

Clinoptilolite-heulandite: applications and basic research

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Structural peculiarities of clinoptilolite and heulandite are reviewed. Special attention is given to partial Si, Al ordering within the tetrahedral framework structure. There is strong evidence that the Si, Al ordering pattern depends on the size, charge, and placing of the original extraframework cations. Even if exchanged to homoionic forms clinoptilolite and heulandite may display different properties depending on the degree and type of Si, Al ordering. In some cation-exchanged heulandites symmetry lowering from the topological symmetry $C2/m$ to Cm or $C\bar{1}$ has been observed due to partial Si, Al ordering and low symmetry site preference of extraframework cations. Major applications of clinoptilolite are reviewed. In the field of pollution abatement not only the natural product but also surface modified clinoptilolites gain importance.

1. INTRODUCTION

Clinoptilolite with the simplified formula $(Na,K)_6Si_{30}Al_6O_{72} \cdot nH_2O$ is the most common natural zeolite found mainly in sedimentary rocks of volcanic origin. Such deposits aroused strong commercial interest because clinoptilolite tuffs are often rather pure and can be mined with simple techniques. Approximately 25 years ago ca. 300,000 tons of zeolitic tuff were mined per year [1]. In 1997 ca. 3.6 Mio tons of natural zeolites (mainly clinoptilolite and chabazite) were worldwide produced [2], ca. 2/3 alone were stopped in China. Demand for natural zeolites has increased rapidly over the past decade, particularly in agricultural applications. Growth rates as high as 10% per year are forecasted [2].

A typical zeolite mining company in the USA, Canada, and Europe has less than 50 employees and produces in open pits 20,000 to 50,000 tons per year. Characteristic clinoptilolite rocks consist of 60-90% clinoptilolite with the remaining being mainly feldspars, clays, glass, and quartz. Depending on quality and specification the price ranges between 50 and 300 US\$ per ton. In North America and Europe a large portion of the production goes into the area of animal hygiene including cat litter and other animal bedding products. The rest is divided among applications in animal feed, fertilizer, environmental absorption, and building materials. Zeolitic building material includes dimension stones, pozzolanic cements and concrete, and lightweight aggregates.

Some of the pioneering zeolite research has been carried out on heulandite with the simplified formula $Ca_4Al_8Si_{28}O_{72} \cdot nH_2O$ because large crystals of this species are available in limited quantities from cavities and vugs in volcanic rocks, e.g. in the Deccan Trap basalts of Western India [3]. Already in 1934 Tiselius [4] studied the temperature, pressure, and concentration dependence of the anisotropic H_2O diffusion in heulandite single-crystals. Other

recent pioneering studies like atomic force microscopy (AFM) and application of heulandites as electrodes will be discussed below.

1.1. Mineralogical nomenclature

Zeolite minerals species shall not be distinguished solely on the basis of the framework Si/Al ratio. An exception is made in the case of heulandite and clinoptilolite; heulandite is defined as the zeolite mineral series having the distinctive framework topology of heulandite (HEU) and the ratio $\text{Si/Al} < 4.0$. Clinoptilolite is defined as the series with the same framework topology and $\text{Si/Al} \geq 4.0$. The exception is based on entrenched usage of the names heulandite and clinoptilolite, and their convenience for recognizing an important chemical feature [5]. Note that in older studies thermal stability has been used to distinguish clinoptilolite from heulandite. This is a derivative property as an aid to identification, and it is not appropriate as the basis for definition.

Individual species in a zeolite mineral series with varying extraframework cations are named by attaching to the series name a suffix indicating the chemical symbol for the extraframework element that is most abundant in atomic properties, e.g. heulandite-Ca, heulandite-Na, clinoptilolite-K, clinoptilolite-Ca etc. [5].

2. CRYSTAL STRUCTURE

The structural topology of the tetrahedral HEU framework [6] is well understood and possesses $C2/m$ space group symmetry with oblate channels confined by ten-membered ($7.5 \times 3.1 \text{ \AA}$) and eight-membered tetrahedral rings ($4.6 \times 3.6 \text{ \AA}$) parallel to the c -axis. Additional eight-membered ring channels ($4.7 \times 2.8 \text{ \AA}$) running parallel to $[100]$ and $[102]$ cross-link the former channels within (010) , giving rise to a two-dimensional channel system parallel to (010) responsible for a layer-like structure (Fig. 1).

