 nm in diameter (i.e. rock pores). Colloids, enzymes or microorganisms as large as bacteria can be trapped within these intraparticle pores. As a results of the large surface area, which is accessible for adhering bacteria, natural zeolites can become effective biofilters when compared with particles having smaller total surface areas such as quartz sand beds (Tarasevich 1994, Baykal and Guven 1997).

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The quality of water prior to treatment can vary considerably. Simple purification technologies, such as the use of chemical additives, may not meet demands for quality water. This is particularly so in cases when too much chemical is applied that may result in hazardous water (e.g. excess organic coagulants may increase the biological oxygen demand (BOD) in the effluent or surplus Al added for phosphate removal may become a harmful contaminant to humans). Fortunately, the use of natural zeolites has the potential to eliminate this problem by removing contaminants from the water via ion-exchange or adsorption processes. Furthermore, abundant deposits of natural zeolites in near-surface sedimentary deposits make their possible use in the treatment of waters and wastewaters very attractive.

## PRODUCTION OF DRINKING WATER

### Removal of $NH_4^+$ and other ions

Natural waters often contain a variety of impurities, including $NH_4^+$, heavy metals, As, $H_2S$, and humic acids. $NH_4^+$ is a common contaminant in natural waters, but its concentration in solution can be reduced below the recommended level for drinking water of <1 mg $NH_4^+$/L by ion-exchange processes. Most natural zeolites in their Na-exchanged form, i.e. Na-clinoptilolite, Na-mordenite, Na-phillipsite, Na-chabazite, and Na-erionite, are selective for $NH_4^+$ as shown experimentally by Ames (1960, 1961) and theoretically by Neveu et al. (1985).

Hlavay (1986) used a natural rhyolitic tuff containing 58 wt % clinoptilolite (Tokaj Hills, Hungary) to remove $NH_4^+$ from natural water. A 0.6- to 1.0-mm size fraction was packed into three columns, and two of the columns were used in series for water treatment while the third column was being regenerated. The exchange sites became exhausted after 470 bed volumes (BV) of the water, containing 1.6 mg $NH_4^+$/L, had passed through the columns. The dynamic ion-exchange capacity of the bed was 0.33 mg $NH_4^+$/g when the breakthrough concentration was 0.2 mg $NH_4^+$/L. The average $NH_4^+$ concentration in the effluent was 0.14 mg/L prior to reaching the breakthrough concentration. During the course of $NH_4^+$ removal, the chemical oxygen demand (COD), reflecting the total amount of oxidizable impurities, the humic acid concentration, and the $Ca^{2+}$ and $Mg^{2+}$ concentrations, did not significantly change.

Several other studies have been published on the use of clinoptilolite-rich rock for removing $NH_4^+$. Xu (1990) prepared distilled water (electrical conductivity <1 µS/m) by first removing $NH_4^+$ using a Chinese clinoptilolite (0.4-0.8 mm) and then passing the water through another commercial cation-exchange column. Linevich et al. (1990) produced drinking water from ground water by removing $NH_4^+$ (≤5.6 mg/L) via ion exchange with clinoptilolite-rich material (Georgian occurrence) and removing $H_2S$ (≤1.5 mg/L) by oxidation with chlorine and sodium hypochlorite, produced electrolytically from a NaCl regeneration solution.

On some occasions, $F^-$ exceeds 1 mg/L in drinking water supplies and must be removed before consumption. In an early use of a modified zeolite, Kravchenko et al. (1990) reacted a crushed clinoptilolite-rich rock with aluminum sulfate as a specific adsorbent for $F^-$. The clinoptilolite was modified by passing a 0.5% aluminum sulfate solution downwards (linear velocity of 10 m/h for 1.0-1.5 h) through a 2-m thick filter layer consisting of 1- to 3-mm clinoptilolite-rich grains from Trans-Carpathia, Ukraine. The filtration bed was then washed with raw artesian water until $Al^{3+}$ in the effluent decreased to 0.5 mg/L. The fluoride content of artesian water containing 2-9 mg $F^-$/L was reduced to below 1 mg $F^-$/L after passing through the modified clinoptilolite-containing column. The $F^-$ increased to 1.0-1.2 mg/L after passing 80 BV of the artesian water



through the column, at which point filtration was stopped and regeneration was performed by treating the column again with the aluminum sulfate solution as described above. According to the authors, $F^-$ is removed either by ion exchange, formation of aluminofluoride complexes bound to cations on exchange sites of clinoptilolite, or by molecular adsorption of fluoride salts; ion exchange seems an unlikely mechanism for this process.

### Ion-exchange and filtration beds

The filtration efficiency of a sand bed can be increased by admixing porous zeolitic rock having a substantially larger surface area than the sand. For example, the surface area of a zeolite-rich rock is ~10 $m^2$/g, whereas a sand has a surface area of ~0.01 $m^2$/g. As might be expected, the increased surface area provides additional area for the adsorption of suspended solids, microorganisms, and other materials in solution. Ammonium ions removed from water may serve as a nutrient source for microorganisms (e.g. nitrifying bacteria) that adhere to crystal surfaces within macro pores of zeolitic rock. Nitrifying bacteria convert the $NH_4^+$ to $NO_3^-$, which can be efficiently removed from water (e.g. see Galindo et al. 2000). Thus, water purification can be achieved by a combination of ion-exchange, filtration, and/or microbiological processes using beds of zeolite-rich materials in addition to other unreactive materials.

A variety of microorganisms, such as *Escherichia coli*, poliovirus, coxackie virus, and bacteriophages, have been effectively removed from drinking water using an $Al_2(SO_4)_3$ coagulant and clinoptilolite-rich material from the Trans-Carpathia region of Ukraine (Grigorieva et al. 1988). The numbers of microorganisms decreased by 50% when clinoptilolite-rich material or coagulant alone were used to treat the water, whereas the two additives together removed 90% of all microorganisms during the same time period. Apparently, the efficient removal of microorganisms was caused by the strong bonding of microorganism-clinoptilolite-coagulant complexes (vide infra).

Natural phillipsite-rich tuff from Tenerife, Canary Islands, Spain was used in a percolation reactor at a constant flow rate of aqueous solution for removing indicator bacteria such as total *coliforms*, fecal *coliforms*, fecal *strepotcocci*, and dissolved organic matter. The amounts of oxidizable impurities were reduced as indicated by composition, BOD, COD, and total bacteria in the effluent (Garcia et al. 1992a). Fixation of bacteria and organic matter occurred not only on zeolite crystal surfaces, but also on the volcanic glass present in the zeolitic rock. The presence of acidic surface groups (i.e. functional groups) on zeolitic and glass surfaces account for the interaction (enhancement or inhibition) with polymeric materials secreted by the cells. Filtration beds consisting of such porous materials offer suitable colonization surfaces for bacteria and a potentially constant supply of nutrients to support the microbial activity from adsorbed and ion-exchanged inorganic and organic ions.

An apparatus for removal of $NH_4^+$, $Fe^{2+}$, $Mn^{2+}$, and As (in the form of $AsO_4^{3-}$) from drinking water has been disclosed in a Hungarian Patent and built in Hungary (Hosszú et al. 1983). The apparatus consists of two columns; the first containing two layers of clinoptilolite-rich materials—one layer of Na-clinoptilolite for $NH_4^+$ ion exchange and another layer of Mn-clinoptilolite for Fe and Mn removal (see below); and a second column filled with $Fe(OH)_3$-coated $TiO_2$ for the adsorption of arsenic. A mechanical filter is placed either between the two columns or after the second column to remove suspended solids that may not be retained by the different materials in the filtration and ion-exchange beds.

Hódi et al. (1994) evaluated a complex method of ion exchange and adsorption (similar to the method described above) for the removal of $NH_4^+$, arsenic, and humic

impurities from natural water for the production of potable water. Efficient removal of $NH_4^+$ was achieved by ion exchange with Na-exchanged clinoptilolite-rich material from Tokaj Hills, Hungary. Humic substances were thereafter removed by adsorption on activated charcoal and, finally, arsenic impurities were removed by $Fe(OH)_3$ previously precipitated on an $Al_2O_3$ substrate. Influent concentrations for $NH_4^+$, $Fe^{2+}$, $Mn^{2+}$, $AsO_4^{3-}$, and COD of 0.86, 0.16, <0.02, 0.14, and 11.1 mg/L, respectively, were reduced to 0.1, <0.02, <0.02, 0.022, and 0.6 mg/L, respectively, in the treated effluent solution.

The mechanical strength of most zeolite-containing tuffs should be satisfactory for use as beds in columns for treating water. Unacceptably friable materials may be treated or altered to enhance their mechanical strength; for example, Aiello et al. (1984) altered the soft Neapolitan yellow tuff from southern Italy that contains phillipsite by subjecting the tuff to hydrothermal treatment with NaOH or KOH at 120-160°C. Pellets were prepared by compressing the treated material at 50 kg/cm$^2$ for >2 days. The ion-exchange capacity of the zeolite was essentially unaffected and the mechanical strength of the material was acceptable for use in ion exchange and filtration beds for water purification.

### Pilot plants and full-scale plants

Several pilot plants and full-scale treatment plants have been constructed and are in operation throughout the world for treatment of natural waters with natural zeolites. Most of these plants use a variety of processes to treat the water, such as ion exchange and filtration as described above. For example, the cation-exchange and filtering properties of clinoptilolite-rich tuff from Georgia were utilized in a pilot plant to remove suspended particles and trace elements from conduit drinking water in Tbilisi, Georgia (Senyavin et al. 1986a). $Cs^+$, $Sr^{2+}$, and $Cu^{2+}$ were removed from natural water of various sources and from synthetically produced model solutions containing around 1 mg/L of these cations. Solutions were passed through clinoptilolite-rich columns, 70 cm in length, at a linear velocity of 6 or 3 m/h. Breakthrough concentrations were registered after 25 h of solution passing through columns containing clinoptilolite rock particles of 0.05-0.2 cm and after 14 h in columns containing clinoptilolite rock particles of 0.3-0.5 cm.

A water reuse demonstration plant in Denver, Colorado, produced high-quality drinking water from secondary municipal wastewater effluents (Ray et al. 1985). The complex treatment involved lime clarification, 1- or 2-stage recarbonation (saturation with $CO_2$), pressure filtration, ion-exchange for $NH_4^+$ removal through a clinoptilolite column, first-stage adsorption on activated carbon, ozonation, second-stage adsorption on activated carbon, reverse osmosis, air stripping, and $ClO_2$ disinfection. Remarkably, water produced in this complex treatment system after two years of operation was lower in total organic carbon (TOC) content and contained fewer trace organics than potable water produced directly from mountain runoff (Rogers et al. 1987). A similar complex purification process for producing drinking water in Ukraine was reported by Kravchenko et al. (1994). The technology consisted of ozonation and multilayer filtration through clinoptilolite-rich material from the Trans-Carpathia area of Ukraine and activated carbon columns supplemented with Fe and Mn removal. Unfortunately, data on the performance of this system were not published.

The growth, composition, and filtering efficiency of algae layers covering the grains of a filter bed were determined in field experiments for the biological treatment of water from the Logan River in Utah, USA (McNair et al. 1987). In this process, termed Slow Sand Filtration (SSF), clinoptilolite (origin unpublished, cation-exchange capacity, CEC, = 1.7-1.9 meq/g) was added to a sand bed to increase surface area and to provide a nitrogen reservoir (via $NH_4^+$ exchange) for the algae covering the filter grains. Removal of organic and inorganic suspended solids was superior in clinoptilolite-amended SSF,



even at filtration rates 2-4 times faster than conventional SSF rates. The growth of the algae coincided with an increase in ability of the amended filter to remove *Giardia lamblia* cyst-size particles. The zeolite-amended SSF system produced drinking water for longer periods of time at higher filtration rates than the conventional SSF that did not contain clinoptilolite. In addition to clinoptilolite, other zeolite-rich materials, including phillipsite and mordenite, have been suggested for use in these types of systems (Hulbert and Currier 1986).

Senyavin et al. (1986b) used clinoptilolite-rich tuff from different deposits in the former Soviet Union (Dzeg, Tedzam, Tshuguev, and Yagodnin deposits) instead of quartz sand as a filtration bed for drinking water purification. A decrease in the number of coliform bacteria, total bacteria, and phyto- and zooplankton was attained after three years of using clinoptilolite-rich materials in the finished water compared with other methods. The mechanical, physical, and chemical properties of clinoptilolite remained essentially unchanged during the three-year test period without regeneration.

### Regeneration of $NH_4^+$-zeolite

Most of the technologies described above use the ion-exchange properties of the zeolite to remove $NH_4^+$. Thus it is fundamentally important to be able to remove $NH_4^+$ from exchange sites so the zeolite may be reused. An $NH_4$-exchanged zeolite can be exchanged or regenerated using 1 N NaCl or KCl solutions, repopulating the exchange sites with either $Na^+$ or $K^+$. The regeneration efficiency is increased when the pH of the regenerating solution is raised above 11, which can be attained by addition of lime (Oláh et al. 1988). High regeneration efficiency can be obtained under these conditions, even at high $NH_4^+$ concentrations in the regenerating solution.

