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ZEOLITES – MATERIALS OF SUSTAINABLE SIGNIFICANCE (SHORT RETROSPECTIVE AND OUTLOOK)

It has been more than 250 years since 1756, when the famous Swedish mineralogist Axel F. Cronstedt first recognized new mineral species in the northern copper mine Svapparaara and called them “zeolite“. Actually, this newly discovered mineral, found in the vugs and cavities of basalt rocks, was a stilbite. For many years thereafter, zeolites, being spectacular crystals which aroused from the volcanic matrix, were of some commercial interest for mineralogists [1].

The word “zeolite“ has Greek roots and means “boiling stones“ (zein = to boil and lithos = stone) which is connected with the visible loss of water observed when the natural zeolite is heated in the mineralogical blowpipe.

Volcanic rocks containing natural zeolites, hydrated aluminosilicate minerals that contain alkaline and earth-alkaline metals, have been mined worldwide perhaps for more than 1000 years, mostly to be used as cement and building stone. Nevertheless, it is believed that zeolitic tuff may have been used already by the ancient Romans and Indians 2000 B.C. for construction of houses, roads, sewage channels, aqueducts, temples and pyramids or, according to one of the life theory hypotheses, zeolites may have even catalyzed the reactions of ammonia and carbon oxides to aminoacids and thus probably generated initial protein precursors for the development of the first living organism on Earth.

Indeed, volcanic tuffs from Pozzuoli (Campania) region and tuffo napolitano have been known to be easily sculptured and shaped (for example, Castel dell’Ovo in Naples was constructed from Vesuvius volcano – figure 1). They may have been used not only by the ancient Roman society, but also all over the world for the construction of many front parts of government buildings also in later periods [2].

The early qualitative observations of natural zeolites were considerably extended in the 1940s by the pioneering work of a renown British professor R.M. Barrer and his

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school in England as well as by Union Carbide Corporation laboratories in the United States. Since that time zeolite science has started to be systematic and zeolites have been sold as an industrial mineral on the markets.

The characteristic behaviour of natural zeolites as molecular sieves for adsorbing small-size gaseous molecules and rejecting larger ones was recognized in the 1930s, particularly in natural chabazite species. Based on Barrer's earlier synthesis experiments, R.M. Milton from the Linde Division of Union Carbide Corporation in Tonawanda, New York, undertook an experimental program aimed at air-separation applications to produce chabazite. Although his initial attempts failed to produce chabazite, he did prepare an entirely new zeolite structure, a structure not found in nature, which had even better adsorption properties than chabazite. This zeolite was, of course, Linde Type A zeolite (LTA), which was one of the mainstays of the worldwide molecular sieves business for several decades [2].



Fig. 1. The front part of Castel dell'Ovo in Napoli was constructed from tuffo napolitano

The development of the environmental applications of natural zeolites was preceded by the development of the permutites, i.e. synthetic amorphous aluminosilicates produced by the above mentioned company, especially for water softening. However, a disadvantage of the permutites was their solubility at pH extremes [3].

Although the process of ion exchange was discovered in 1850, it was not applied as an industrial separation process until 1905, when a German chemist Richard Gans demonstrated it could be used as a unique process for both water softening and the removal of iron and manganese ions.

The extensive development of the new organic ion exchangers, e.g. sulfonated and aminated copolymers of styrene and divinylbenzene, after the 2nd World War (WW II),

with superior stability and ease of regeneration, enabled a rapid expansion of industrial applications of the ion exchange processes [4].

Greater stability of some natural zeolites vs. organic resin ion exchangers under certain conditions and their high selectivity towards particular ions allowed for the development of new environmental applications of zeolites. Generally, this did not involve the substitution of other exchangers for zeolites in existing applications but rather the development of entirely new processes for which the existing ion exchangers were not well suited.

In the 1950s, Union Carbide Corporation (at present Dow Chemicals) and some oil companies, especially Shell Development Company in the USA, Canada and Mexico, started to use the natural zeolites (erionite, chabazite and mordenite) as cheap molecular sieve amendments for the purification and desiccation of low-grade natural gas streams.