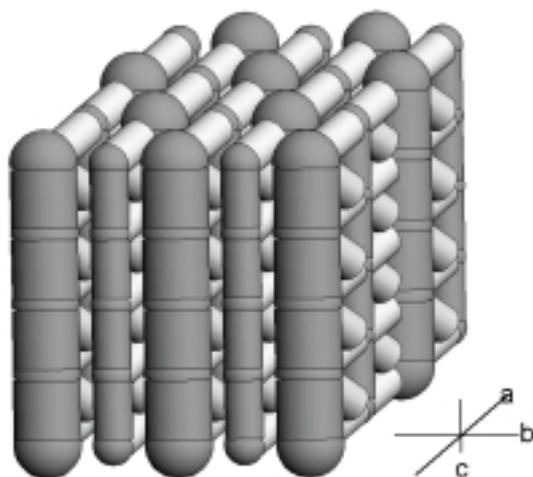


Fig. 1. Columnar model of the two-dimensional channel arrangement parallel to (010) in HEU frameworks. The dark gray columns parallel to $[001]$ represent eight- and ten-membered ring channels. These channels are cross-linked by the light gray eight-membered ring channels running parallel to $[100]$ and $[102]$.

There is still doubt about the true symmetry of clinoptilolite and heulandite. Ventriglia [7] determined heulandite to be piezoelectric but none of the subsequent studies on natural samples could confirm this low symmetry (either space group Cm or $C1$). The possible reason for acentricity is partial Si, Al ordering within the various tetrahedral sites which is difficult to resolve by analytical or structural techniques. Thus $C2/m$ is the maximum symmetry which may be lowered to $C2$, Cm , $C\bar{1}$, and $C1$. In addition, multiple polymorphs, distinguished by different distributions of partially Si, Al ordered tetrahedra, exist in each space group. In a review of $C2/m$ heulandites and clinoptilolites it was found that: (i) in all cases the tetrahedron T2 had the highest Al concentration but below 50%, (ii) the tetrahedron with the second richest Al occupation (below 25% Al) could either be T1, T3, T4, or T5 depending on the sample [8]. In analogy to alkali feldspars it can be postulated that each clinoptilolite or heulandite may be structurally different, even if a constant Si/Al ratio is maintained. This problem is not only of academic interest but has also strong influence on cation diffusion, cation exchange, gas sorption, and catalytic properties, etc.

2.1. Examples of inconsistent properties

Gunter et al. [9] used three different natural HEU samples of the following composition, H-I: $Ca_{3.6}K_{0.8}Al_{8.8}Si_{27.4}O_{72} \cdot 26.1 H_2O$, H-II: $Ca_{2.1}Mg_{0.3}Na_{2.5}K_{0.3}Al_{8.0}Si_{28.2}O_{72} \cdot 25.5 H_2O$, and H-III: $Ca_{3.7}Na_{1.3}K_{0.1}Al_{8.9}Si_{27.1}O_{72} \cdot 21.4 H_2O$ to study Pb^{2+} exchange. The crystals were crushed to 100-500 μm and stirred for 4 weeks in 2 M solution of NaCl at 100°C to obtain standard conditions (Na-exchanged varieties). After this time only sample H-III was completely Na-exchanged whereas samples H-I and H-II still revealed significant concentrations of the original extraframework cations in the core of the crystals. In a second step Na-exchanged crystals were treated in a similar way for 3 weeks in 2 M solution of lead acetate to obtain Pb^{2+} -exchanged varieties. However, only sample H-III completely exchanged. In particular, sample H-I with a tetrahedral framework composition almost identical to sample H-III revealed only Pb^{2+} exchange in a very narrow seam on the rim and around cracks. The reason for this different exchange behavior was not understood [9].

Tarasevich et al. [10] performed K^+ and Pb^{2+} exchange experiments on Na-exchanged forms of two different natural clinoptilolite samples and noted different selectivity for these samples although the difference in the SiO_2/Al_2O_3 ratio was insignificant and the cation exchange capacities were virtually the same. It should be noted that the selectivity was only different on a quantitative scale. The characteristic exchange sequence of *low-field strength* zeolites [11, 12] remained uninfluenced. Tarasevich et al. [10] speculated that some specific features of the clinoptilolite structure are responsible for the difference in selectivity. One of their sample formed in nature as Ca-rich variety whereas the other as clinoptilolite-Na. It was suggested [10] that an originally Ca^{2+} -rich clinoptilolite crystallizes for effective charge balance with a different Si, Al distribution compared to a Na^+ -rich clinoptilolite with similar Si/Al ratio. Thus even in its Na-exchanged form both clinoptilolites have a ‘memory’ in the sense that the originally Ca^{2+} rich sample has a stronger selectivity for Pb^{2+} (of similar charge and size) than the originally Na^+ rich sample which is more selective for K^+ . This memory effect is imprinted by the Si, Al distribution.

