

Environmental applications of natural zeolitic materials based on their ion-exchange properties

Carmine Colella



SK98K0310

*Dipartimento di Ingegneria dei Materiali e della Produzione, Università Federico II,
Piazzale V. Tecchio, 80 - 80125 Napoli, Italy*

Summary

Natural zeolites, such as clinoptilolite, chabazite, phillipsite and mordenite, exhibit good selectivities for some water pollutants, e.g., Cs^+ , NH_4^+ and Pb^{2+} . Zeolite-rich tuffs may be therefore utilized for removing the above and other cations from wastewaters before discharge. Continuous processes with fixed beds are usually employed for water purification, such as those in service in the USA for ammonium removal from municipal sewages. Direct addition of the ion exchanger is needed when the pollutant must be removed from soil and trapped in the zeolite framework. Discontinuous processes (addition of zeolite to the waste solution) are also possible, provided the polluted zeolitic sludge is stabilized-solidified in a cement matrix before disposal.

Introduction

Water pollution is matter of deep concern. Toxic cations, such as many heavy metal cations or ammonium, may be detrimental for the aquatic life and may reach also man through the food chain. This is why strict limitations have been imposed by many countries to wastewater discharge in the aquatic bodies (sea, rivers, lakes).

Municipal sewages or wastewaters of industrial origin must therefore be submitted to chemical and/or biological treatments prior to discharge. Cation abatement is achieved usually by precipitation, whereas ammonium is removed biologically, but both treatments may turn sometimes unsatisfactory, e.g., the limit for discharge is missed, because of peculiar troubles of chemical and/or physical origin (1). Ion exchange can be a feasible alternative to the usual chemical and biological methods. Zeolites in particular have demonstrated excellent selectivities for hazardous cations, reasonable reaction kinetics, and very moderate environmental impact. Natural zeolites present in addition the advantages of large diffusion and low costs.

This paper intends to review the main successful uses and prospects of applications of natural zeolites as cation-exchangers in the environmental pollution control.

Chemistry of natural zeolites

Natural zeolites, which can be conveniently utilized in processes of technological relevance, are those present in the large sedimentary tuff deposits, often of volcanic origin, widespread all over the world (2). Zeolites which are exploited or exploitable as ion exchangers are limited to four types: chabazite, clinoptilolite-heulandite, mordenite and phillipsite. All these types may be classified as siliceous zeolites, as their Si/Al ratio ranges between roughly 3 for phillipsite and chabazite and at least 4 for clinoptilolite and mordenite. Accordingly, considering that the zeolite percentage in the original rocks is normally greater than 50%, the average cation exchange capacity stands in the range 1.5-2.5 meq/g.

Cation selectivity and exchange kinetics

Although selectivity is a function of several parameters, either depending on the framework type and composition and on the nature of the cations in competition, a simple relationship of the selectivity with the framework composition may be worked out. Since the siliceous zeolites, as those of sedimentary origin, present a low anionic field strength, in a uni-univalent cation exchange, cations with low charge density, such as cesium and ammonium, are preferred. In the di-divalent exchange zeolites prefer in any case large cations, irrespective of their framework composition. Finally, in the uni-divalent exchange

selectivity is determined by the hydration energies more than by the cation-lattice interaction. Accordingly natural zeolites evidence a marked preference for cations with low hydration energy, e.g., lead.

With reference to the exchange kinetics, as the tuff pore dimensions are in the range 10^2 - 10^5 Å (4), cation diffusion is not affected by the porous matrix of the rock, so that the zeolite-rich tuffs behave as pure zeolites. Rate constants of the exchange reactions of Na-exchanged clinoptilolite-, chabazite- or phillipsite-rich tuffs for most heavy metal cations are in the range of 10^{-3} - 10^{-1} l/meq-min (5,6).

Continuous and discontinuous removal processes

Removal of hazardous cations by ion exchange using natural zeolites is commonly devised as a continuous process. Fixed beds of zeolite tuff grains are percolated by the water containing the cation(s) to be removed up to exhaustion and then regenerated by eluting them with a concentrated salt solution. Discontinuous removal processes (addition of zeolite to the waste solution) are also considered, when the efficiency of the continuous process is low, but in this case an additional procedure for stabilizing the pollutant-loaded zeolitic sludge, for instance in a cement matrix, is needed.

The main use of natural zeolites as cation exchangers for environmental protection have been reviewed recently by Pansini (7). The main fields in which the use of natural zeolites is advisable are:

- (a) *Removal of ammonium from municipal sewages.* Clinoptilolite is being used in some large-scale facilities in the United States, where ammonia is removed and recovered as ammonium sulphate fertilizer solution. Improvement in the process, still at level of pilot or demonstration plants, have been introduced with the RIM-NUT process, in which either ammonium or phosphate are removed and recovered as a solid fertilizer (8). Application of zeolites for ammonium removal in aquaculture is also reported in the literature.
- (b) *Removal of heavy metals from wastewaters.* These processes, either continuous or discontinuous, are still at level of laboratory tests. Zeolites utilized are clinoptilolite, phillipsite, chabazite; cations tested, are mainly lead, chromium, cadmium. Treatment of acid mine drainage has been also considered.
- (c) *Removal of radionuclides from nuclear power plant waters.* The decontamination of radioactive waste solutions is favoured by the high selectivity of natural zeolites for cesium, which is usually separated by ion exchange in fixed beds and then recovered as salt (Hartford Atomic Energy Project) or disposed as a solid waste (Idaho Nat. Eng. Lab.). Zeolite mixtures are usually necessary for the joint removal of cesium and strontium, because of the poor selectivity of natural zeolites for the latter contaminant. Mixtures of natural and synthetic zeolites have been used also for reducing the environmental impact of major accidents occurring in nuclear power plants, like those occurred in Three Mile Island, USA, and in Chernobyl (Russia). Preliminary data regarding other less common radionuclides are also available in the literature.

References

1. J.W. Patterson, *Wastewater treatment technology*, Ann Arbor Science Publishers, Ann Arbor, Michigan, 1975.
2. D.B. Hawkins, in *Zeoagriculture. Use of natural zeolites in agriculture and aquaculture*, W.G. Pond and F.A. Mumpton Eds., Westview Press, Boulder, Colorado, 1984, p. 69-78.
3. C. Colella, *Mineralium Deposita* **31**, 554-562 (1996).
4. V. Albino and C. Colella, in *Atti 2° Convegno Naz. AIMAT*, P. Giordano Orsini Ed., Univ. Trento (Italy), 1994, Vol. I, p. 497-504.
5. G. Blanchard, M. Maunaye and G. Martin, *Water Res.* **18**, 1501-1507 (1984).
6. C. Colella, M. de' Gennaro, A. Langella and M. Pansini, *Separation Science and Technology* **33**, 467-481 (1998).
7. M. Pansini, *Mineralium Deposita* **31**, 563-575 (1996).
8. L. Liberti, A. Lopez, V. Amicarelli and G. Boghetich, in *Natural Zeolites '93. Occurrence, Properties, Use*, D.W. Ming and F. A. Mumpton Eds., ICNZ, Brockport, N.Y., 1995, p. 351-362.