In the following years, new diagnostic methods, mostly X-ray powder diffraction, contributed to discovering dozens of bedded rocks of volcanic origin that appeared to consist of uninteresting clay or low-grade bentonites which actually contained near-monomineralic assemblages of micrometer-size zeolite crystals. The largest known deposit of clinoptilolite in the United States was found in the Mojave Desert near Hector, California, within a deposit of bentonite called Hectorite, because of its proximity to Hector. High-grade clinoptilolite ores of similar quality to Hector clinoptilolite, with almost monoionic varieties and over 90%-zeolite mineral content, were opened in Castle Creek (Idaho), Buckhorn (New Mexico) and Fish Creek Mountains (Nevada). The occurrence of the clinoptilolite was reported in 66 ores of the country; moreover, the U.S. zeolites were predominantly in the sodium form [2], [5], [6].



Fig. 2. A view of an open-pit mine of clinoptilolite-rich tuff in Eastern Slovakia (left) and erionite-rich localities in Cappadocia, Turkey (right)

Nowadays over 1000 occurrences of zeolite minerals have been reported, predominantly from sedimentary rocks of volcanic origin in more than 40 countries of the world, e.g. USA, Mexico, Cuba, Chile, Argentina, South Korea, Japan, China, New Zealand, South Africa, Tanzania, Kenya, Iran, Israel, Bulgaria, Romania, Hungary, Slovakia, Slovenia, Ukraine, Croatia, Georgia, Turkey, Italy and many others. Most of the mines are designed to exploit clinoptilolite or mordenite, although chabazite and phillipsite are also mined. Mining a zeolitic deposit is relatively simple compared to the mining of most other mineral commodities. Zeolite-bearing formations are generally at or close to the surface and require the removal of only small amounts of overburden to expose the ore (figure 2).

Most zeolites in sedimentary rocks are formed from volcanic ash or other pyroclastics in the reaction of the amorphous aluminosilicate glasses with pervading pore water. Others originate from the alteration of pre-existing feldspars, feldspathoids, biogenic silica or poorly crystalline clay minerals. The factors controlling whether a zeolite or clay mineral will form is still insufficiently understood, however temperature, pressure, reaction time, alkalinity and dissolved salts in pores solutions seem to be the dominant factors.

Although the zeolites have attractive ion-exchange properties, until the early 1960s they were not found to be of significant commercial use as ion exchangers. This was largely due to the lack of availability and lack of knowledge of their properties. The first environmental application was developed by L.L. Ames in 1961 for the treatment of high-level alkaline wastes from the PUREX processing of spent nuclear fuel. Here, zeolite's high stability in ionizing radiation and in aqueous solutions at elevated temperatures and at the elevated pH levels together with their excellent selectivities towards certain radioisotopes was the reason why these minerals were applied for the recovery and concentration of Cs(137) and Sr(90) radioisotopes in long-term storage.

The zeolite ion-exchange process was developed and used also in the Hanford Atomic Energy Project for the separation of radioactive cesium from highly radioactive liquid wastes. The cesium content in the wastes was in the order of 0.1 mmol per litre and approximately 4.5 mol per litre of sodium concentration. The separation of the radioactive cesium from high-level liquid waste, prior to the evaporation and solidification of the waste in large underground storage tanks, was necessary on account of the excessive heat generation resulting from Cs(137) fission reactions in salt cake. The waste was pumped downflow through a bed of chabazite-bearing material until cesium breakthrough occurred [7].

In the Idaho National Engineering Laboratory, low-level radioactive wastewater from an irradiated fuel-storage basin was passed through four clinoptilolite columns in parallel. Each column consisted of two drums connected in series. When radionuclides broke through the bottom drums, the top drums were replaced and removed from use, sealed and buried as solid waste [8].