Additional exchange isotherms Pb^{2+} (solution) $\rightarrow 2Na^+$ (clinoptilolite) were recorded [13, 14] under comparable conditions as in [10]. However, a maximum exchange level of ca. 80% [13, 14] is in contrast to ca. 95% for two different samples [10]. Such discrepancies in the exchange behavior were discussed by Langella et al. [14] concluding that the cation exchange

selectivity of clinoptilolite is markedly dependent on its original cationic composition, as not all the cationic sites in the structure can be made available for exchange. The pronounced differences in the exchange isotherms (Fig. 2), reported by various research groups [10, 13-16], are mainly due to assumption of different cation exchange capacities (CEC) for clinoptilolite. The CEC values are either experimentally determined by different methods or calculated from the chemical composition of clinoptilolite [13, 17]. In most cases, a so-called Na-exchanged clinoptilolite is not completely Na-exchanged but still preserves additional extraframework cations [13, 16]. Furthermore, surface analytical investigations on cation-exchanged heulandite have demonstrated that metal accumulation on the crystal surface due to adsorption of soluble and surface precipitation of insoluble hydrolysis products must be considered [18].

2.2. The memory effect in HEU frameworks

Support for the hypothesis of imprinted Si, Al distributions during crystal growth depending on the environment and conditions [10] comes from three different approaches: (i) study of growth texture of natural crystals [19], (ii) structure modeling applying lattice energy minimization techniques to HEU frameworks with Na and Ca as extraframework cations [20-23], and (iii) synthesis of HEU frameworks prepared from aluminosilicate gels at 180°C in the presence of alkali hydroxides [24].

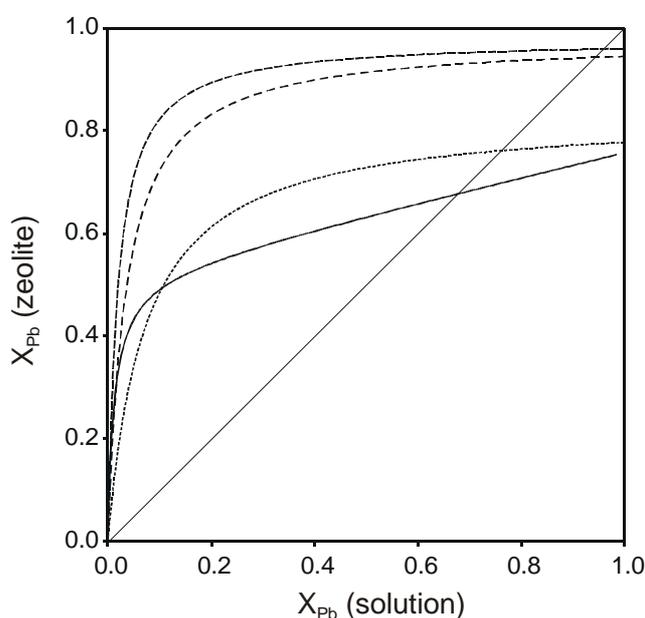


Fig. 2. Experimentally determined exchange isotherms for $\text{Pb}^{2+} \rightarrow 2 \text{Na}^+$ in different natural clinoptilolites at 20 - 25°C and at 0.1 total solution normality: intermediate and long dashed curves [10], dotted curve [13], solid curve [14]. The discrepancies of the curves are explained by differences in CEC, extraframework cation distribution, and partial Si, Al ordering.

Akizuki et al. [19], using optical and X-ray techniques, found within one macroscopic ‘single crystal’ of heulandite domains of triclinic and monoclinic symmetry. The symmetry is different from growth sector to growth sector. The two-dimensional atomic arrangement exposed on a growth-step surface of a tetrahedral (Si, Al) framework differs on each surface. Depending on whether an extraframework cation is adsorbed on the surface, Al^{3+} (for charge balance) or Si^{4+} will be incorporated into the adjacent tetrahedron. Thus the degree of partial Si, Al ordering is different from growth sector to growth sector depending on its crystallographic orientation and type of extraframework occupant [19]. In other words, each crystal is composed of various polymorphs intergrown in a twin-like relationship.

Channon et al. [20] and Ruiz-Salvador et al. [21-23] calculated the minimum energy Si, Al arrangement for H_2O -free clinoptilolite-Na, heulandite-Ca, and solid solution members and determined different Al site preferences depending on type and placing of extraframework cations. Characteristic of such models is that for each bulk composition there are always several possible extraframework cation distributions leading to different Si, Al arrangements. Although these calculations were performed for anhydrous species, at least a corresponding difference in Al preference may be expected during crystal growth in a natural hydrous system.

Zhao et al. [24] noticed during HEU framework synthesis that for a given aluminosilicate-gel composition the Si/Al ratio in the zeolite framework strongly depended on the applied alkali hydroxide. Na and K produced HEU zeolites with an Si/Al ratio significantly higher than the one in the starting gel, the opposite was found for Li, whereas clinoptilolite-Rb had a composition close to the gel. These results may be interpreted that depending on the alkali cation, a different crystal growth mechanism operates. Thus during crystallization different growth surfaces are exposed leading to a different distribution of Al tetrahedra [19].