Kalló (1990) achieved a regeneration efficiency of 80% by recycling 40 BV of 20 g KCl/L regenerating solution at pH = 7 through clinoptilolite-rich material. The exhausted regenerating solution contained 500 mg $NH_4^+$/L. The efficiency was increased to 88% and the $NH_4^+$ content of the regenerating solution was as high as 6000 mg/L at pH = 11-12. Nearly all dissolved $NH_4^+$ in solution was degassed from the regeneration solution at pH > 11 as $NH_3$ by air stripping. Hlavay (1986) achieved similar regeneration of $NH_4^+$-exchanged clinoptilolite-rich tuff by passing a solution of 20 g NaCl/L adjusted to pH > 11.5 by the addition of lime. Ammonia was stripped from the regenerating solution with air and the column was backwashed with 20 BV of de-ammoniated water in order to remove $CaCO_3$ and $Fe(OH)_3$ precipitates from the zeolite bed. No reduction in cation-exchange capacity was observed during 10 exchange-regeneration cycles.

Semmens et al. (1977) evaluated a biological method for regeneration of $NH_4$-exchanged clinoptilolite. Nitrifying bacteria converted $NH_4^+$ to $NO_3^-$ on the surface of porous zeolitic tuff in oxygen-enriched air. The nitrification process results in the formation of acidic or H-exchanged clinoptilolite. Because nitrifying bacteria activity is reduced in acidic media, a neutral pH was maintained by a continuous addition of soda. Complete regeneration was achieved within two hours if the concentration of dissolved oxygen was >6 mg/L. The CEC of the clinoptilolite-rich tuff did not change after 40 exhaustion-regeneration cycles.

Ammonia can also be evolved from exchange sites by heating clinoptilolite between 350-450°C in a stream of air (Szymansky et al. 1960). After $NH_3$ devolatilization, H-exchanged sites are formed, and the clinoptilolite-rich material can again be used for the ion exchange of $NH_4^+$, which is highly selective over $H_3O^+$. Because of the high-energy costs and the technical difficulties associated with the heating process, this method is not generally used in water treatment.

Albertin et al. (1994) used a recycled 5% NaCl brine to remove $NH_4^+$ from spent zeolite columns. This method overcame difficulties encountered with the discharge of saline solutions used for regeneration of exhausted clinoptilolite-rich and phillipsite-rich columns producing drinking water in a pilot plant near Venice, Italy. The brine is stored in a tank, and $NH_4^+$ is removed from solution by break-point chlorination where chlorine is introduced until excess chlorine appears in the regenerating solution. At this point most of the $NH_4^+$ has been oxidized by the break-point chlorination process and is evolved from solution as $N_2$ gas.

## MUNICIPAL AND AGRICULTURAL WASTEWATER TREATMENT

### Removal of $NH_4^+$

Ammonium ion concentrations are at least one order of magnitude higher in municipal wastewaters than in natural waters and inorganic and organic impurities also occur in greater amounts. Furthermore, suspended solids (SS) are normally present in municipal wastewaters. Conventional biological wastewater treatment, which reduces the concentration of oxidizable impurities and produces secondary effluent, can be improved by aeration that results in nitrification of $NH_4^+$ by nitrifying bacteria. The nitrate is subsequently removed by denitrification under anaerobic conditions. Both steps are time consuming, require large treatment installations, and consume energy. Removal of $NH_4^+$ can be accomplished by ion exchange as described above. Permutite-type inorganic cation-exchange materials (i.e. synthetic aluminosilicates that are crystallographically amorphous) and the various organic ion-exchange resins have poor selectivities for $NH_4^+$; therefore, they have unacceptably low $NH_4^+$ exchange capacities and low regeneration efficiencies. Consequently, high operation costs and problems with the disposal of large volumes of brine are encountered. Clinoptilolite's high selectivity for $NH_4^+$ makes it promising for use in the removal of $NH_4^+$ from municipal wastewater. Several plants have been designed and built to treat municipal wastes using clinoptilolite-rich materials. A 27,000 $m^3$/d capacity plant at Lake Tahoe, California, used several hundred tons of clinoptilolite-rich tuff from the Hector deposit in California (Butterfield and Borgerding 1981), and even larger plants with 45,000 and 245,000 $m^3$/d capacities have been built in Virginia, USA (Gunn 1979). Several studies that illustrate the effective use of zeolite-rich materials for the removal of $NH_4^+$ and other impurities from municipal wastewaters are reported below.

Typically only a fraction of a zeolite's CEC is utilized before the breakthrough concentration of $NH_4^+$ is reached in a dynamic exchange system (i.e. flow-through, column exchange system). For example, Czárán et al. (1988) reported that only 0.2-0.3 mmol $NH_4^+$/g exchanged onto clinoptilolite-rich material under dynamic exchange conditions, instead of the theoretically maximum $NH_4^+$ exchange capacity of 1.1-1.4 mmol $NH_4^+$/g. The exchange capacity under dynamic exchange conditions depends on several factors, such as the particle size of clinoptilolite grains, $NH_4^+$ concentration and pH in the wastewater influent, flow rate of solution through columns, and contact time with the zeolite-rich material (e.g. length of exchange columns or filter beds). Smaller particle-size materials usually result in higher effective exchange capacities for $NH_4^+$; however, flow resistance through the bed often increases due to reduced permeability. Kalló (1990) suggested that the optimum particle size for clinoptilolite-rich material for $NH_4^+$ removal in these types of exchange systems is 0.5-2 mm. As might be expected, the effective $NH_4^+$ exchange capacity increases for zeolite-rich material as the $NH_4^+$ influent concentration increases (Kalló 1990). Horvathova (1986) suggested that an influent solution of pH 7 is optimum for $NH_4^+$ exchange under dynamic conditions. The effective $NH_4^+$ exchange capacity decreases as the flow rate increases through the column, and



Kalló (1990) recommended a flow rate of ~10 BV/h for optimum exchange of $NH_4^+$ in clinoptilolite-rich materials.

Although synthetic zeolites have higher total cation-exchange capacities, natural zeolites exhibit greater selectivity for $NH_4^+$. Metropoulos et al. (1993) compared $NH_4^+$ removal using Na-exchanged clinoptilolite-rich tuff from North Greece, mordenite-rich material from Nevada, USA, and natural ferrierite from Nevada, with Na-, K-, and Ca-forms of synthetic zeolite A (Carlo Erba, Italy). The Na-exchanged natural zeolites showed higher selectivities for $NH_4^+$ than synthetic zeolite A. Although the clinoptilolite-rich tuff had a lower CEC, it exhibited the best performance in $NH_4^+$ removal because of its high selectivity for $NH_4^+$ and its high ion-exchange rate.

Metabolic ammonia is a major pollutant in aquaculture systems, and natural zeolites along with other ion-exchange materials have been used to remove $NH_4^+$ from such polluted waters. For example, toxic $NH_4^+$ was removed from fish water tanks at the Seattle Aquarium in Seattle, Washington, by recycling the contaminated water through filter beds of clinoptilolite-rich material (Mumaw et al. 1981). The $NH_4^+$ concentrations in aquarium tank wastewater, which contained between 0.3-0.5 mg/L metabolic $NH_4^+$, was reduced to less than 0.1 mg $NH_4^+$/L by passing the water through a filter bed containing 850 kg of clinoptilolite-rich material at a flow rate of 190 L/min. The clinoptilolite-rich material retained 1 g $NH_4^+$/kg after about 10 days operation, at which point the clinoptilolite-rich filter bed was regenerated by back washing with saltwater.

Ciambelli et al. (1985a) determined the physicochemical characteristics and the $NH_4^+$ ion-exchange properties of Neapolitan yellow tuff from Italy, which contains mostly phillipsite and some chabazite, and compared it with clinoptilolite-rich tuff from near Hector, California. The $Na^+/NH_4^+$ cation-exchange isotherms indicated that phillipsite is more selective for $NH_4^+$ than clinoptilolite and the rate of cation exchange is higher for phillipsite than for clinoptilolite (Aiello and Nastro 1984). When Na-forms of the two zeolites were ion exchanged with solutions containing different competing cations, e.g. to simulate aquaculture systems, $NH_4^+$ uptake was found to be comparable for the two zeolites. However, phillipsite exhibited higher selectivity for $NH_4^+$ at equilibrium than clinoptilolite. Nevertheless, the practical application of phillipsite-rich tuff is rather limited because its mechanical strength is lower than that of most clinoptilolite-containing rock (see Liberti et al. 1986a).

Throughout the years, many methods have been studied for treating wastewaters associated with animal production, e.g. wastewater from cattle, swine, and poultry sewage pits or lagoons. Natural zeolites have been effectively used to treat these wastewaters. Passaglia and Azzolini (1994) reported the use of zeolite-rich tuff from Italy, containing different amounts of chabazite and phillipsite, for treating wastewater from swine sewage. Sewage wastewater was percolated through fixed beds of zeolite-rich materials in their original form (i.e. native exchange cations) and in their Na-exchanged forms after regeneration with NaCl. Effective $NH_4^+$ exchange capacities of zeolite-rich materials in their original form ranged from 0.4-0.9 meq $NH_4^+$/g. Sodium and $Ca^{2+}$ were the primary cations removed by $NH_4^+$ from zeolite exchange sites. Potassium ions were also removed from the sewage wastewater, although more $NH_4^+$ was exchanged by the zeolites, likely due to its greater concentration in the wastewater suppressing the exchange of $K^+$. Effective $NH_4^+$ exchange capacities of Na-forms of the zeolites after regeneration with the Na solution increased to 1.2-1.7 meq $NH_4^+$/g.

Wastewater (150 $m^3$/d) from a pig farm with 10,000 pigs was treated in a cascade multi-step system using mechanical, chemical, and biological processes (Zubály et al. 1991). Large suspended particles were first removed by grating the sewage. Particles

removed by the grate were composted and used as organic fertilizer. Suspended particles, colloids and dissolved organic and inorganic species not removed by the grate were then passed through a channel (six 20 m sections separated by barrages). Approximately 20 $m^3$ of clinoptilolite-rich tuff (3-10 mm) from the Tokaj Hills deposit in Hungary were placed in each section. The zeolite filters removed 100% of oils and fats, 98% of suspended solids, and 95% of dissolved organic and inorganic impurities from the wastewater. Zeolite filters successively removed these impurities for two years at which point they became exhausted. The exhausted zeolite material was used as a fertilizer. Effluent from the treated wastewater was used to water trees in an orchard operation. These studies suggest that zeolites may be used to treat these types of wastewaters; however, additional studies are needed to determine whether zeolites can efficiently and economically remove pollutants such as $NH_4^+$ from wastewaters of animal production in large feedlots.

**Zeolite bed regeneration**

As pointed out above, zeolite beds must be regenerated so that the zeolite can be economically reused once the beds have been exhausted after the treatment of municipal or agricultural wastewaters. For most applications, cations, e.g. $Na^+$, that easily exchange with $NH_4^+$ are used in the regeneration process. Several processes that have been successfully used to remove $NH_4^+$ from spent zeolite beds are described below.

A clinoptilolite-rich bed was effectively regenerated with solutions of 3% NaCl or $CaCl_2$ after the bed had been used to remove $NH_4^+$ from biologically treated wastewater (Linne and Semmens 1985). Some BV of treated water in which $NH_4^+$ had been removed was fed back through the outlet of the clinoptilolite-rich bed in order to remove precipitated impurities, which concentrated upstream in the bed, i.e. from the inlet to the outlet of the bed. This backwashing did not, however, affect the efficiency of $NH_4^+$ removal and aided in preventing plugging of the bed by the salt impurities.

A clinoptilolite-rich tuff of high $NH_4^+$ exchange capacity (2.18 meq $NH_4^+$/g) from near Death Valley Junction, California, was used in packed columns for removal of $NH_4^+$ from pond waters (Williford and Reynolds 1992). Although columns were regularly regenerated with salt solution the cation-exchange capacity decreased with use. The decrease was attributed to the presence of organic material, especially algae in the natural pond water, which partly coated the external surfaces of zeolite grains, thereby decreasing the accessibility of $NH_4^+$ to zeolite exchange sites. Frequent back flushing of the zeolite column was required in order to avoid fouling of the system by algae and other organics.

Phillipsite-rich tuff from Italy was used to remove >95% $NH_4^+$ from municipal wastewater (Ciambelli et al. 1985b). The phillipsite-rich tuff was exhausted after 350 BV of municipal wastewater had passed through the columns. Exhausted beds were regenerated with NaCl solution that resulted in complete $Na^+$ exchange and the zeolite's effective $NH_4^+$ exchange capacity increased after regeneration. The phillipsite exhibited no loss of $NH_4^+$ exchange capacity after 35 cycles of operation.

