ZEOLITE STABILITY CONSTRAINTS ON RADIOACTIVE WASTE ISOLATION IN ZEOLITE-BEARING VOLCANIC ROCKS

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ABSTRACT

Silicic tufts of the southern Great Basin and basalts of the Columbia River Plateau are under investigation as potential host rocks for high- and intermediate-level radioactive wastes. Non-welded and partially welded tufts may contain major amounts (>50%) of the zeolite minerals: clinoptilolite, mordenite, and analcime. Densely welded tufts and some basalt flows may contain clinoptilolite as fracture filling which limits permeability of these rocks. The cation exchange properties of these zeolite minerals allow them to pose a natural barrier to the migration of cationic species of various radionuclides in aqueous solutions. However, these minerals are unstable at elevated temperatures and at low water vapor pressures, and they may break down either by reversible dehydration or by irreversible mineralogical reactions. All of the breakdown reactions occurring with increased temperature involve a net volume reduction and evolution of fluids. Thus, they may provide both a pathway (shrinkage fractures) and a driving force (fluid pressure) for release of radionuclides to the biosphere. These reactions may be avoided by keeping zeolite-bearing horizons saturated with water and below about 85°C. This may restrict allowable gross thermal loadings in radioactive waste repositories in zeolite-bearing volcanic rocks.

INTRODUCTION

Silicic tufts which have undergone variable amounts of zeolitization are under consideration as a medium for the long-term isolation of high-level radioactive wastes (Smyth et al. 1978; Smyth and Sykes 1980; Sykes and Smyth 1980). One potential site in such a medium is located in southern Nye County, Nevada (Heiken and Bierver 1978; Sykes et al. 1979; Spengler et al. 1979; Bish et al. 1981) at Yucca Mountain, on and immediately adjacent to the Nevada Test Site (NTS). The principal zeolite phases in these rocks are clinoptilolite, mordenite, and analcime. They may comprise 90% or more of some horizons. The zeolites can act as a cation exchange medium to retard migration of some radionuclides in ground water. Cation exchange properties of these minerals have been reviewed by Vaughan (1978) and Smyth and Capurso (1981), and extensive studies have been carried out to measure sorption behavior of some zeolite-bearing rocks (Wolfsberg et al. 1979; Vine et al. 1980). However, major mineralogical changes appear to have occurred in these rocks at temperatures below 100°C. The four major zeolite zones described by Iijima (1975, 1980) have been recognized in these rocks (Bish et al. 1981). Major changes seem possible or likely if the rocks are heated further. Inasmuch as heat-generating wastes may be placed in such a medium, it is imperative to understand the types of mineralogical reactions and the conditions under which they may occur so that such reactions may either be avoided or allowed in the repository design.

Reactions that may occur in these rocks at temperatures below 200°C are of two types: simple reversible dehydration and complex mineralogical phase changes. The first of these involves the loss of loosely bound water of hydration in the zeolite. This water is not required for stoichiometry of the zeolite and may be lost reversibly without damage to the aluminosilicate framework. However, loss of the water can cause contraction of the unit cell (and hence individual grains) of as much as 10% by volume (Boles 1971, 1972) with concomitant development and propagation of fractures and loss of mechanical strength. The second type of reaction involves complete recrystallization and exchange of cations and or water with the environment. Such reactions may evolve (or incorporate).
significant quantities of water, result in volume changes in large quantities of rock, and alter physical and chemical properties of rock and incorporated fluids. The object of this paper is to review the stability relationships of the principal zeolites which are common in silicic tuffs and in fractures in basalts (clinoptilolite, mordenite, and analcime), and to infer any possible constraints on siting and thermal loading of a radioactive waste repository in such rocks. Of particular importance are dehydration and mineralogical reactions that occur among these phases at temperatures below 200°C.