2.3. Low symmetry HEU frameworks

There is also direct experimental evidence for low symmetry HEU frameworks. In a series of exchange experiments (K, NH_4 , Rb, Cs, Cd, and various alkylammonium ions) using as starting material the same Na-exchanged heulandite from Nasik (India) with the original composition $\text{Na}_{0.96}\text{K}_{0.09}\text{Ca}_{3.54}\text{Al}_{8.62}\text{Si}_{27.51}\text{O}_{72} \cdot n\text{H}_2\text{O}$, different space groups ($C2/m$, Cm , and $C\bar{1}$) were analyzed for the exchanged products [25-28]. The differences in symmetry were also reflected in different patterns of Si, Al ordering. There are two explanation for this observation: (i) The large single-crystals (up to 0.5 mm in maximum dimension) from Nasik were structurally inhomogeneous [19], (ii) the crystals were all triclinic, space group $C1$, and the observed space group depended on whether the exchanged cations occupied a position on a special position of local $2/m$, or m , or $\bar{1}$ symmetry enhancing the symmetry information of the Si, Al distribution in the framework. The difference of partial Si, Al ordering alone (deviating from $C2/m$ symmetry) is not sufficiently pronounced to be resolved from an X-ray single-crystal experiment. Notice that not necessarily the ‘true’ Si, Al distribution will be resolved in such a diffraction experiment but only the contribution from the Si, Al arrangement that is in resonance with the ‘signals’ from the extraframework occupant. Probably a combination of both inhomogeneity and low symmetry enhancement is the reason for the observation of different space groups. Yang and Armbruster [25] studied the structure of two Cs-exchanged crystals both had $C\bar{1}$ symmetry but one crystal displayed a more pronounced Si, Al ordering pattern than the other one. This example suggests an

inhomogeneous starting material [19]. For all hitherto analyzed triclinic HEU frameworks the deviation of the α and β angles from 90° was below 0.5° [19, 25, 28, 29].

2.4. Consequences for further research

The above observations and discussions indicate that HEU frameworks behave differently compared to most synthetic zeolites with disordered or partly disordered Si, Al distribution. Even for a given Si/Al ratio the exact exchange behavior of a HEU framework can not be predicted based on the existing knowledge. One of the reasons is the low topological symmetry ($C2/m$) of the HEU framework compared to the cubic frameworks of e.g. LTA or FAU. In low symmetry structures the distribution of Si and Al, or the existence of numerous polymorphs, plays a much more important role than in a high symmetry framework. In summary, we have to accept the conclusion [14] that for any ‘sophisticated’ practical application of natural clinoptilolites specific studies on representative samples from the deposit that is being examined for its exploitation potential have to be carried out.

Even exact knowledge of the exchange behavior of well defined synthetic HEU frameworks [24] would not circumvent this problem. For a natural sample we never know its original formation condition and extraframework composition. It could well be that subsequent penetrating fluids in the deposit altered the original composition.

The positive aspect of the structural complexity of HEU frameworks is that it offers the chance to learn more about tailor-made design of synthetic tetrahedral framework structures with only partly ordered Si, Al distribution.

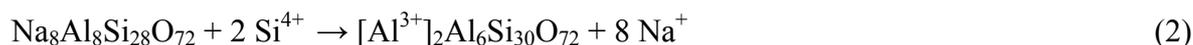
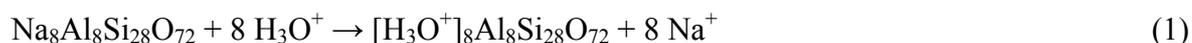
2.5. The Si, Al distribution in ‘activated’ clinoptilolite

For most catalytic applications ‘activated’ zeolites are required. There are two standard routes how this activation can be achieved. Fairly well understood is ion-exchange to clinoptilolite- NH_4 with subsequent release of H_2O and NH_3 upon heat treatment above 843 K leading to anhydrous clinoptilolite-H with Brønsted centers [e.g. 30, 31]. Upon dehydroxylation at higher temperature the concentration of Brønsted sites (acidic hydroxyl groups) decreases and Lewis sites are formed. Heat treatment of clinoptilolite- NH_4 above 673 K leads also to partial dealumination of the framework and migration of Al to extraframework sites [32, 33].