Homonnay et al. (1993) disclosed in a patent a process for the regeneration of $NH_4$-exchanged clinoptilolite-rich material with Na-hypochlorite solution containing 0.5-1 mg/L iodine or bromine as a catalyst, which accelerated the oxidation of $NH_4^+$. Nontoxic nitrogen compounds form during the course of this oxidative regeneration; however, the ion-exchange capacity of clinoptilolite is unaffected and the regenerating solution can be recycled. Unfortunately, the authors did not suggest a practical application for the regeneration process.



Biological regeneration of $NH_4$-clinoptilolite has also been suggested as a means of regenerating zeolite beds used to treat municipal wastewaters, similar to the regeneration described earlier for the manufacture of drinking water. A clinoptilolite-rich tuff filtration system was used to remove $NH_4^+$ from fish rearing ponds at the Eagle Creek National Fish Hatchery in Oregon, USA (Horsch and Holway 1984). Daily agitation of the filter bed with air prevented the conduits from plugging and the clinoptilolite-rich materials from fouling with organic and particulate matter. Nitrification (i.e. oxidation of $NH_4^+$ to $NO_2^-$ to $NO_3^-$ by nitrifying bacteria) began in the filtration system 15 days after start up of the treatment process, i.e. after the start of $NH_4^+$ removal from the rearing pond water. The $NH_4^+$ removal efficiency of clinoptilolite used as a biological filter was 89%. At no time did $NH_4^+$ or $NO_2^-$ reach toxic levels. Oxidative bacterial regeneration of the clinoptilolite filter was accomplished within one week after it was taken off line from removing $NH_4^+$ from the pond water, making this process an alternative to brine regeneration of clinoptilolite.

Instead of regenerating $NH_4^+$-spent zeolite beds, the spent zeolite may be used as a fertilizer in agricultural applications (Mori and Tsuneyoshi 1986). An $NH_4^+$-spent mordenite (presumably from Itado, Japan) with an N content of 1 mg/g was applied to rice paddy fields at an application rate of 5 kg/$m^2$. The cation-exchange capacity of the soil was increased threefold by the amendment and the authors suggested that the zeolite may be used as a slow-release fertilizer (see Ming and Allen, this volume).

Preston and Alleman (1994) also reported the use of a clinoptilolite-rich material for $NH_4^+$ removal via ion exchange and as a biofilter medium for the oxidation of $NH_4^+$ by nitrifying bacteria. Nitrifying bacteria produce protons during the oxidation of $NH_4^+$, hence this process can increase solution acidity over time. The slightly alkaline $NH_4^+$ wastewater will usually neutralize the solution; however, neutralization of the acidity by the addition of lime may be required to maintain a slightly alkaline solution. The metabolism of nitrifying bacteria decreases with increasing acidity, eventually ending in bacteria death. Preston and Alleman (1994) found that this system remained viable through numerous cycles, and a single cycle may reach a maximum operation period of 60 h. They suggested that the negatively charged nitrifying bacteria are electrostatically bound or immobilized on zeolite crystal surfaces. The immobilization of nitrifying bacteria on clinoptilolite may enhance the nitrification process in wastewater treatment.

Simultaneous nitrification and denitrification have been suggested for removal of nitrogen from municipal wastewater (Halling-Soerensen and Hjuler 1992). A clinoptilolite-rich material was used as a support medium for microorganisms. The porous structure of the rock provided alternating aerobic and anoxic conditions, where an aerobic pattern developed as zeolitic grains contacted water high in dissolved oxygen that enhanced nitrification. Oxygen is consumed and $H^+$ is produced during the nitrification process, until anoxic conditions develop and denitrification begins. Simplified reactions for nitrification and denitrification can be expressed as follows:

$$Z^- NH_4^+ + 2\ O_2 \rightarrow Z^- H^+ + HNO_3 + H_2O \qquad \text{(nitrification)}$$

$$2\ HNO_3 + 5\ H_2 \rightarrow N_2 + 6\ H_2O \qquad \text{(denitrification)}$$

where $Z^-$ is the zeolite substrate. Reducing agents other than $H_2$ (e.g. ethanol) may be used in the denitrification process. The biological reactors were operated for 6 months during which the influent wastewater contained between 30 and 5000 mg $NH_4^+$/L. These reactors removed a maximum of 13.5 kg N/$m^3$d with an efficiency of 95.8%. Nitrogen removal in this process is faster than with technologies using suspended cultures, i.e. without any support for the microorganisms.

Clinoptilolite has been used in combination with aerated mechanical sand filters for removal of peak concentrations of $NH_4^+$ from domestic wastewater (Baykal and Guven 1997). High-efficiency $NH_4^+$ removal was achieved when sufficient time was allowed for the development of nitrifying bacteria colonies. The effective $NH_4^+$ exchange capacity of clinoptilolite decreased 10% after 10 cycles of regular operation and regeneration.

The simple removal of N and P nutrients by sorption from secondary water of biologically treated municipal wastewater has been attempted using natural zeolites. Up to 62% $NH_4^+$ and 15% P were removed by adding 2-50 g/L powdered zeolitic rock (presumably clinoptilolite-rich rock from Australia) to the secondary wastewater (Komarowski et al. 1994).

### Zeolites as coagulating agents

Natural zeolites may be used along with other compounds as coagulating agents to remove suspended solids from wastewater. This approach is especially attractive for the removal of microorganisms, e.g. in removal of bacteria from drinking water using clinoptilolite-rich tuff and $Al_2(SO_4)_3$ as described above (Grigorieva et al. 1988). Adherence of microorganisms to zeolite particles may also increase biological activity, such as in the ZeoFlocc process described in detail below.

Kvopkova et al. (1988) removed petroleum contaminants from the wastewater of a textile plant by a flocculation process. The textile plant wastewater effluent contained 12.6 mg/L petroleum products with a COD of 537 mg/L and was treated by three different coagulating agents: (a) 1.4 mmol/L $FeSO_4$ and 3.2 mmol/L CaO; (b) same as (a) plus 0.2 mg/L polyacrylamide; and (c) same as (a) plus 100 mg/L clinoptilolite-rich tuff from Eastern Slovakia and 2.5 mg/L diethylenetriamine-stearic acid condensate ($C_{10}$-$C_{30}$ carboxylated or quaternary amines). Residual levels of the petroleum products and COD values were lowest in the effluent receiving the clinoptilolite treatment after sedimentation (see Table 1).

**Table 1.** Removal of petroleum products and chemical oxygen demand (COD) from wastewater of a textile plant treated with various flocculation agents (Kvopkova et al. 1988).

| *Flocculant dosage* | *Petroleum products* | *COD* |
|---|---|---|
| | *mg/L* | *mg/L* |
| None added | 12.6 | 537 |
| (a) 1.4 mmol $FeSO_4$/L and 3.2 mmol CaO/L | 3.2 | 192 |
| (b) Same as in (a) and 0.2 mg polyacrylamide/L | 2.7 | 172 |
| (c) Same as in (a) and 100 mg clinoptilolite/L with 2.5 mg diethylenetriamine-stearic acid condensate/L | 2.1 | 153 |

### Complex treatment technologies

Municipal wastewaters often contain considerable amounts of phosphorous impurities, mainly as $PO_4^{3-}$ in the range of 5-30 mg P/L, which can usually be removed in the form of insoluble compounds such as phosphates of multivalent metals. The solubility of di- and trivalent metal orthophosphates is relatively low, e.g. a few mg P/L depending on pH, temperature, and ion concentrations. The widely accepted method for removing phosphate is to precipitate phosphate by adding lime (e.g. $CaCO_3$) to the wastewater. Although this method is simple, it often results in a treated wastewater stream with some $PO_4$ because the solubility of $Ca_3(PO_4)_2$, formed from the lime addition, is not negligible. Calcium-exchanged zeolites may offer an effective alternative for the removal of phosphate from municipal wastewater. For example, Ca-clinoptilolite-rich tuff from Japan added to wastewater resulted in the precipitation of phosphates. Apparently, $Ca^{2+}$ on the zeolite exchange sites reacted with solution phosphate to precipitate complex calcium phosphate salts associated with the zeolite (Kurita Water 1985).



Several more complex treatment processes have been designed that use natural zeolites for the removal of $NH_4^+$, phosphates, and other contaminants from wastewaters. Two of these processes (RIM-NUT and ZeoFlocc processes) are briefly described below.

***RIM-NUT process.*** A promising technology was developed by Liberti et al. (1984) for removing $NH_4^+$ and phosphates from domestic secondary effluent (i.e. biologically oxidized, settled, and chlorinated effluent). Compounds in the secondary effluent serve as nutrients for microorganisms, which are responsible for creating eutrophic conditions in the wastewater (i.e. depletion of dissolved $O_2$ by microorganisms). A process termed RIM-NUT (from the Italian phrase for "removal of nutrients") was developed as a method for reducing the eutrophic potential of municipal and industrial wastewater by combining ion exchange from natural zeolites with precipitation processes to selectively remove $NH_4^+$ and/or phosphate ions from the wastewater. A pilot plant of 10 $m^3/h$ capacity was built in the West Bari Sanitation Station in Italy and a flow diagram of the process is shown in Figure 1 (Liberti et al. 1986a).

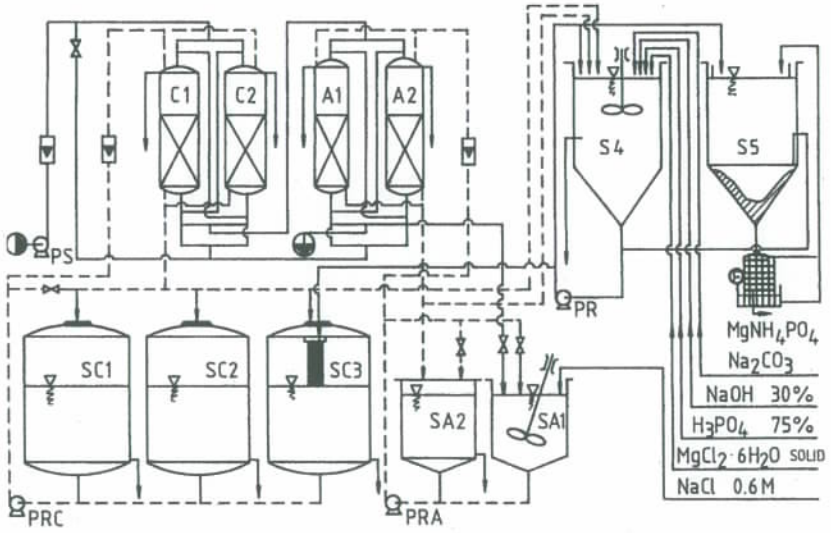


**Figure 1.** Flow sheet of the RIM-NUT process plant (C1 & C2 = cationic-exchange columns 1 & 2; A1 & A2 = anionic-exchange columns 1 & 2; SC1, SC2, & SC3 = cationic regeneration reservoirs 1, 2, & 3; SA1 & SA2 = anionic regeneration reservoirs 1 & 2; S4 & S5 = settler thickener tanks 4 & 5; F = filtration apparatus; solid line (—) = wastewater treatment streams; dashed lines (---) = 0.6 N NaCl regeneration streams; PS, PRC, PRA, & PR = pumps of different capacities (Liberti et al. 1986a).

The process is based on a combination of $NH_4^+$ and $PO_4^{3-}$ ion-exchange reactions, where a zeolite (in this case clinoptilolite-rich tuff from the Anaconda Copper Company, Denver, Colorado) was used to remove $NH_4^+$ according to the following reaction:

$$Na^+\text{-}Z^- + NH_4^+ \Leftrightarrow NH_4^+\text{-}Z^- + Na^+$$

where $Z^-$ is the negatively charged zeolite framework. A strongly basic anion-exchange resin (e.g. Amberlite IRA 458 from Rohm and Haas, Philadelphia, Pennsylvania, or Kastel A 501 D from Ausimont-Montedison, Milano, Italy) was used to exchange $PO_4^{3-}$ from the wastewater as follows:

$$2\ R^+\text{-}Cl^- + HPO_4^{2-} \Leftrightarrow R_2^{2+}\text{-}HPO_4^{2-} + 2\ Cl^-$$

where $R^+$ is the anion-exchange resin.