STABILITY REVIEW

Dehydration Stability.—Literature on the thermal stability of clinoptilolite, heulandite, mordenite, and analcime is complex and, in places, conflicting. Laboratory studies of zeolite stability are of two principal types: those done at one atmosphere pressure or less, and those done at elevated water pressures. The former principally address dehydration reactions to metastable states, while the latter address the thermodynamic stability of clinoptilolite relative to other zeolite phases. Both types of reaction may constrain design of a waste repository in or near clinoptilolite-bearing rocks. Literature on the thermodynamic stability of these zeolites will be reviewed under "Mineralogical Stability" below. The dehydration of these minerals may cause water loss under unsaturated conditions, possibly affecting the stability of mine tunnels, or, in a worse case, control temperature and water pressure conditions during a thermal excursion. In either case, the reactions warrant investigation.

Because heating tests in dry atmospheres have been used to differentiate clinoptilolite from heulandite (Mumpfen 1960; Alietti 1972; Boles 1972), there exists considerable information on the thermal stability of these minerals under such conditions. Breger et al. (1970) describe a complex polymorphism in clinoptilolite based on X-ray powder diffraction and infrared spectroscopy. These and subsequent workers (Boles 1971, 1972; Alietti 1972) describe discrete contracted phases, a B phase and an intermediate I phase, which occur on heating in the range 200 to 300°C, followed by cooling. The more alcalic and silicic the clinoptilolite, the higher the temperature at which the contracted phases appear. The more calcic and aluminous heulanlites become X-ray amorphous above 250°C, while the more alcalic and silicic clinoptilolites do not become X-ray amorphous until heated above 750°C. The contracted crystalline phases were observed to revert to the normal structure after cooling and being allowed to re-equilibrate with atmospheric moisture. It is inferred that the contracted phases result from reversible loss of loosely bound water with concomitant collapse of the aluminosilicate framework. The contracted phases appear to have decreased in volume by as much as 10%. Single-crystal observations of the dehydration of these minerals are in progress (Mortier and Pearce 1980), so it should soon be possible to conclude whether the contracted phases are discrete, definable states, or whether all intermediate states may exist. Such observations should be extremely useful for interpretation of dehydration phenomena and how they might affect physical properties, mechanical strength in particular.

Mordenite behaves similarly to clinoptilolite on dehydration (e.g., Schlenker et al. 1979a, 1979b). It loses loosely bound water on increased temperature up to about 300°C. Water loss is accompanied by a reduction in unit cell volume of as much as 8%. Loss of crystallinity begins above 400°C. No detailed information on the dehydration behavior of analcime was found in the literature. Analcime might be expected to exhibit similar effects; however, they will probably be much less pronounced and occur at higher temperatures due to the substantially lower water content, higher density, and apparent higher temperature of paragenesis of analcime relative to clinoptilolite and mordenite.

Mineralogical Stability.—Zeolite grade metamorphism was defined to be the lowest grade of regional metamorphic alteration of rocks by Fyfe et al. (1958) based on the early work of Coombs (1954). It occurs at temperatures below 200°C and pressures below 300 MPa (3 Kb) (e.g., Winkler 1965; Turner and Verhoogen 1960) and is typical of low-grade burial and contact metamorphic assemblages (Hay 1966; Coombs 1970; Sheppard 1971; Hay 1978). It is only recently that the zeolite
grade has been subdivided into zones which are consistent, mappable, and correlated between rocks of differing composition, and that temperatures have been tentatively assigned to boundaries (Iijima 1975, 1978, 1980). The temperature ranges of these zones are also known to vary with the composition of pore fluids, particularly with sodium concentration.

Zeolite zones defined by Iijima (1975, 1980) are based on zeolite mineralogies replacing volcanic glass in two types of sequences: an alkali zeolite reaction series and a calcic reaction series. Zone boundaries are defined on the basis of the more common alkali series which is typical of diagenetically altered silicic tuff. "Four diagenetic zones are constructed: namely, Zone I is a zeolite-free zone characterized by glass shards which alter principally, or sometimes wholly, to smectite and opal; Zone II is a zone characterized by clinoptilolite, mordenite, or both which originate from acidic glass; Zone III is a zone characterized by analcime replacing the precursor zeolites, which often coexist as relic; and Zone IV is a zone characterized by albite replacing analcime." (Iijima 1980, p. 108). The mineralogy of the various zones is shown diagrammatically in Figure 1.