The second mechanism is based on acid treatment of the ‘raw’ zeolite [e.g. 34]. It was hitherto believed that the extraframework cations are replaced by H_3O^+ and the tetrahedral framework is altered by loss of Al. According to Sychev et al. [34] ^{27}Al and ^{29}Si NMR spectra of acid treated clinoptilolite-Na indicated that tetrahedral fragments consisting of SiO_4 tetrahedra connected to two AlO_4 tetrahedra are attacked, decreasing (for 2M HCl) the Al concentration from originally 5.9 to 4.1 pfu. Misaelides et al. [35] leached natural heulandites for 48 h with HCl solution of varying concentration (0.001 to 2 M) and noticed for samples treated with 1 and 2 M HCl partial surface amorphization and decreasing Al concentrations from the interior to the rim. The rim approached characteristics of amorphous silica gel [35-37]. Yamamoto et al. [38] imaged by atomic force microscopy the (010) surface of heulandite leached with 0.2 N H_2SO_4 and found pits caused by layer-to-layer dissolution. Heulandite-Na exposed for 15 weeks at 423 K to 0.5 M RECl_3 solution (pH 2.8) led to surface erosion and almost complete extraction of Na also in the center of heulandite crystals [39]. The loss of Al in the center of the crystals was low. Subsequent X-ray single-crystal structure analysis [39] indicated partial rearrangement of framework Al to hydrated extraframework Al, where Al

preferred octahedral coordination. Thus not only H_3O^+ but also Al^{3+} appeared as extraframework cations.

In other words acid leaching of heulandite causes (i) Al and extraframework cation depletion on the surface leading to an amorphous silica layer and (ii) depletion of extraframework cations in the core of the crystals where the HEU framework is still intact. In extreme cases all extraframework cations are lost and for charge balance two different exchange mechanisms operate:



These data indicate that the structural state of acid leached heulandite or clinoptilolite is only poorly defined. The acidity of the solution, the time and temperature of leaching, crystal size, original crystal structure and composition have a strong influence on the leached structure. Variation of any of these parameters may cause variations in the structural state and in the associated catalytic behavior of the leached material.

3. RECENT PIONEERING STUDIES

3.1. Atomic force microscopy (AFM)

Selective catalytic reactions occur also by molecular recognition on the external surface of zeolite crystals and therefore surface-structural information is vital for understanding catalytic mechanisms [40]. Large natural crystals of heulandite are available from various deposits and for this reason some of the pioneering AFM imaging of zeolite surfaces has been performed on these minerals [41-45]. ‘Molecular resolution’ was obtained for the heulandite (010) face that is densely packed without giving access to the two-dimensional channel system. This face was selected because it is prominent in natural crystals and (010) is also a perfect cleavage plane. In contrast, the resolution of the (100) surface, characterized by channel mouths of the eight-membered ring channels, was considerably poorer. Channel in- or outlets could not be resolved but appeared as undifferentiated grooves. Yamamoto et al. [45] argued that the lower resolution is caused by the tip-sample interactions on corrugated surfaces due to the channel mouths. In addition, it must be considered that faces like (100) are always decorated by traces of the perfect (010) cleavage and have therefore a rough surface. Corresponding low-resolution results were obtained for channel mouths in natural stilbite and mordenite. However, the ordered pore structure characterized by 12-membered rings could be imaged on the (001) face of a synthetic mordenite after scrapping off amorphous coatings [46].

Crystal growth induced steps ($n \times 9 \text{ \AA}$) on the heulandite (010) surface are either one or multiple tetrahedral layers thick [45]. Similar features have previously been observed on (010) cleavage plates [42]. In addition, growth spirals [44] and etch pits [38] on heulandite (010) faces were imaged.

Adsorption of pyridine bases is generally applied to test the surface acid properties of zeolites. Adsorbed pyridine base molecules interact with the surface acid site and the strength of the interaction can be monitored by spectroscopic methods. Komiyama et al. [47] obtained in situ molecular AFM images of well ordered arrays of pyridine and β -picoline on the (010)

surfaces of heulandite and stilbite and examined their orientation by semi-empirical molecular orbital calculations.

3.2. Clinoptilolite – heulandite electrodes for analytical application

A carbon paste electrode modified with Cu^{2+} -doped clinoptilolite powder has been evaluated as an amperometric sensor for non-electroactive NH_4^+ in flow injection analyses [48]. The conductivity of heulandite single crystals parallel to [100] has been studied under isothermal conditions as a function of the H_2O content, small polar organic molecule concentration, and charge compensating cations. Results indicate that heulandite electrodes will be applicable for analytical purposes in aqueous solution [49].

4. APPLICATION

4.1. Ion exchange and adsorption

Clinoptilolite and heulandite are low field strength zeolites for which the cation specificities $\text{Cs}^+ > \text{Rb}^+ > \text{NH}_4^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+ > \text{H}^+$, and $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$ are predicted [11, 12]. Corresponding theoretical estimates yielded $\text{Ba}^{2+} > \text{Pb}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+}$ [16] but experiments revealed $\text{Pb}^{2+} \approx \text{Ba}^{2+} \gg \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Cd}^{2+}$. Using clinoptilolite-Na as reference $\text{NH}_4^+ > \text{Pb}^{2+} > \text{Na}^+ > \text{Cd}^{2+} > \text{Cu}^{2+} \approx \text{Zn}^{2+}$ [14] and $\text{Pb}^{2+} > \text{NH}_4^+ > \text{Cu}^{2+} \approx \text{Cd}^{2+} > \text{Zn}^{2+} \approx \text{Co}^{2+} > \text{Ni}^{2+} > \text{Hg}^{2+}$ [15] has been determined.