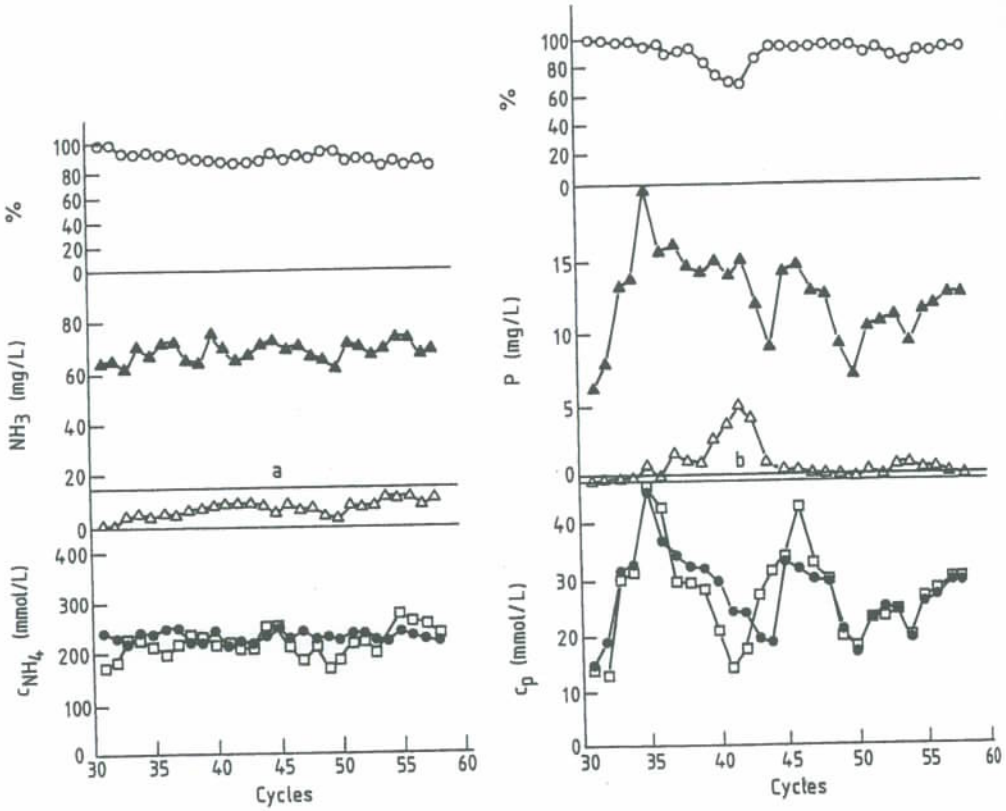


**Figure 2 (left).** Removal of $NH_4^+$ during the RIM-NUT process for successive exhaustion-regeneration cycles [Key for symbols: o = % removal of nutrient $NH_4^+$; Δ = $NH_4^+$ concentration in secondary effluent; a = Italian regulatory limit for discharge of $NH_4^+$ into sea; • = ion exchange capacity of clinoptilolite in service; □ = release of $NH_4^+$ in regeneration, $C_{NH4}$ = exchange capacity with respect to $NH_4$ (mole $NH_4^+/m^3$ of exchanger) (Liberti et al. 1986b).]

**Figure 3 (right).** Removal of $HPO_4^{2-}$ during the RIM-NUT process for successive exhaustion-regeneration cycles. [Key to symbols same as in Fig. 2 except for P instead of $NH_4^+$; line labeled b is the Italian regulatory limit for phosphorus discharge into lakes) (Liberti et al. 1986b).]



Two cation (C1 and C2 in Fig. 1) and two anion (A1 and A2 in Fig. 1) exchangers of 0.45 $m^3$ each were installed to ensure continuous operation by alternating between ion exchange and regeneration. Removal efficiencies for $NH_4^+$ and hydrophosphate are shown in Figures 2 and 3, respectively (Liberti et al. 1986b). The average phosphate removal from the wastewater was ≥95%. A major decrease of efficiency was observed during cycles 37-42 (Fig. 3) when the inlet concentrations of other anions were high, i.e. 105 mg $NO_3^-$/L and 55 mg $SO_4^{2-}$/L were present in the influent in addition to 15 mg $PO_4^{3-}$/L, and these anions likely retarded or slowed the exchange of $HPO_4^{2-}$ on the anion-exchange resin.

Ion exchangers were regenerated with 0.6 N NaCl after passing 70 BV of wastewater for 3 h through the exchange columns. The regeneration of clinoptilolite was carried out four times with 6 BV of NaCl and the anion-exchange resin was regenerated with 2 BV of NaCl. The initial portions of the exhausted solutions, which contained $NH_4^+$ and $HPO_4^{2-}$ in the highest concentrations, were accumulated in a settler tank (S4 in Fig. 1). Magnesium and phosphate salts (e.g. $MgCl_2$ and NaOH + $H_3PO_4$) were added to regeneration solutions (which contained $NH_4^+$ and $HPO_4^{2-}$) in order to establish a stoichiometric ratio of $Mg:NH_4:PO_4 = 1:1:1$ at pH = 9. A $MgNH_4PO_4$ precipitate formed according to the reaction:

$$Mg^{2+} + NH_4^+ + HPO_4^{2-} \rightarrow MgNH_4PO_4 + H^+$$

The end product ($MgNH_4PO_4$) resulted in the production of a slow-release premium quality fertilizer with 7% organic content, which originated from the suspended solids (SS) and bio-resistant organics in the wastewater. The product contained negligible traces of heavy metals and had no pathogenic hazards. Heavy metals, if present, were likely removed by clinoptilolite at the high pH of wastewater during the treatment. The negatively charged pathogenic bacteria, which adsorbed on positively charged quaternary ammonium groups of the strongly basic anion-exchange resin, were killed by osmotic shock during the elution of ion exchangers with the concentrated NaCl regeneration solution and by the alkalinity of the precipitating solution (Liberti et al. 1987). After six months of operation (treatment of 120,000 BV of municipal secondary effluent), both ion exchangers were fouled to some extent by strongly bound contaminants or ions. Libertí et al. (1987) reported that both clinoptilolite and the ion-exchange resin lost ~3% of their effective ion-exchange capacities. The economic feasibility of this process is still being evaluated and is primarily influenced by the price and amount of the additional chemicals required to produce the high-grade, premium fertilizer (Liberti et al. 1987). A second plant using the RIM-NUT process was built and evaluated in South Lyon, Michigan, USA (Liberti et al. 1988).

A less sophisticated method was suggested for simultaneous removal of $NH_4^+$ and $PO_4^{3-}$ from wastewater effluents using phillipsite-rich tuff (Garcia et al. 1992b). Volcanic tuff with abundant phillipsite (Tenerife, Canary Islands, Spain) was studied as a water purifying bed for removing inorganic contaminants, pathogenic bacteria, and dissolved organic matter. The input and output concentrations were determined at constant flow rate. The percolation bed retarded about 70% of the total $NH_4^+$ and 14% of the total $PO_4^{3-}$ after 10 days of operation. Phosphate removal was attributed to the precipitation of Ca and Mg phosphates. Calcium and $Mg^{2+}$ were introduced into solution after being replaced at zeolite exchange sites by $NH_4^+$. The removal of soluble organic matter resulted in 20-50% reduction of COD and in complete removal of bacteria in the processed wastewater.

***ZeoFlocc process.*** The ZeoFlocc process is based on the ability of microorganisms to adhere to zeolite-rich particles, thereby increasing the biological activity and efficiency of municipal wastewater treatment. ZeoFlocc is a patented process that derives its roots

from zeolite (Zeo) and the flocculation (Flocc) of bacteria with the zeolite (Kiss et al. 1990). The ZeoFlocc technology is being used in Hungary, Germany, Austria, Switzerland, and Australia and the estimated wastewater treated by this technique is now over 400,000 $m^3$/d.

The increase of biological activity in the ZeoFlocc process can be attributed to the formation of bacteria-flocs around zeolite particles that result in a greater number of smaller bacteria flocs. The sizes of bacteria flocs without zeolite additions are between 0.4 to 2 mm, whereas the bacteria flocs associated with zeolite particles are smaller than 0.3 mm. As might be expected, the transport of oxygen and nutrients requires shorter time in the smaller flocs than in the larger ones. It is also likely that the nitrification process is accelerated because $NH_4^+$ is available as a nutrient source from zeolite exchange sites. As an example, the addition of 50 g of clinoptilolite-rich powder from Tokaj Hills, Hungary, with a particle size of 40-160 µm (note the small particle size) to 1 $m^3$ of wastewater increased the rate of the biological wastewater process by at least 25% (Oláh et al. 1991). Kallo (1995) conducted a comparison test of the ZeoFlocc process using clinoptilolite-rich materials, synthetic zeolites, perlite, and charcoal. The rates of oxygen consumption in the biological treatment of sludge wastewaters were 4, 4, 7, 32, and 77 mg $O_2$/Lh when the same relative amounts of synthetic zeolites A and X, perlite, charcoal, and clinoptilolite-rich tuff from Tokaj Hills, Hungary, respectively, were added to the wastewater.

Simultaneous removal of $PO_4^{3-}$ during the ZeoFlocc process may be achieved by adding trivalent metal cations, particularly $Fe^{3+}$, to municipal wastewaters. For example, by adding 1.16-1.95 atoms of Fe as a concentrated solution of $FeClSO_4$, which is a secondary by-product of iron manufacturing called Ongroflok, and a suspended clinoptilolite powder from Tokaj Hills, Hungary, to the equivalent of 1 atom of P in the wastewater, the $PO_4^{3-}$ content of the wastewater effluent was decreased from 15-20 mg/L to 1-1.5 mg/L (Oláh et al. 1989). Without the addition of the suspended zeolite, 1.7-2.5 atoms of Fe for each P atom in wastewater were required for similar phosphate removal.

The results of the ZeoFlocc process with clinoptilolite and $Fe^{3+}$ additives for biological treatment plants of different capacities are summarized in Table 2 (Kalló 1995). The clinoptilolite and $Fe^{3+}$ additions significantly decreased the effluent COD, BOD, $NH_4^+$, $PO_4^{3-}$, and suspended solids and increased $NO_3^-$ for the various capacities compared with control tests without the additives. The significant increase in the $NO_3^-$ content with zeolite addition suggests faster rates of nitrification and therefore an increase in biological activity compared with treatments not receiving zeolite additives. The nitrification rate was slowed by increasing the biological load from 0.04 to 0.14 kg BOD/kg d (e.g. see BOD values in Table 2 for treatment plants of 100 and 43 $m^3$/d capacity) and more $NH_4^+$ remained in the effluent (e.g. 10 and 1 mg $NH_4^+$/L for 43 and 100 $m^3$/d treatment plants, respectively). The remaining $NH_4^+$ can be removed from the effluent by ion exchange with clinoptilolite-rich materials as discussed above (Kalló 1995).

The changes in the removal of phosphates from wastewater treated with clinoptilolite and $Fe^{3+}$ for a 2000 $m^3$/d treatment plant are shown over a 60-day period in Figure 4 (Oláh et al. 1991). Clinoptilolite and $Fe^{3+}$ additions maintained the effluent P concentration below the limit allowed from biologically treated water during most of the 60-day ZeoFlocc process. The high phosphate removal efficiency in the ZeoFlocc process is due to retention of Fe (or Al) in zeolitic rock as oxides and/or hydroxides that react with the phosphate ions by specific adsorption processes. Phosphate concentrations in the effluent begin to increase two days after clinoptilolite and $Fe^{3+}$ additions are stopped (see last 6 days in Fig. 4). When only $Fe^{3+}$ is introduced in the biological treatment, $PO_4^{3-}$ concentrations in the effluent begin to increase about 12 hours after the $Fe^{3+}$ addition is stopped.



**Table 2.** Mean composition of wastewater in biological treatment plants of various capacities for a 2-week period after establishment of steady-state conditions (Kallo 1995).

| | | Additives | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| *Capacity* | *Sewage*† | *Clinoptilolite* | *$Fe^{3+}$* | *COD*‡ | *BOD** | *$NH_4^+$* | *$NO_3^-$* | *$PO_4^{3-}$* | *Susp. solid* |
| *$m^3$/d* | | mg/L | | | | | | | |
| **43** | Inlet | | | 161 | 89 | 32.5 | 1.6 | 4.0 | 88 |
| | Control | - | - | 69 | 16 | 28.6 | 16 | 3.0 | 27 |
| | Test | 65 | 17.5 | 44 | 9 | 10.0 | 30 | 0.4 | 15 |
| **100** | Inlet | | | 306 | 155 | 32.1 | 0.7 | 5.4 | 144 |
| | Control | - | - | 54 | 13 | 20.3 | 24 | 3.8 | 17 |
| | Test | 43 | 23.2 | 36 | 8 | 1.0 | 57 | 0.5 | 9 |
| **400** | Inlet | | | 83 | 32 | 22.3 | 2.3 | 2.9 | 22 |
| | Control | - | - | 37 | 8 | 0.8 | 53 | 2.2 | 10 |
| | Test | 35 | 16.0 | 28 | 5 | 0.6 | 85 | 1.0 | 5 |
| **1850** | Inlet | | | 411 | 194 | 41.1 | 0.6 | 5.5 | 69 |
| | Control | - | - | 68 | 19 | 6.4 | 28.2 | 3.6 | 35 |
| | Test | 44 | 20.9 | 63 | 18 | 2.8 | 42.1 | 0.9 | 18 |

† Inlet = raw sewage inlet to aerator; Control = sewage treated without additive after primary settling tank; Test = sewage treated with additive after primary settling tank

‡ COD = Chemical Oxygen Demand * BOD = Biological Oxygen Demand

Recently, highly dispersed FeOOH-coated clinoptilolite has been found to be a more effective agent to add to the ZeoFlocc process for phosphate removal from wastewater (Illés et al. 1997). The FeOOH coating on clinoptilolite is achieved by dry grinding (in air) powders of $FeSO_4 \cdot 7H_2O$ (by-product of iron manufacturing), lime or limestone, and a clinoptilolite-rich material (Tokaj Hills, Hungary). The grinding results in the solid-state transformation of $FeSO_4 \cdot 7H_2O$ into a highly dispersed, FeOOH-coated clinoptilolite support. Kalló and Papp (1999) have shown that this material is effective in removing phosphate from wastewaters, and the biological activity for the FeOOH-coated clinoptilolite system is similar to the clinoptilolite and $Fe^{3+}$ system.