Fig. 3. Natural clinoptilolite columns for ammonium removal and the inside of the regeneration hall at Tahoe Truckee Sanitation Agency in California

Clinoptilolite helped in a variety of ways by tackling the dramatic detrimental effects of the Chernobyl accident in 1986, when about a half million tonnes of clinoptilolite-bearing materials from all former the Soviet Union zeolite opencasts were successfully used to reduce and buffer the huge radioactive explosion [7], [9]. In addition, filters of clinoptilolite tuffs were suggested to extract radionuclides from the drainage water of the encapsulated Chernobyl nuclear power plant. The filtration reduced radiocesium(137) by 95% and radiostrontium(90) by 50–60%. The decontamination of potable water from the Dnieper River using a combination of dust-like clinoptilolite with aluminium sulfate coagulation, followed by clinoptilolite filtration, led to a drastic decrease of radioactivity. In Bulgaria, 10% clinoptilolite was added to the cow feed which reduced radiocesium content in the produced milk by 30%.

The presence of clinoptilolite and mordenite in undersaturated tuffs at Yucca Mountain in Nevada drew attention as a possible high-level radioactive waste repository. These two zeolites can retard radionuclides migration through cation exchange, due to their exchange capacities as high as 2.0 meq per gram for Cs(137) and Sr(90). This is important as there exists a significant hazard to the environment from waste canisters allowing reliable containment for over 1000 years [10], [11].

Later the environmental application of clinoptilolite by the Ames and Mercer concerned excellent ammonium-ion selectivity of clinoptilolite and led to the development of the ammonium-removal process from municipal wastewater in the early 1970s. These authors together with The Plant Engineering Service CH₂M-Hill proposed a tertiary treatment unit for Battelle Northwest/ South Tahoe Public Utility District to protect the quality of the Truckee River in California (figure 3). The regional facilities using naturally occurring clinoptilolite for ammonium removal in tertiary sewage treatment became fully operational in the early 1980s and since then their operation has been uninterrupted, it is the only industrial plant using natural zeolite in the world [12].

The current world production of synthetic zeolites is estimated at about 1.4 million metric tons per year. Almost 80% of synthetic zeolites are used in laundry detergents. The petroleum industry is the most important consumer of zeolite-based catalysts. All the world gasoline is produced or upgraded using zeolites. Methanol, as the main product from the Fischer-Tropsch reaction, can be efficiently converted to high-octane fuels by using a ZSM catalyst (MTG Process) and thus it offers the opportunity to produce fuels from alternative sources rather than the from deficient crude oil. China is the largest manufacturer of zeolites with an estimated output of 2.5 Mpta or 65% of world output. Cuba accounts for a further 15% of the world production. Other significant producers include Germany, Japan and South Korea.

The ability to release beneficial elements while capturing and binding others, often less desirable ones, makes zeolite an ideal media for the selective adsorption of certain elements and compounds from soil, water and air. Zeolite can exchange calcium for the ammonia naturally produced in the animal digestive process. It not only reduces the amount of ammonia which is released as harmful gas, but also remains in the manure as added nitrogen, thereby increasing the nutrient value of the manure used as a fertilizer. 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 of rumen microbes as well as changing the body fat and milk content [13]. Copper- and silver-exchanged zeolites are used as antimicrobial agents in dust masks, plastic films and antifouling paints to control barnacle growth on boats. Zeolite-based oxygen-concentrator systems are widely used in the production of medical-grade oxygen due to the zeolitic molecular sieve effect able to remove and purify oxygen separated from nitrogen in air (Pressure Swing Absorption).

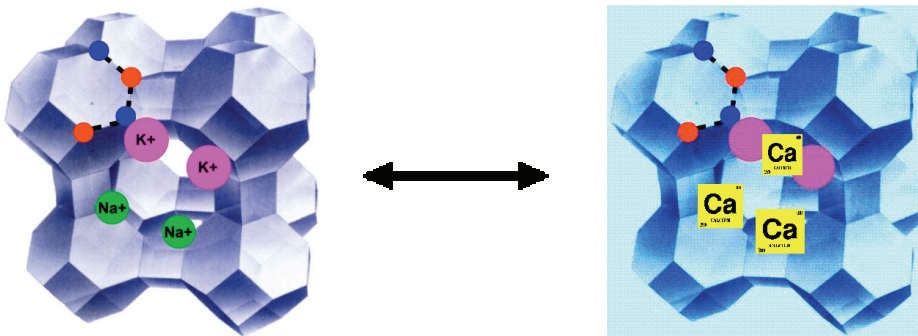


Fig. 4. Synthetic zeolites A and X are used in detergents for water hardness removal