Charge-balancing cations present on the surface of very fine-grained clinoptilolite can be replaced by high-molecular-weight quaternary amines [50], such as hexadecyltrimethylammonium (HDTMA) whereas the internal zeolite cavities remain accessible for small cations. Surfactant modified zeolites (SMZ) absorb CrO_4^{2-} , benzene, and perchloroethylene (PCE) suggesting that a stable HDTMA bilayer (Fig. 3) formed on the external surface of the zeolite. Nonpolar organic solutes are sorbed by the organic phase whereas anions (CrO_4^{2-}) are retained on the outward pointing positively charged headgroups of the surfactant bilayer [50]. Various types of surfactants on clinoptilolite were applied to extract benzene, toluene, and xylenes from petrochemical spills [51]. HDTMA modified clinoptilolite exhibits enhanced sorption of U^{6+} [52, 53].

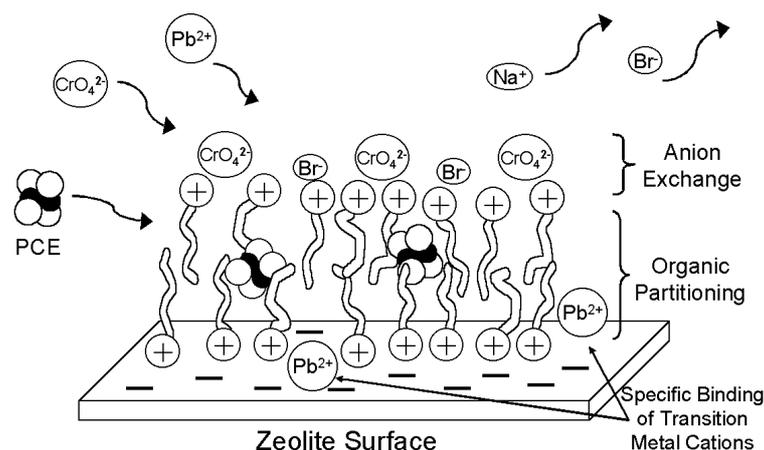


Fig. 3. Sketchy drawing of HDTMA forming a bilayer (tail to tail) on the surface of clinoptilolite [50]. Nonpolar organic molecules (PCE) partition into the bilayer, anions (CrO_4^{2-}) exchange with the counterions of the surfactant, cations (Pb^{2+}) bind to the zeolite surface.

δ -MnO₂ precipitated on the clinoptilolite surface was successfully applied for removal of Mn³⁺ from surface and deep-well water [54, 55] and for the treatment of paint-shop effluents [56].

4.1.1. Pollution abatement

Pilot studies of NH₄⁺ removal from municipal wastewater by using clinoptilolite-containing tuff were reported from various countries. After exchange and subsequent regeneration of the zeolite with NaCl/KCl solutions ammonia was stripped from the solution and an ammonium-phosphate fertilizer was produced. The Tahoe-Truckee Sanitation Agency, California, treated between 1978 and 1993 8·10⁷ m³ wastewater applying a clinoptilolite tuff for ammonia exchange. The system was designed to accommodate a flow rate of 26,100 m³/day of wastewater and to extract 19.5 mg NH₄/liter (507 kg) from a feedwater containing ca 25 mg/liter [57]. Ca-saturated clinoptilolite is used for ammonia removal from NASA's advanced life support wastewater system [58] to establish long term human presence in space. Natural zeolites are also produced for Pb²⁺ and Cd²⁺ removal from wastewater [e.g. 59, 60] and many other environmental application [61].

Low-cost surfactant-modified zeolites (SMZ) have been prepared in multi-ton quantities for use as subsurface permeable barriers to ground-water contaminant migration [50]. Most other studies on SMZ comprise small-scale laboratory experiments [e.g. 62, 63].

4.1.2. The 1986 Chernobyl disaster

In the USA and Great Britain phillipsite-, clinoptilolite-, and chabazite-rich tuffs are routinely applied for the decontamination of radioactive wastewater to remove Cs and Sr radioisotopes [e.g. 64]. However, these are small-scale operations compared to the extensive use of natural zeolites at Chernobyl.

During the Chernobyl disaster thirty to forty times the radioactivity of the atomic bombs dropped on Hiroshima and Nagasaki were released. The main radioactive isotopes from the Chernobyl accident were ¹³⁷Cs, ¹³⁴Cs, ⁹⁰Sr, and ⁸⁹Sr. The details of zeolite applications at Chernobyl remain rather obscure because of a secrecy problem still remaining after disintegration of the former Soviet Union. About 500,000 tons of zeolite rocks, mainly containing clinoptilolite, were processed at various deposits in Ukraine, Georgia, and Russia specifically for use at Chernobyl [65]. The majority of the zeolites was used for the construction of protective barriers and for agricultural applications in polluted areas.