Flocs produced with zeolite seeds are of higher bulk density than flocs without zeolite seeds; therefore, the zeolite/bacteria flocs settle faster, thereby reducing the concentration of suspended solids in the effluent leaving the secondary settling tank

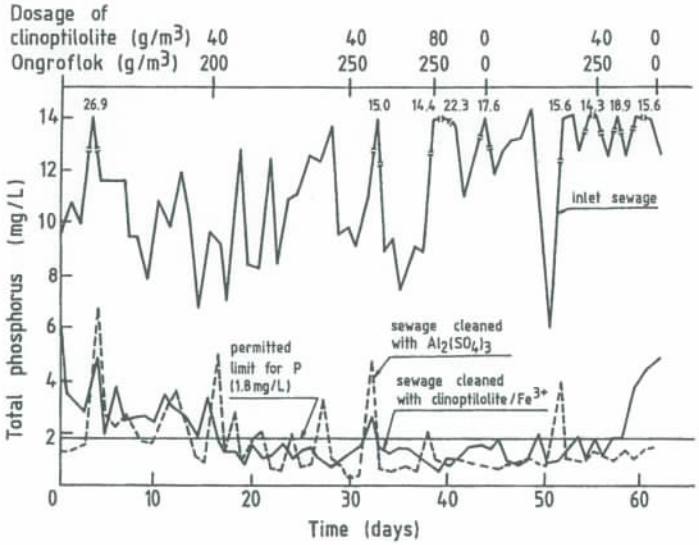


**Figure 4.** Comparison of phosphorus concentrations in inlet raw sewage to phosphorus concentrations in biologically treated effluents with either additions of clinoptilolite + $Fe^{3+}$ or with aluminum sulfate (Kalló 1995).

(e.g. see the corresponding values for suspended solids in Table 2). It has been reported (Fujiwara et al. 1987) that the separation of sludge solids from a supernatant is facilitated by adding 0.3 wt % clinoptilolite to the sludge. The settling rate of the sludge was nearly twice as fast with the clinoptilolite flocculent as that observed with a commercial flocculent. Sludge removed during the ZeoFlocc process has a higher sedimentation rate than that removed in conventional biological treatment (Oláh et al. 1989, Mucsy 1992). The volume of zeolite-containing sludge, which is easier to dewater, is nearly 50% less than the sludge without zeolite additives under similar conditions. Composting of zeolite-containing sludge proceeds similarly to unamended sludge, but water leached through zeolite-containing sludge contains only 2/3 of the $NH_4^+$ and oxidizable compounds compared with water leached from unamended sludge (Papp 1992).

Kalló (2000) added 0, 10, 20, and 30 vol % composted sludge amended with clinoptilolite-rich tuff to a substrate consisting of 50% sand and 50% peat (Table 3). No elemental toxicities were observed in lettuce and cabbage grown in the sludge amended soils and plant productivity increased with increasing clinoptilolite/sludge content in the soil. Yields of onion, spinach, tomato, and bean were similarly increased by the addition of ZeoFlocc-treated sludge (Kalló 1995). Heavy-metal accumulation in plants grown in soils amended with ZeoFlocc-treated sludge did not exceed levels permitted for human consumption. The Zn plant tissue concentrations of several plant types grown in soils amended with ZeoFlocc-treated sludge are listed in Table 4. It is likely that $Zn^{2+}$ and other heavy metals are exchanged onto zeolite exchange sites, where these heavy metals are very slowly released into solution at soil pHs of greater that 4 (Dyer 1988).

Clinoptilolite-rich tuff has been added directly to sewage sludge in attempts to reduce the release of heavy metals when the treated sludge is applied as a beneficial source of organic matter and plant nutrients (Weber et al. 1983). Varying amounts of anaerobically digested municipal wastewater sludge and clinoptilolite granules (< 0.8 mm) from the Washakie Basin deposit in Wyoming, USA, were added to soil. The uptake of Cu, Cd, Zn, Mo, and Ni by sorghum-sudangrass grown in the sludge and zeolite-



**Table 3.** Plant productivity of cabbage lettuce and common white cabbage grown in soil amended with varying amounts of sludge treated with clinoptilolite-rich materials as a by-product of the ZeoFlocc process (Kalló 2000).

| *Added sludge to soil* | *Cabbage lettuce* | *Common white cabbage* |
|---|---|---|
| *volume %* | *g/plant* | *g/plant* |
| 0 | 220 | 3760 |
| 10 | 237 | 4110 |
| 20 | 244 | 4600 |
| 30 | 257 | 4730 |

**Table 4.** Zinc content of vegetables grown in soil amended with varying amounts of sludge treated with clinoptilolite-rich materials during the ZeoFlocc process (Kalló 2000).

| *Added sludge* | *Red pepper* | *Cabbage lettuce* | *Spinach* | *Radish* | *Onion* |
|---|---|---|---|---|---|
| *volume %* | *mg Zn/kg* | | | | |
| 0 | 35 | 65 | 81 | 28 | 29 |
| 10 | 46 | 125 | 104 | 33 | 46 |
| 20 | 44 | 134 | 105 | 44 | 53 |
| 30 | 55 | 155 | 145 | 42 | 56 |

amended soils did not vary significantly from plants grown in sludge amended soils without zeolite amendments. The results presented here indicate that the addition of clinoptilolite-rich tuff along with the sludge is less effective for retention of heavy metal retardation when compared plants grown in soils where clinoptilolite has been added to the sludge during the ZeoFlocc process as described above.

## REMOVAL OF HARMFUL METAL CATIONS FROM WATER

Natural zeolites can be used as ion exchangers for removal of *radioactive* cations such as $Cs^+$ and $Sr^{2+}$ and *heavy-metal* cations such as $Cu^{2+}$, $Cd^{2+}$, $Zn^{2+}$, $Ni^{2+}$ and $Pb^{2+}$. Radioactive $Cs^+$ and $Sr^{2+}$ may be present in recycling waters of atomic power stations or as environmental contaminants after accidents at atomic power stations. Heavy- or transition-metal cations appear in wastewaters of many sources, e.g. in the electroplating industry, photographic material processing, tannery processing, coke manufacturing industry, or even in well water as iron and manganese. The zeolite-rich material chosen for use in removing these potentially harmful cations from wastewater must rely on their cation-exchange selectivities for the appropriate cation as well as their chemical, physical, and thermal stabilities.

### Cesium and strontium

Ames (1959) concluded that clinoptilolite-rich tuff from Hector, California, was the most promising of 15 different zeolites tested for $Cs^+$ removal from solutions containing competing cations such as $Al^{3+}$, $Fe^{3+}$, $Ba^{2+}$, $Sr^{2+}$, $Ca^{2+}$, $Mg^{2+}$, $Rb^+$, $K^+$, $NH_4^+$, $Na^+$, and $Li^+$ in large concentrations. The concentrations of competing cations ranged from 0.5 to 6.0 N, whereas that of $Cs^+$ was as low as $1.75 \times 10^{-8}$ N $^{137}Cs^+$. $Cs^+$ breakthrough was

determined at linear flow rates of 0.9-10 m/h at 25 and 60°C. The high selectivity of clinoptilolite for $Cs^+$ was shown by the effective removal of $Cs^+$ in spite of the high concentration differences between $Cs^+$ and competing cations. Ames (1960) recorded the earliest application of clinoptilolite-rich material in removal of radioactive cations. He used clinoptilolite-rich tuff from the Hector deposit in California, to selectively remove $^{137}Cs$ and $^{90}Sr$ from the low-level radioactive wastewater of nuclear power plants. The advantage of natural zeolites over organic ion-exchange resins lies in their resistance to degradation in the presence of ionizing radiation and their low solubility. Zeolites can also be used for long-term storage of long-lived radioisotopes by drying a zeolite exchanged with radionuclide cations at 200°C and sealing the zeolite in a stainless steel container. Another radioisotope storage method is conversion of a radioisotope-loaded zeolite to glass (e.g. heating in air at 1100°C) having an extremely low radioisotope leaching rate (Sherman 1978).

Mercer and Ames (1978) presented a detailed description of the use of natural zeolites for the removal and fixation of radionuclides, including (1) removal of $^{137}Cs$ from high-level radioactive wastes; (2) decontamination of low- and intermediate-level wastes; and (3) fixation of radioactive wastes for long-term storage. They found that other natural zeolites, including chabazite, erionite, and mordenite, in addition to clinoptilolite, have high selectivities for $Cs^+$. Examples that illustrate these and other uses of zeolites for the removal of $^{137}Cs^+$ and $^{90}Sr^{2+}$ are given in Table 5.

**Table 5.** Applications of zeolites for the treatment of $Cs^+$ and $Sr^{2+}$ radioactive wastes (Mercer and Ames 1978, Dyer 1984).

| *Type of effluent* | *Location* | *Zeolite used* | *Isotopes removed* | *Plant details* |
|---|---|---|---|---|
| High-level radioactive waste | Hanford Nuclear Lab., Washington, USA | Linde AW-500 (chabazite) | $^{137}Cs$ | 8.4 $m^3$ zeolite bed processed millions of gallons of waste |
| Purification of product from above | Hanford Nuclear Lab., Washington, USA | Large-port mordenite | $^{137}Cs$, $^{90}Sr$ | Full-scale plant |
| Process condensate wastewater | Hanford Nuclear Lab., Washington, USA | Large-port mordenite | $^{137}Cs$, $^{90}Sr$ | |
| Low-level wastewater from fuel storage pond | Idaho National Engineering Laboratory, Idaho, USA | clinoptilolite (cp) | $^{137}Cs$, $^{90}Sr$ | 4 _ 0.15 $m^3$ cp columns 1900 $m^3$ water treated/$m^3$ zeolite |
| Evaporator overheads and miscellaneous wastewater | Savannah River Plant, Aiken, South Carolina, USA | Linde AW-500 (Chabazite) | $^{137}Cs$ | Treated 3077-10192 $m^3$ of overheads and 2019-1538 $m^3$ of miscellaneous wastewater/$m^3$ zeolite |
| Wastewater from fuel storage | British Nuclear Fuels, Sellafield, UK | clinoptilolite | $^{137}Cs$, $^{90}Sr$ | 4000 $m^3$ water/d processed |



Early success in using clinoptilolite-rich materials for $Cs^+$ and $Sr^{2+}$ removal in the nuclear industry was not reflected by worldwide applications of the zeolite for this purpose. One of the reasons contributing to the low usage worldwide was the general unavailability of clinoptilolite-rich materials and the lack of availability of a high-grade, clinoptilolite-rich rock at that time. Since then, clinoptilolite deposits have been located throughout the world and some of these deposits contain high-grade clinoptilolite (e.g. the Itaya mine in Japan and several deposits in the western USA). Because of the increased availability of high-grade clinoptilolite, its current use has increased in the treatment of radioactive wastes (Dyer 1984). Clinoptilolite is used in the United Kingdom to treat pond waters at installations of the British Nuclear Fuels and Central Electricity Generating Board, and its use is becoming standard practice in some areas.