Pet litter, animal feed and water purification account for more than 70% of the market sales tonnage (figure 4). Zeolite filtration is used in some marine aquaria to keep nutrient concentrations low for the benefit of corals adapted to nutrient-depleted

waters. The versatility of surface-modified clinoptilolite is not fully explored yet; however, low-cost surfactant-modified zeolites are prepared in multi-ton quantities for the use as subsurface permeable barriers against groundwater-contaminant migration (figure 5).

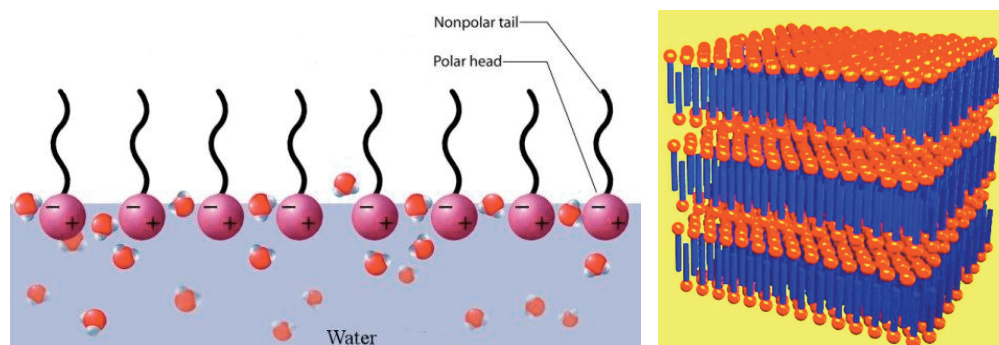


Fig. 5. Sketch of mono- and bilayer surfactant used for zeolitic surface modification

The above description of versatile applications of bilayer zeolite may have to be finished by mentioning the challenging zeoionic space vegetables, i.e. tiny radish roots, grown at the MIR orbital space station in 1990 as well as NASA Advanced Life Support using Ca-saturated clinoptilolite for ammonia removal in the wastewater system which was designed to enable long-term human survival in space [14].

It may be concluded that better knowledge of natural zeolite properties together with growing needs for selective, stable ion exchangers in pollution abatement, water treatment, energy production, agriculture, aquaculture, animal nutrition, metal processing, biomedical applications and other uses have contributed to the exciting practical development of these unique minerals (figure 6).



Fig. 6. Zeocem Company in Slovakia produces various agricultural clinoptilolite-based substrates for soil fertilizing

Nevertheless, the rapid escalation of the prices of raw materials may place these volcanogenic sedimentary rocks at an improved price-performance position compared to those produced synthetically or may permanently increase the number of crystalline zeolite-type or other porous carbon- or silica-based substances, even in the future.

Thanks to the chemical and mineralogical variability of zeolitic rocks and thanks to their moderate ion-exchange and selectivity properties, the exploration of new zeolite ores in the individual countries has initiated unpredictably wide national research and versatile industrial applications of these tuffaceous materials all over the world.

The progress in marketing natural zeolites as building stones, as lightweight aggregate and pozzolans in cements and concretes, as a filler in paper, in the uptake of Cs and Sr from nuclear waste and fallout, as soil amendments in agronomy and horticulture, in the removal of ammonia from municipal, industrial and agricultural waste and drinking water, as energy supplier in solar refrigerators, as dietary supplements in animal diets, as consumer deodorizers, in pet litters, in the uptake of ammonia from animal manures, as ammonia filters in kidney-dialysis units and as a zeoponic substrate for growing plants on space missions and their recent success in healing cuts and wounds are encouraging, given that natural zeolites are considered a commodity of great potential the application of which is a promise of further expansion in the future [15].

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