Decontamination of potable water of the Dnieper river by using a combination of dust-like clinoptilolite and aluminum sulfate followed by filtration through clinoptilolite layers led to a drastic decrease of radioactivity [66, 67]. In addition, filters of clinoptilolite tuffs were suggested to extract radionucleides from the drainage water of the encapsulated Chernobyl nuclear power plant. Filtration reduced ¹³⁷Cs by 95% and ⁹⁰Sr by 50-60%. After one year the filters carrying a radioactivity of 10⁻⁵ Ci/kg were exchanged and buried [66].

To reduce Cs radionucleides in cow milk in Bulgaria 10% clinoptilolite was added to the cow feed resulting in 30% Cs reduction in the milk [68]. For Cs decontamination of children chocolate and biscuits were prepared containing 2-30 wt.% pure and powdery clinoptilolite [68]. In Western Europe clinoptilolite was tested to reduce radionucleide levels in soil [69], plants [70], sheep [71], broiler chicken [72], and fruit juice [73].

4.1.3. Agronomic and horticultural applications

The purpose of zeolite application in this field is slow-release fertilization or a combination of ion-exchange and mineral dissolution reactions. Mainly K- or NH₄-saturated clinoptilolites

are used [74]. The term *zeoponics* can be applied to the cultivation of plants in any artificial soil in which zeolite minerals constitute an important component, e.g. in microgravity environments or lunar outposts [75]. The first *zeoponic* space vegetables grown from seeds were tiny radish roots produced on MIR OS in 1990 [76].

4.1.4. Animal hygiene and bedding products

Application of clinoptilolite in this area is favorable because of its high NH_4^+ exchange capacity and surface absorption of odors (e.g. ethylene, aldehydes, mercaptans, ketones, H_2S). Cat litter is sold in small bags yielding a profitable price of ca. 800 US\$ per ton [77]. Clinoptilolite occupies only a small niche in this market. The majority of cat litter is produced from clays. The annual volume of cat litter worldwide consumed equals about the annual production of natural zeolites.

4.1.5. Nutrition and health

The physiological effects of clinoptilolite appear to be related to their high cation-exchange capacity, which affects tissue uptake and utilization of NH_4^+ , Pb^{2+} , Cd^{2+} , Cu^{2+} , Cs^+ , and other cations in animals [78]. Clinoptilolite appears to be stable in the gastrointestinal tract and reduces ammonia toxicity in pigs and sheep. In ruminants clinoptilolite alters rumen fermentation, thereby modifying volatile fatty acid production by rumen microbes and changing milk and body fat content. Pigs, chickens, and turkeys are protected from mycotoxins in contaminated grains. The aflatoxin concentration in milk is reduced if cows are fed aflatoxin-contaminated feeds. The details of this protection mechanism is not yet understood but adsorption on the zeolite-surface may play an important role. In general, addition of 1 to 5 wt.% clinoptilolite to the diet of animals has been shown to improve growth and feed utilization and to reduce the incidence and severity of diarrhea in pigs, cattle, sheep, and chickens. Ag-exchanged clinoptilolite eliminates the microorganisms *E. coli* and *S. faecalis* from water after 2 h of contact time [79]. Clinoptilolite application is not restricted to animals but an anti-diarrheic drug (ENTEREX) has also been developed for humans [80]. Preliminary studies have been performed to test the potential use of clinoptilolite as a matrix for slow drug release [81, 82].

4.1.6. Gas separation

The gas adsorption characteristic of clinoptilolite strongly depends on the extraframework cations [83]. Nitrogen uptake, relative to methane, increases significantly away from the either pure Ca- or K-exchanged form. It is suggested that a specific K-Ca distribution within the structural channels may act as hydration controlled nano-valve [84] permitting diffusion of N_2 but repelling CH_4 . Partly exchanged clinoptilolites applied for N_2 and O_2 separation from air yielded increasing separation rates for the sequence $\text{K} > \text{Rb} > \text{Na} > \text{Cs} > \text{Li}$ [85]. There are several patents describing separation of CH_4 from N_2 , hydrocarbons from CO_2 and N_2 , O_2 enrichment in air, and SO_2 separation from air.