As noted above, clinoptilolite-rich material is attractive for treating radioactive wastes because of its high selectivity for $Cs^+$ and $Sr^{2+}$. The ion-exchange distribution coefficients for $Cs^+$ and $Sr^{2+}$ in clinoptilolite when the counter ion is $Ca^{2+}$ and the normality of the solution is 0.0003 are listed as follows (Nikashina and Zaborskaya 1977):

$$K_{Cs} = 5.5 \times 10^4 \text{ (meq } Cs^+/g_{clinoptilolite})/(\text{meq } Cs^+/\text{ml } H_2O) \text{ and}$$

$$K_{Sr} = 3 \times 10^3 \text{ (meq } Sr^{2+}/g_{clinoptilolite})/(\text{meq } Sr^{2+}/\text{ml } H_2O).$$

The high selectivity of clinoptilolite for $Cs^+$ and $Sr^{2+}$ was instrumental in fostering its use for removal of radioactive isotopes from the discharge water of nuclear power plants in the former Soviet Union (Tarasevich 1981). This selectivity property was exploited in developing technology to decontaminate effluents produced from cleaning clothes in washing machines after the Chernobyl accident in 1986. Water with $10^{-4}$ to $10^{-5}$ Ci/L activity was filtered through a bed of clinoptilolite-rich granules from the Trans-Carpathian area of Ukraine. The removal of $^{137}Cs$ was 80-100% in static batch processes and 40-80% in dynamic flow-through column systems. The adsorption capacity for clinoptilolite-rich material was $4 \times 10^{-6}$ Ci/kg under dynamic flow-through conditions (Zaitsev et al. 1995). In another application, nearly 500,000 tons of zeolitic-rich rock from the Trans-Carpathia area was used in an attempt decontaminate rivers polluted with these radioactive wastes after the Chernobyl accident.

Natural zeolites have also been used to reduce the migration of radioactive cations in contaminated soils. For example, the uptake of $Sr^{2+}$ by *sorghum-sudangrass* from a Sr-contaminated soil amended with 32 t/ha of clinoptilolite-rich tuff from Washakie Basin, Fort Le Clede, Wyoming, USA, decreased from 38 to 24 mg $Sr^{2+}$/kg, and no reductions were detected in plant uptake for other cations such as $Mg^{2+}$, $Na^+$, $Fe^{3+}$, and $Mn^{2+}$ (Weber et al. 1983). Other potential applications to reduce or eliminate radioactive $Cs^+$ and $Sr^{2+}$ contamination by adding natural zeolites to soils are discussed by Ming and Allen (this volume).

## Heavy metals

In most cases, it is cheaper to mine natural zeolites in near-surface deposits than to produce an equivalent quantity of synthetic zeolites because the price of natural zeolites is usually about 80-90% lower than that of the cheapest synthetic zeolites. As a result of the low cost of natural zeolites and the fact that their native exchangeable cations are relatively safe to humans, plants, and animals (e.g. $Na^+$, $Ca^{2+}$, $Mg^{2+}$, $K^+$), natural zeolites are especially attractive alternatives for removing undesirable heavy-metal ions from effluent wastewaters mainly of industrial origin (Kesraoui-Ouki et al. 1994). The exchange of multivalent metal ions can be achieved over a pH range between 3-6. However, the pH must be sufficiently low to ensure the solubility of metals (i.e. cationic form in solution) but high enough to minimize $H^+$ exchange instead of metal cation

exchange onto zeolite exchange sites and to minimize destruction of zeolite structure by hydrolysis (Dyer 1988). Zeolites are highly selective for various heavy metals and have been considered suitable for the removal of heavy metals from wastewaters (Blanchard et al. 1984, Rustamov et al. 1991, Takasaka et al. 1991). Natural zeolites have been investigated for removal of $Mn^{2+}$, $Fe^{2+}$, $Hg^{2+}$, $Cr^{3+}$, $Ag^{+}$, $Cu^{2+}$, $Cd^{2+}$, $Zn^{2+}$, $Pb^{2+}$, $Co^{2+}$, and $Ni^{2+}$ from various wastewaters.

Semmens and Martin (1988) investigated the selectivity of clinoptilolite (Anaconda Copper Company, Denver, Colorado) for $Ba^{2+}$, $Pb^{2+}$, $Cu^{2+}$, $Cd^{2+}$, and $Zn^{2+}$. They suggested that the CEC of clinoptilolite depends significantly on how the zeolite is pretreated and they recommended conditioning the zeolite with 0.5 N NaCl solutions for at least two exhaustion-regeneration cycles before measuring equilibrium effective CECs, which should approach theoretically expected CECs. Semmens and Seyfarth (1978) earlier observed a similar increase in CEC from 1.69 meq/g to 2.23 meq/g when clinoptilolite-rich tuff from near Buckhorn, New Mexico, USA, was conditioned by two sequential treatments with 0.5 N $NH_4Cl$ and 1 N NaCl. Zamzow and Eichbaum (1990) also observed an increase in the effective CEC of conditioned clinoptilolite-rich material used to remove heavy metals such as $Pb^{2+}$, $Cd^{2+}$, $Cu^{2+}$, $Co^{2+}$, $Zn^{2+}$, $Ni^{2+}$, and $Hg^{2+}$. They reported that the concentrations of metal ions in the effluent of the regeneration solution were 30 times higher than in the contaminated wastewater.

$Mn^{2+}$ has been removed from drinking water using simple ion exchange with natural zeolites (White et al. 1995). Clinoptilolite-rich tuff from Northern Romania was used in its native form and in modified forms by independent exchange with $Li^{+}$, $Na^{+}$, $NH_4^{+}$, $K^{+}$, $Mg^{2+}$, $Ca^{2+}$, $Fe^{2+}$, and $Fe^{3+}$. Clinoptilolite-rich materials exchanged with $Li^{+}$ or $Na^{+}$ were the most effective forms for $Mn^{2+}$ removal and the $Ca^{2+}$-form performed the poorest in removing $Mn^{2+}$. Nearly 67% more $Mn^{2+}$ was exchanged onto K-clinoptilolite than onto the natural exchange form. Ion-exchange distribution coefficients of $Mn^{2+}$ (defined as Mn content of the zeolite in mg/kg divided by Mn content of solution in mg/L) for $Li^{+}$, $Na^{+}$, $K^{+}$, and $Ca^{2+}$ were 900, 700, 280, and 100, respectively, when the initial $Mn^{2+}$ concentration was 10 mg/L. These values decreased to 400, 510, 250, and 50 mg/L, respectively, if 10 mg/L $Fe^{2+}$ was also present. Kinetics of ion exchange indicated that the rate-limiting step was film diffusion around the grains of zeolitic rock.

Misaelidis and Godelitsas (1995) investigated the removal of $Hg^{2+}$ from aqueous solutions of low concentration (10 to 500 mg $Hg^{2+}$/L) with Na-exchanged clinoptilolite-rich tuff from Greece and Na-exchanged heulandite crystals. They found that Na-exchange of clinoptilolite and heulandite enhanced the uptake of $Hg^{2+}$ by nearly 50%. For the highest solution concentration (500 mg $Hg^{2+}$/L), 43 mg $Hg^{2+}$/g was bound to Na-clinoptilolite, whereas 16 mg $Hg^{2+}$/g was bound to Na-heulandite. Mercury was thought to be bound by ion exchange, adsorption, and surface precipitation. However, Homonnai et al. (1996) reported that the $NH_4$-exchanged form of clinoptilolite-rich tuff from the Trans-Carpathian area in Ukraine had the capacity to adsorb only 4-7 mg $Hg^{2+}$/g, which likely reflects the higher selectivity of $NH_4^{+}$ over $Hg^{2+}$ on the exchange sites of clinoptilolite.

The high selectivity of clinoptilolite and mordenite for $NH_4^{+}$ also suppresses the uptake of $Zn^{2+}$ in solutions containing both $NH_4^{+}$ and $Zn^{2+}$. For example, Kang (1989) found that more $NH_4^{+}$ is bound to clinoptilolite-rich and mordenite-rich tuff than $Zn^{2+}$ at concentrations $1\text{-}7 \times 10^{-3}$ N. The exchange of $NH_4^{+}$ ranged from 0.44 to 0.50 meq/g and $Zn^{2+}$ exchange ranged from 0.07 to 0.17 meq/g for clinoptilolite- and mordenite-rich materials from Korea that had been equilibrated with a $1 \times 10^{-3}$ N $NH_4^{+}$ and $7 \times 10^{-3}$ N $Zn^{2+}$ solution, respectively. The adsorption of $Zn^{2+}$ is decreased by the presence of $NH_4^{+}$, but the exchange of $NH_4^{+}$ is not affected by the presence of $Zn^{2+}$.



These findings are in accordance with the drastic reduction of $Mn^{2+}$, $Cu^{2+}$, and $Ag^{+}$ exchange capacities of natural zeolites in the presence of $NH_4^{+}$ in wastewater (Otterstedt et al. 1989). They compared the uptake of these metals by clinoptilolite-rich tuff, mordenite-rich tuff, and synthetic zeolite A when the $NH_4^{+}$ concentration was ~50 mg/L. Synthetic zeolite A is not as selective for $NH_4^{+}$ as clinoptilolite or mordenite, and they found that synthetic zeolite A was ≥10 times more effective than clinoptilolite and ≥20 times more effective than mordenite in removal of $Cu^{2+}$. Synthetic zeolite A was ≥40 times more effective than clinoptilolite for removal of $Ag^{+}$ and ≥15 times more effective than clinoptilolite for removal of $Mn^{2+}$. These differences in exchange of heavy metals are due to lower ion-exchange distribution coefficients between $NH_4^{+}$ and these metal ions for synthetic zeolite A than for clinoptilolite and mordenite.

Some authors, however, have suggested that $Cu^{2+}$ removal from solutions with $NH_4$-exchanged clinoptilolite approaches 100%, presumably at lower concentrations than those usually encountered in wastewater (Kalita and Chelishchev 1995). Blanchard et al. (1984) achieved the simultaneous removal of $NH_4^{+}$ and heavy metals from drinking water by clinoptilolite-rich material (origin not reported, CEC of zeolitic rock was 2.2 meq/g). The concentration of heavy metals in the feed solution was 0.2 mg/L in addition to 2.6 mg $NH_4^{+}$/L. Heavy-metal concentrations in the effluent water after passing through the clinoptilolite rich material were significantly reduced. Breakthrough concentrations of several µg/L were obtained after passing 175, 220, 225, and 470 BV of wastewater through the clinoptilolite-rich bed for $Cd^{2+}$, $Zn^{2+}$, $Cu^{2+}$, and $Pb^{2+}$, respectively. A breakthrough $NH_4^{+}$ concentration of 0.15 mg/L was obtained after 480 BV had passed through the bed at a flow rate of 10 BV/h. Regeneration of spent clinoptilolite-rich beds was performed with 20 g NaCl/L at pH 4.0-4.5 in order to avoid precipitation of metal hydroxides.

It is well known that ion-exchange selectivities depend on the ion concentration of the metals in the wastewater to be treated. Cation-exchange selectivities for most transition or heavy-metal cations become higher compared with alkali or alkaline-earth cations by lowering the concentrations of transition and heavy-metal cations in solution (see Pabalan and Bertetti, this volume). Therefore, the concentration range of the metals to be removed in wastewater treatment will affect the sequence of ion-exchange selectivities and must be taken into consideration for effective treatment. Examples of cation-exchange selectivity sequences of clinoptilolite-rich materials for various heavy metals are listed in Table 6 (see references for details on effects of solution pH and ionic concentrations).

**Table 6.** Cation-exchange selectivity sequences of clinoptilolite-rich samples for heavy metals.

| *Selectivity sequence* | *Reference* |
|---|---|
| Pb»Cd>Cu»Zn | Fujimori & Moriya (1973) |
| Pb>Cd>Zn>Cu | Semmens & Seyfarth (1978) |
| Pb>$NH_4$>Cu,Cd>Zn,Co>Ni>Hg | Blanchard et al. (1984) |
| Cs>Pb>Fe>Cu>Zn,Cd,Co>Ni>Mn>Cr | Horvathova & Kachanak (1987) |
| Pb>Cd>Cu>Co>$Cr^{3+}$>Zn>Ni>Hg | Zamzov & Eichbaum (1990) |
| Pb>Cu>Zn>Co>Ni | Kalita & Chelishchev (1995) |

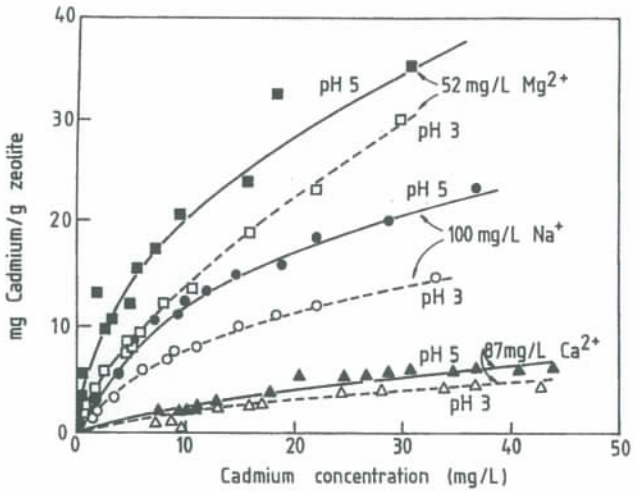


**Figure 5.** Cadmium ion exchange isotherms at 20°C for a clinoptilolite-rich tuff from the Anaconda Copper Company, Denver, Colorado, USA, in the presence of $Mg^{2+}$, $Na^+$, and $Ca^{2+}$ competing cations (illustrated in mg/L on figure) at pH 3.0 and 5.0 [*x*-axis is $Cd^{2+}$ in solution, *y*-axis is $Cd^{2+}$ exchanged onto zeolite exchange sites (Semmens and Martin 1980)].

