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## Natural Zeolites And Nuclear-Waste Management: The Case Of Yucca Mountain, Nevada, Usa

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Natural microporous zeolites first gained widespread attention in radioactive waste applications after the pioneering research of Ames in the late 1950's. In particular, clinoptilolite was demonstrated to be effective in removing Cs and Sr from process wastewaters. We now know that zeolite-rich rocks can retard, via simple cation exchange, the migration of radionuclides occurring in solution as simple cations (e.g., Cs<sup>+</sup>, Sr<sup>2+</sup>, and Ba<sup>2+</sup>). In addition to possessing very high cation-exchange capacities (~2 meq/g), clinoptilolite and mordenite have high selectivities for Cs, Ba, and Sr. Their high selectivities mean that these zeolites can sorb Cs, Ba, and Sr from solutions, even when these cations are present in small amounts together with large amounts of other competing cationic species. Both their high cation-exchange capacities and their selectivity for Cs and Sr are key in their use in radioactive waste applications.

The cation-sorbing capabilities of the natural zeolites, clinoptilolite and mordenite, were emphasized early in studies of the potential high-level radioactive waste repository at Yucca Mountain, Nevada. Indeed, the presence of zeolites at Yucca Mountain and the minerals' cation-exchange properties first drew attention to volcanic tuffs as possible hosts for radioactive waste disposal. However, further studies of natural zeolites at Yucca Mountain over the past two decades have illustrated that many different aspects of zeolite mineralogy are fundamentally important in radioactive waste isolation. Interestingly, sorption of simple cationic radionuclides by natural zeolites is only of minor significance in a geologic repository due to (1) the short half-lives ( $\leq 30$  yrs) of most of these radionuclides (e.g., <sup>137</sup>Cs and <sup>90</sup>Sr); and (2) generally high sorption coefficients of many other common minerals for simple cationic species. It is commonly considered that the primary heat-producing radionuclides, <sup>137</sup>Cs and <sup>90</sup>Sr, will have decayed long before the engineered portion of a repository (e.g., the waste canister) is breached. Although at least one isotope of Cs (<sup>135</sup>Cs) has a half-life sufficiently long ( $2.3 \times 10^6$  yr) to be of concern, the most important radionuclide migration issues in a geologic repository for high-level radioactive waste concern *anionic* species (e.g., TcO<sub>3</sub><sup>-</sup>, NpO<sub>2</sub>CO<sub>3</sub><sup>-</sup>, and I<sup>-</sup>) and long-lived *actinides* (e.g., Np and Pu) that often form large, complex aqueous species such as NpO<sub>2</sub><sup>+</sup> and UO<sub>2</sub><sup>2+</sup>. Few, if any, minerals at Yucca Mountain, or in nature in general, interact significantly with anionic species. However, minor and trace minerals such as smectite and Fe and Mn oxides and hydroxides can be important in retarding the migration of complex actinide species such as neptunyl. These details of the importance of zeolites in retarding the migration of radionuclides point to some of the limitations of natural microporous materials in real-world applications. Many of the radionuclides important in radioactive waste isolation form aqueous species too large to be accommodated in the extraframework positions in natural zeolites. However, the exchange capacities of clinoptilolite and mordenite are so large and their selectivities for Cs and Sr so great that their presence should not be discounted. The short-lived nuclides of Cs and Sr

account for 2/3 to 3/4 of the total activity in high-level waste at 100 years, and the presence of these zeolites provides assurance against significant movement of any simple cationic radionuclide. The fact that natural zeolites can act as efficient retardation barriers to the migration of Cs and Sr is confirmed by detailed trace-element studies on Yucca Mountain tuffs. Even thin layers of zeolitic tuff have effectively retarded the downward migration of Sr in the past.

In addition to the problems posed by the large radionuclide inventories in high-level radioactive waste, it is now well known that geologic emplacement of such waste will heat large volumes of rock, depending on the exact distribution and density of waste canisters. The potential repository horizon at Yucca Mountain is in the vadose (unsaturated) zone, and both zeolites and smectite will be important sources and sinks of water and thermal energy during dehydration/rehydration. These sources and sinks must be considered when modeling the long-term thermohydrologic behavior of Yucca Mountain. For example, simple calculations considering both the water content of clinoptilolite and the measured porosity of zeolitic tuff at Yucca Mountain show that a clinoptilolite-rich tuff contains approximately as much water in its structure as contained in the rock pores at 92% saturation (approximate measured saturation value in the vadose-zone zeolitic tuff). Heating a rock containing 80% clinoptilolite to 200°C will release an amount of water equivalent to ~27% of the available porosity and will result in a small but potentially significant volume decrease. Likewise, on cooling, partially dehydrated zeolites will rehydrate, readily taking up any free water initially available in the rock pores. Given the importance of water as a transport medium, it is clear that clinoptilolite and mordenite are extremely significant as both *sources* and *sinks* of water in the vadose zone. In addition, dehydration and hydration reactions of clinoptilolite and mordenite in the vadose zone can have important impacts on the total enthalpy of the natural system. Because the H<sub>2</sub>O molecules in clinoptilolite extraframework sites are energetically distinct from liquid water, the energy to heat and dehydrate a given amount of clinoptilolite to 200°C is 71 to 81% greater than the energy to simply heat the material, without dehydration, to the same temperature. Thus, the presence of hydrated natural zeolites can exert a considerable damping effect on the thermal evolution of a repository.

Finally, mineral reactions such as the transformation of clinoptilolite to analcime, may also be important if temperatures are sufficiently high. Such reactions are particularly important because they give rise to large volume reductions and production of water. Observed natural paragenetic sequences suggest that clinoptilolite may react to analcime at temperatures as low as 90-100°C, although the exact temperature depends on the associated aqueous silica activity. Crystallization of one mole of analcime from clinoptilolite produces 16 moles of silica, which may either be precipitated (as cristobalite or quartz) or may be carried away as aqueous silica. The reaction also produces 48 moles of H<sub>2</sub>O for each mole of analcime produced. Perhaps more importantly, the reaction results in a volume decrease of 21.5% if quartz is produced or 16.9% if cristobalite is produced. Clearly, the reaction of clinoptilolite to analcime would have profound effects on the rock mineralogic and hydrologic properties, resulting in a rock containing a much less sorptive zeolite (analcime). The large associated volume decrease would greatly impact the hydrologic properties of the rock.

These examples show the variety of ways in which natural microporous zeolites are important in a high-level radioactive waste application. Most importantly, the examples illustrate that the importance of zeolites extends far beyond simple cation-exchange interactions to phenomena that can affect the entire thermohydrologic system.