4.2. Catalysis

As examples, xylene isomerization, toluene hydrodemethylation, *n*-butene isomerization, dehydration of methanol to demethyl ether, hydration of acetylene to acetaldehyde [31], catalytic reduction of NO [86] have been described to be successful if applying different varieties of treated clinoptilolite (cation exchanged or 'activated'). For a rough estimate about the importance of clinoptilolite for catalytic applications a search in the *Chemical Abstracts*

was performed (*clinoptilolite and catalysis*) leading to 413 hits between 1966 and 1999 (1-32 papers per year). Due to the low number of publications per year the histogram (Fig. 4) reveals a fairly coarse structure but a maximum in the early eighties and a minimum in the early nineties with a subsequent increase to recent times is recognized. If the statistical *clinoptilolite* data are normalized to the total number of papers dealing with *zeolite and catalysis* (31,034 hits) the maximum in the early eighties (ca. 3 % of the papers on *zeolite catalysis*) becomes even more prominent (Fig. 4). A closer look at research subjects in the statistical peak area does not indicate any specific invention that could be responsible for the increased scientific activity at this time. However, during increased activity (early eighties) more than 70% of the listed papers were written in Russian. In contrast, in 1998 ca. 60% were written in English (20% in Russian) but ca. 40% of the research institutions still belonged to countries of the former Soviet Union. The shallow minimum in the early nineties is characterized by a decreased publication activity in the former Soviet Union.

Thus the statistical pattern is governed by the political development in Eastern Europe. During the cold war East European countries had no excess to the major producers of synthetic zeolites thus they developed technologies to use their abundant natural deposits for catalytic applications. The disintegration of the Soviet Union, accompanied by a political and economic crisis, led to a decrease of research activity in this field. The slight recovery of this trend in recent time is associated with an increased number of English papers written by East Europeans (lift of the iron curtain). One may extrapolate that in the future natural zeolites will become less important for catalytic applications.

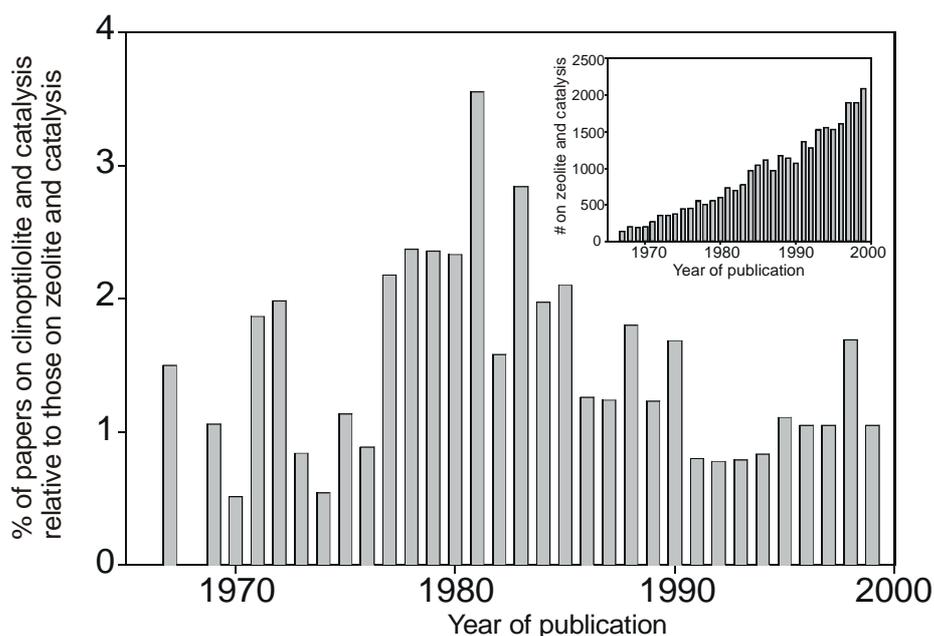


Fig. 4. Histogram of papers listed in the *Chemical Abstracts* dealing with *clinoptilolite and catalysis*. The inset displays a histogram of papers on *zeolite and catalysis*. This histogram is used to normalize the *clinoptilolite and catalysis* histogram. Notice the maximum in the early eighties caused by an increased research activity in the former Soviet Union.

5. OUTLOOK

The highest profits for clinoptilolite seem to be achieved in the field of cat litter, animal bedding, and odor absorbents. With increasing environmental conscious applications in pollution abatement gain importance, in particular, if large amounts of ion exchanger or absorber are needed. The versatility of surface modified clinoptilolite is not fully explored yet. As the recent example of U^{6+} sorption [52,53] on the surfactant indicates, many other applications seem possible where the advantages of the porous bulk structure are combined with specific properties of well-chosen surfactants.

Most of the basic research work concentrated on ion exchange behavior studied in form of exchange isotherms. Nevertheless kinetic aspects are equally important [9, 87, 88] and there is a lack of knowledge, in particular for structurally and chemically well-defined clinoptilolites. Structure modeling has to be expanded to hydrous systems [89] to provide better understanding of H_2O interactions with extraframework cations and the inner cavity or channel surface. HEU frameworks are interesting research subjects because of the only partly ordered Si, Al distribution, the low symmetry of the framework, and the different types of channel systems. In this respect understanding of structure and properties of clinoptilolite provides a key for zeolites in general.

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