As mentioned earlier, the influence of pH is very important for efficient removal of heavy metals by ion exchange. A decrease in pH will decrease the effective CEC for heavy metals because $H_3O^+$ will compete for zeolite exchange sites (see Fig. 5; Semmens and Martin 1980). These authors also found that under similar solution concentrations and pH values selectivity coefficients for clinoptilolite-rich material (Anaconda Copper Company, Denver, Colorado) decreased in the order $Pb^{2+} > Ag^+ > Cd^{2+}$ in the presence of the same counter ions $Mg^{2+}$, $Na^+$, and $Ca^{2+}$. The exchange of $Cd^{2+}$ and $Pb^{2+}$ onto clinoptilolite exchange sites was least inhibited by $Mg^{2+}$, followed by $Na^+$ and $Ca^{2+}$. The exchange of $Ag^+$ was also least inhibited by $Mg^{2+}$, but $Na^+$ inhibited the exchange more than $Ca^{2+}$.

Heavy metals on saturated or exhausted zeolites can be effectively regenerated with a solution containing 20-25 g NaCl/L, which has been adjusted to a pH of 4-4.5 with HCl (Blanchard et al. 1984). The heavy-metal ions can be more effectively removed from high concentration regenerating solution than from the low heavy metal concentrations wastewater. The heavy metals are precipitated as hydroxides by increasing the pH to 6 or 7, depending on the type and concentration of heavy-metal ions in the regenerating solution.

An alternative to ion-exchange processes for the removal of heavy metals from wastewaters is the adsorption of heavy metals on zeolite surfaces coated with a suitable adsorbent. For example, soluble $Fe^{2+}$ and $Mn^{2+}$ are often present in well waters at concentrations of 0.1-2 mg/L, which is too high for human consumption. The removal of $Fe^{2+}$ and $Mn^{2+}$ can be accomplished simultaneously by adsorption of these ions on $MnO_2$ that has been precipitated onto the surfaces of zeolite particles embedded in the porous rock. The $MnO_2$ adsorbent must have high surface area and high mechanical strength. The zeolite-$MnO_2$ product is called "manganese zeolite" or "zeomangan" and various zeolites have been used in this process, including clinoptilolite-rich tuff from Fuatsui, Akita Prefecture, Japan (Torii 1978) and Tokaj Hills, Hungary (Polyák et al. 1995) and chabazite-rich tuff from Italy (Aiello et al. 1979). In addition to adsorption of $Fe^{2+}$ and



$Mn^{2+}$ on the $MnO_2$ coating, these bivalent cations may also be exchanged onto the exchange sites in the zeolite.

Polyák et al. (1995) have presented a method to prepare zeomangan. The zeolite is first exchanged into its $K^+$ form by ion exchange with 20 g KCl/L. Then up to 12-15% of the $K^+$ is exchanged by $Mn^{2+}$ with a solution containing 169 g $MnSO_4$/L. The K,Mn-zeolite is percolated with a solution of 10 g $KMnO_4$/L. The resulting product is an $MnO_2$-coated zeolite where the reaction for the precipitation of $MnO_2$ is as follows:

$$3\ Mn^{2+} + 2\ MnO_4^- + 2\ H_2O \rightarrow 5\ MnO_2 + 4\ H^+$$

The oxygen content of the precipitated $MnO_2$ is slightly lower than that expected for stoichiometric $MnO_2$. The actual composition corresponds to the formula $MnO_{1.89\text{-}1.93}$. Consequently, the coating contains $Mn^{2+}$ and some $Mn^{3+}$. The surface charge of the $MnO_2$ is dependent on the solution pH. The zero point of charge ($pH_{zpc}$) is pH 1.56; hence, surfaces become negatively charged above the $pH_{zpc}$ and provide sites for the exchange of $Mn^{2+}$ (and $Cd^{2+}$, $Zn^{2+}$, $Cu^{2+}$, and $Pb^{2+}$ if they are present in the wastewater, e.g. Polyák et al. 1995).

The $MnO_2$ will also oxidize $Fe^{2+}$ to $Fe^{3+}$ according to the reaction:

$$MnO_2 + 2\ Fe^{2+} + 4\ H_2O \rightarrow 2\ Fe(OH)_3 + Mn^{2+} + 2\ H^+$$

Once oxidation occurs, $Fe^{3+}$ precipitates as ferric hydroxide on the $MnO_2$-coated zeolite, thereby removing Fe from the water stream. Well water is treated by flowing the water stream through the $MnO_2$-coated zeolite. The capacity of the $MnO_2$-coated zeolite to extract $Fe^{2+}$ and $Mn^{2+}$ depends on their concentrations in the well water and the flow rate of water through the bed. Capacities to adsorb $Fe^{2+}$ and $Mn^{2+}$on $MnO_2$-coated chabazite are summarized in Table 7 for different concentrations of $Fe^{2+}$ and $Mn^{2+}$ and flow rates through the bed.

The $MnO_2$-coated zeolite is usually regenerated by passing 10 BV of 0.05-0.1 N HCl, followed by washing the bed material with 10 BV of 10 g $KMnO_4$/L. When the

**Table 7.** $Fe^{2+}$ and $Mn^{2+}$ adsorption capacities on $MnO_2$-coated chabazite used to treat well waters until a breakthrough concentration of 0.1 mg/L was achieved (calculated from the data of Aiello et al. 1979).

| *Cation composition in influent* | | *Flow rate through column* | **Adsorbed cations* | |
|---|---|---|---|---|
| $Fe^{2+}$ | $Mn^{2+}$ | | $Fe^{2+}$ | $Mn^{2+}$ |
| ----------*mg/L*---------- | | *BV/h*† | ----------*mmol/g*------- | |
| 1 | - | 48 | 0.11 | - |
| 2.5 | - | 48 | 0.19 | - |
| 5 | - | 48 | 0.19 | - |
| 2 | 0.5 | 48 | 0.21 | 0.04 |
| 1.25 | 1.25 | 32 | 0.15 | 0.13 |
| 1.25 | 1.25 | 48 | 0.14 | 0.10 |
| 1.25 | 1.25 | 64 | 0.06 | 0.07 |

*Adsorbed on $MnO_2$-coated chabazite †BV/h = bed volumes/h

exhausted adsorbent is leached with the HCl solution at pH = 1.5-2, the adsorbed cations are removed in higher concentrations than in the original wastewater and can thus be more effectively precipitated by increasing the pH of the regenerating solution. The $KMnO_4$ solution reoxidizes the reduced $MnO_2$ on the zeolite support. Exhaustion-regeneration cycles can be repeated 5-8 times without loss of the adsorption capacity.

Many industries, such as photographic processing, electroplating, metal finishing, ore mining and mineral processing, coal mining and processing, and oil refining, have potential problems associated with heavy-metal contamination in wastewaters or in runoff waters. Effluents generally contain heavy metals in low concentrations in the presence of high salt concentrations; hence, the use of ion-exchange technologies must be evaluated on a case-by-case basis. It is also important to note that ion-exchange equilibria determined in batch or static systems differ from ion-exchange capacities measured in flow-through or dynamic systems (Semmens and Martin 1980). Ion-exchange equilibria and selectivities provide some information on the rates of ion exchange under dynamic conditions, but the rate of exchange is dependent on inter- and intra-particle diffusion. The former can be influenced by particle size of the zeolite and flow rate through the exchange column. Previous studies suggest that the optimum zeolite particle size is 0.3-0.8 mm and the flow rate through a column is 8-16 BV/h (Semmens and Martin 1980, Guangsheng et al. 1988, Kalló 1995).

In addition to the reduction of potential toxic metals, another objective of heavy-metal removal from wastewaters should be metal recovery and reuse. These metals are usually valuable to industry, but, in most cases, they cannot be economically recovered by conventional concentrating techniques. Technologies should be evaluated that recover heavy metals from regenerating solutions of ion-exchange processes to enhance their potential economic recovery.

## INDUSTRIAL WASTEWATER TREATMENT

As mentioned earlier, because of their unique ion-exchange properties, adsorption capabilities, mechanical, chemical, and thermal resistance, and low price, natural zeolites may be applied for the treatment of wastewater and sewage produced by industry. As might be expected, ion-exchange selectivities of natural zeolites play an important role in removal of $NH_4^+$, and at low concentrations (below $10^{-3}$ N) they may be used in removal of heavy-metal cations from industrial wastewaters. Adsorption of organic and inorganic molecules is influenced by the molecular sieving properties of zeolites and additional adsorption may take place in pores in the zeolitic rock. The mechanical strength of most zeolitic rocks is satisfactory for most technical purposes such as filling in fixed bed ion exchangers or adsorbents, e.g. in trickling filter beds (Mercer and Ames 1978). Zeolite granules can often be manufactured from zeolite-rich rocks or tuffs by simple crushing and sieving; hence, expensive pelletization is not needed as in the case with synthetic zeolites, which are usually produced as fine powders with micrometer grain size. Natural zeolites are stable in the pH range of 4-9 and at solution temperatures up to the boiling point of water (or even above). They are not soluble in any organic solvent. They can often be dehydrated-hydrated many times without significant hysteresis. Some natural zeolites are stable at least up to 500°C in air, hydrogen, carbon monoxide, and other gases. Apart from airborne dust hazards, natural zeolites do not pose any environmental problems, and on the contrary are able to retard harmful substances in the environment as described earlier. The cost of mining natural zeolites is less than one fifth the cost of manufacturing the least expensive synthetic zeolite products. Hence, there are numerous properties that make natural zeolites attractive for treating industrial wastewaters. However, the optimum conditions for the use of natural zeolites in a given wastewater



treatment application must be determined experimentally. Several practical and potential uses of natural zeolites in the treatment of industrial wastewaters are listed below.

Clinoptilolite-rich tuff from South Korea has been used to remove $NH_4^+$ from coke-oven wastewater (Ha 1987). The clinoptilolite was transformed into its Na-form in order to extend the effective capacity for $NH_4^+$ exchange. The $NH_4^+$ breakthrough concentration was reached after 55-60 BV of wastewater containing 20-30 meq $NH_4^+$/L passed through the column. The exhausted bed was regenerated with 2 N NaCl. The $NH_4^+$ exchange capacity of the clinoptilolite column decreased by less than 10% after four regenerations with fresh regenerating solution. Approximately 95% of the effective $NH_4^+$ CEC could be restored if the spent clinoptilolite was regenerated with 10 BV of NaCl. The first 20% of regenerating solution eluted from the spent clinoptilolite column contained high concentration of $NH_4^+$ (0.5-0.8 M) and was replaced with fresh regenerating solution. Ammonia may be removed from the spent regenerating solutions by stripping with air as described above.

Korobchanskii et al. (1987) exploited the ion-exchange properties of a clinoptilolite-rich tuff from the Trans-Carpathian region of Ukraine to remove $NH_4^+$ from wastewater from a coke oven after initially treating the wastewater with a series of processes including settling, sand filtration, and/or coagulation with $FeCl_3$. A breakthrough concentration of 5 mg $NH_4^+$/L was reached after passing 7 BV of the influent wastewater with a concentration of 700 mg $NH_4^+$/L at a rate of 2 BV/h through the clinoptilolite-containing column. Approximately 50-60% of the cation-exchange capacity of the 1- to 2- mm clinoptilolite grains was utilized under these dynamic conditions. Regeneration of spent clinoptilolite was achieved by passing a 10% solution of $H_2SO_4$ through the spent clinoptilolite column. The effective $NH_4^+$ exchange capacity remained unchanged at 8.2 mg $NH_4^+$/g after 3 sorption-desorption cycles. Ammonium sulfate was the by-product of the regeneration process.

Clinoptilolite-rich tuff from Georgia was used for the removal of mercury from chlorine production wastewater (Mamedov et al. 1985). Mercury contents of the wastewater to be treated varied between 6.4 and 52.0 mg/L. The lowest ratio of the $Hg^{2+}$ in the treated effluent to the wastewater influent was 0.04 and the effective $Hg^{2+}$ exchange capacity of the clinoptilolite-rich tuff was 11 mg $Hg^{2+}$/g (around 1/10 of CEC). The flow rate through the clinoptilolite column (particle size of about 1.6 mm) was 1.5 BV/h.

A Na-clinoptilolite from Georgia was used to remove $Ag^+$ by ion exchange from liquid wastes from photographic material processing (Rustamov and Makhmudov 1988). Liquid waste containing 0.14 meq $Ag^+$/L was passed through a Na-exchanged clinoptilolite column with a linear flow rate 27 m/h. Spent clinoptilolite columns were eluted with 1 N $NaNO_3$ solution at 1.8 m/h. Silver concentrations in regenerating solutions were 14 times higher than in the initial liquid waste.

Guangsheng et al. (1988) showed that Na-exchanged clinoptilolite-rich material from Nenjiang, China, could efficiently remove $Cu^{2+}$ from electroplating effluents. The pH of the wastewater, which contained 20-30 mg $Cu^{2+}$/L, was adjusted to 4-5 for attaining the optimum conditions for $Cu^{2+}$ exchange onto zeolite exchange sites. This process removed all of the $Cu^{2+}$ from the electroplating wastewater. The effective $Cu^{2+}$ exchange capacities decreased from 1.14 to 0.87 meq/g when the linear velocity was increased from 3 to 9 m/h. Approximately 90-97% of the exchanged $Cu^{2+}$ was recovered during regeneration with 2 BV of a saturated NaCl solution. No reductions in the CEC were observed after 29 successive exhaustion-regeneration cycles.

Magnesium chloride and $H_3PO_4$ were used to flocculate particles in the effluents from a goatskin tannery in order to reduce sludge production and to produce sludge that

is much easier to dewater (Bilotta and Vallero 1984). These flocculents were more efficient in removing COD, suspended solids, Cr, $SO_4^{2-}$, and $NH_4^+$ compared with conventional biological treatment methods. As might be expected, a clinoptilolite-rich tuff may be used to reduce the $NH_4^+$ concentration in the effluent after treatment with the flocculents. For example, an effluent with an $NH_4^+$ concentration of 90-100 mg/L was decreased to 25-30 mg $NH_4^+$/L after passing through a column containing clinoptilolite-rich materials. Most of the discussion in this chapter has been directed toward the use of clinoptilolite-rich materials. However, Colella et al. (1984) found in laboratory tests that phillipsite-rich tuff from near Naples, Italy, was more efficient than clinoptilolite-rich tuff for $NH_4^+$ removal from tannery wastewaters The phillipsite-rich tuff had a higher CEC of 2.28 meq/g compared with a CEC of 1.2 meq/g for the clinoptilolite-rich tuff. In addition to removing $NH_4^+$ from the tannery wastewater, the COD was reduced by 28% with phillipsite-rich tuff and by 24% with clinoptilolite-rich tuff compared with wastewater not treated with the zeolites.

A conventional nitrification-denitrification process was compared with an ion-exchange process using clinoptilolite-rich tuff from Slovakia for removal of $NH_4^+$ from shoe manufacturing wastewater (Chmielewska-Horvathova et al. 1992). The pilot plant consisted of 2 alternating pressure filters containing 70 L of clinoptilolite-rich material (0.3- to 1.0-cm grain size) and treated 20 $m^3$/d wastewater. Regeneration of spent clinoptilolite beds was achieved by passing NaCl solution through the columns and then, $NH_3$ was stripped from the spent regenerating solution by air. As an example, the operation costs for the ion-exchange/regeneration process are 22% higher than the biological nitrification-denitrification process for a plant of 6000 $m^3$/d capacity, but investment costs are 27% lower for the clinoptilolite ion-exchange process compared to the nitrification-denitrification process, not taking into account the high energy consumption of long time aeration required for the biological degradation.

Some organic impurities may be removed by adsorption on zeolites. For example, dichloropropanol ($ClCH_2$-(OH)CH-$CH_2Cl$) has been removed from aqueous solution by adsorption on mordenite-rich tuff from Eastern Crimea area of Ukraine (Kakhramanova et al. 1983). The adsorption takes place on the external surfaces of mordenite crystals because the size of hydrated dichloropropanol prevents penetration into the zeolite's channels to access extraframework sites. Adsorption of dichloropropanol was the highest (4.2 $mg/L_{mordenite}$) when mordenite-rich tuff was pre-treated with $[(C_2H_5)_2NH_2]^+Cl^-$, which exchanges onto the exchange sites in mordenite, and the wastewater stream was passed through the zeolite bed under dynamic flow conditions. Even traces of dichloropropanol can be removed from wastewater by passing the stream through a zeolite-rich bed.

Various toxic chlorinated organic compounds (e.g. trichloroethylene, chloroform, dichloroethane, perchloroethylene, epichlorohydrin, etc.) in wastewaters (1.0-1.3 g/L) have been removed by adsorption on the crystal surfaces of clinoptilolite-rich and mordenite-rich materials (Rustamov et al. 1992). Adsorption capacities of these zeolites for chlorinated organic compounds were increased by initially exchanging either amines or $Cu^{2+}$ onto zeolite exchange sites. For example, clinoptilolite-rich material exchanged with $CH_3NH_2$.HCl and $Cu^{2+}$ increased the sorption of epichlorohydrin from 2.08 to 3.14 and 4.40 wt %, respectively. Mordenite-rich material exchanged with the sample ions increased the adsorption of epichlorohydrin from 1.56 to 2.70 and 3.28 wt %, respectively. For comparison, the sorption capacity of charcoal was 3.00 wt % under the same conditions. The charcoal lost around 75% of its adsorption capacity for epichlorohydrin after 10 regenerations, whereas clinoptilolite-rich material exchanged with $CH_3NH_2$.HCl lost less than 20% of its adsorption capacity for epichlorohydrin.



Korean workers used an unspecified local zeolite (presumably clinoptilolite) to remove color from wastewater of a dyeing process (Doh and Park 1980) Their studies confirmed the earlier work of Iso et al. (1976) on the use of clinoptilolite-rich material to remove color from wastewaters produced in dyeing processes. Iso et al. (1976) reported that the amount of COD impurities adsorbed on clinoptilolite-rich materials at equilibrium was nearly equal to that adsorbed on granular active carbon, both of which were around 10 mg COD/g.

Although zeolites have a permanent positive framework charge, balanced by exchangeable cations, it is possible in some cases to use zeolites for removal of anionic contaminants by modifying the zeolite surfaces. Anionic impurities were removed from the water circulating system of a paper manufacturing company using clinoptilolite-rich tuff from Tokaj Hills, Hungary (Baumann and Heinzel 1996). Clinoptilolite was initially treated at 200-500°C with polyaluminum chloride, which is hydrolyzed on zeolitic surfaces to form a cationic polymer coating. Epichlorohydrin, epichlorohydrin derivatives, and/or dicyandiamid ($HN=C(NH_2)$-NH-C≡N) were effectively adsorbed on the treated zeolite substrate.

Wastewater produced in yeast production plants was more effectively treated in anaerobic reactors containing zeolitic tuff (41% clinoptilolite and 40% mordenite contents from Cuba) as a support medium than in reactors containing ceramic Raschig rings, PVC pellets, or limestone as support media (Sanchez and Roque-Malherbe 1987). An initial BOD of 20,000 mg/L was decreased by 65% after passing 10 BV of wastewater through the zeolite gravel bed, whereas wastewater passed through ceramic rings, PVC pellets, and limestone gravel decreased the BOD by 52, 40, and 34%, respectively. This supports earlier claims (see above) that the zeolite support media can increase the biological activity of bacteria, where the zeolite concentrates nutrient sources (i.e. $NH_4^+$) for bacteria and provides an excellent support medium for their growth.

## CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

The high selectivity of natural zeolites for $NH_4^+$ has prompted their use to treat a variety of natural waters and wastewaters from municipal, industrial, and agricultural sources. Natural zeolites also offer the possibility of removing minute amount of heavy-metal ions and radioactive $Cs^+$ and $Sr^{2+}$ from wastewaters, even in the presence of competing alkali or alkaline-earth cations. In addition to intracrystalline cation exchange, the crystal surfaces of natural zeolites may act as adsorption sites or filters for organic molecules and microorganisms, which may contribute significantly in the treatment of wastewaters. In some cases, the technology of using natural zeolites has been elevated to the point where they are used to treat large-scale municipal and industrial wastewaters. However, numerous questions remain unanswered and additional areas of research must be pursued before natural zeolites may be used to their full potential to treat water and wastewater.

A promising area for the use of natural zeolites is in the adsorption of herbicides, insecticides, and fungicides so that the zeolite retards the migration of these agents into groundwater and runoff. Only recently have studies begun to examine this potential area (see Ming and Allen, this volume), and considerable work remains on the modification of zeolite surfaces to make them effective in adsorbing anionic or organic species. There are indications that natural zeolites, mainly clinoptilolite and mordenite, may adsorb traces of dioxin from air incineration plant emissions as well as from wastewaters (private communication from Metallurgische Gesellschaft/LURGI/ GmbH, Germany). Obviously, mechanisms and properties of dioxin adsorption on natural zeolites must be addressed. Another area that requires further studies is what to do with the heavy metals or other

wastewater impurities removed by natural zeolites. New technologies need to be developed to economically recover and reuse these potentially valuable commodities.

Several of the recent, more complex water-treatment processes that use natural zeolites have potential for widespread use in wastewater treatment. For example, removal of phosphate from wastewater by adsorption on FeOOH-coated zeolites and the modification of natural zeolites as a substrate to produce more effectively bacteria flocs for biological treatment of wastewater are promising technologies. Studies are required to determine whether these technologies can be efficiently and economically used to treat wastewaters compared with more traditional wastewater-treatment processes.

There may be new technologies that use natural zeolites for the treatment of municipal, agricultural, and industrial wastewaters. For example, natural zeolites might be used in the treatment of recycled water in swimming pools to remove $NH_4^+$ and chloroamine formed after chlorination disinfection. Natural zeolites may be used in applications for the removal of $NH_4^+$ via ion exchange from wastewaters of fish-farming ponds or in transportation of live fish and subsequent release of $Ca^{2+}$ and $Mg^{2+}$ into solution where they will precipitate as carbonates in $HCO_3^-$-rich water. New technologies that utilize natural zeolites may be developed to treat liquid manures produced during animal production. These are only a few examples and, no doubt, many other potential applications will become evident as we deal with the never-ending problem of treating contaminated waters and wastewaters. These potential applications and others require sound scientific research, including the thorough chemical, physical, and mineralogical characterization of the zeolite-rich materials used in these applications. Natural zeolites provide numerous possibilities to treat wastewaters with environmentally friendly materials and these unique minerals are far from being fully exploited.

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16

# Use of Zeolitic Tuff in the Building Industry

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## INTRODUCTION

Zeolite-rich volcanic tuffs are widely distributed in almost every country of the world, where they are present in low-, medium-, or high-grade million-ton deposits. Even though the formation of the zeolite minerals may have followed different genetic paths, the zeolitic rocks have in common a matrix of finely crystalline zeolite that cements the other non-zeolitic particles and is responsible for the overall mechanical properties of the material. Zeolitic tuffs have been employed since pre-historic times in construction, mostly as dimension stone. This use is still the most common of natural zeolites in the building industry, although other applications have recently come to the forefront, such as lightweight aggregate or as additives for manufacturing blended cements.

Given the fact that much of this material is excavated and used locally and that the market demand is strongly affected by the trends of the building industry, estimates of the worldwide zeolitic tuff production for construction purposes are difficult to make. In Italy, where the use of zeolitic tuff as dimension stone is commonplace, about 75 quarries were reported in operation in 1992 with total production of about $3 \times 10^6$ tons per year (Aiello 1995). More recently, this production has decreased, due to the crisis of the building industry, and in 1998 it amounted to about $1.5 \times 10^6$ tons per year. In Japan, the production of tuff as dimension stone is currently about $4 \times 10^5$ tons per year (N. Kuchitsu, National Research Institute of Cultural Properties, Tokyo, Japan, pers. comm., 1996). Considering that zeolitic tuff is used as dimension stone in many other countries as well, e.g. Bulgaria, Cuba, Germany, Greece, Hungary, Mexico, Romania, and Turkey, the current worldwide zeolitic tuff consumption as dimension stone is about $3 \times 10^6$ tons per year.

Information is even more scarce on the use of natural zeolites as additions to cement, because the recourse to zeolitic tuff as a pozzolanic material is rather recent and is widespread only in those locations in which other pozzolanic materials, such as natural pozzolan, fly ash, silica fume, etc., are not readily available. The use of zeolitic tuffs as cement additives is common in Bulgaria, China, Cuba, Germany, Jordan, Russia, Turkey, United States, and Yugoslavia. It is of interest to note that in China, in 1989, about $7 \times 10^7$ tons of blended cement, about one third of the total cement production of the country, was manufactured with 10 to 30 wt % natural zeolite (Kasai et al. 1992). Mumpton (1996) also reported that in Serbia (Yugoslavia) about $10^5$ tons per year of clinoptilolite-rich tuff are

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# NATURAL ZEOLITES:

## OCCURRENCE, PROPERTIES, APPLICATIONS

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*COVER:* Representation of the crystal structure of heulandite viewed down the *c*-axis, with *b* vertical. Ten-membered and eight-membered tetrahedral rings form channels parallel to *c*. In the channels,

small green spheres represent Na atoms,
larger light-blue spheres represent K atoms,
small yellow spheres represent Ca atoms,
large blue spheres represent $H_2O$ molecules.

[Figure courtesy of M.E. Gunter; cf. Fig. 16, p. 41, this volume.]

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