Several lines of evidence have been used to establish temperatures of boundaries between zones. The top of Zone III, marked by the appearance of analcime, has been observed in drill holes penetrating thick sequences of Quaternary marine tuffs currently undergoing burial diagenesis in the Niigata, Akita, and Tenpoku oil fields of Japan (Iijima and Utada 1971; Iijima 1975, 1978, 1980; Iijima and Ohwa 1980). Borehole logs give a narrow temperature range of 84 to 91°C for the transition. It appears to occur over a large depth range (1700 to 3500 m), indicating that temperature rather than pressure (total or water) is the controlling variable. This is in very good agreement with the experimental work of Boles (1971) who converted clinoptilolite to analcime at 100°C in pore fluids of 0.1M NaCl plus 0.01M NaCO₃ in 21 days. In the drill holes, the top of Zone IV is observed at 120 to 124°C over a depth range of 2500 to 4500 m, again indicating that temperature rather than pressure is the controlling variable.

The top of Zone II is observed at temperatures of 25 to 60°C over a depth range of 635 to 1900 m. The wider temperature range indicates that this reaction is perhaps more sensitive to pressure or pore water composition.

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**Fig. 1.—Zeolite zone mineralogy for alkali and calcic zeolite series (after Iijima 1980). Approximate temperatures of boundaries between zones at bottom of figure are given by Iijima, 1980 and for marine tuffs with high concentrations of Na⁺ in pore fluids (Iijima and Ohwa 1980).**
FIG. 2.—Plot of Na concentration vs temperature for reactions bounding zeolite zones (after Iijima 1975). The lowest temperature and concentration field is for the assemblage alkali clinoptilolite + silica + H₂O and corresponds to Zone II (fig. 1). The reaction of this assemblage to analcime + quartz + H₂O is delineated by three data points: temperatures of saline alkaline lakes, those of thick marine tufts, and the laboratory experiment of Boles (1972). The reaction of the assemblage analcime + quartz + H₂O (Zone III) to albite + quartz + H₂O is bounded by four data points: saline alkaline lakes (e.g., Mariner and Surdam 1970), thick marine tufts (Iijima and Ohwa 1980), weakly alkaline geothermal waters (e.g., Honda and Muffler 1970) and some laboratory experiments (e.g., Liou 1971; Saha 1959). The composition of water from drill hole J-13 in Jackass Flat is plotted at the approximate ambient temperature of possible repository horizons at Yucca Mountain.

Iijima (1975) has summarized the effects of pore water composition on the temperatures of the Zone II/III and Zone III/IV boundaries. His conclusions are presented diagrammatically in figure 2 and permit a rough extrapolation to lower sodium concentrations. If sufficient sodium is available for conversion of alkali clinoptilolite to analcime at concentrations below 1000 ppm, then the reaction should proceed at temperatures of 90 to 100°C at concentrations typical of waters in tuff with open continental hydrologic systems.

In summary, the zeolite grade of metamorphism consists of four major zones with completely different mineralogies. Relatively small increases in temperature can completely alter physical and chemical properties of rocks in this grade. Temperature and sodium concentration have been identified as major controlling variables; however, in certain circumstances, other variables such as water pressure and activities of H⁺, K⁺, and Si⁴⁺ may become important. Reactions between zones require recrystallization with or without an intervening liquid phase and are therefore likely to be sluggish. Little is known about the kinetics of these reactions or the thermodynamic properties of these zeolites, in part because hydration states are difficult to define.

The most reliable indication of temperature boundaries between zones is based on field, rather than laboratory, evidence. This is true because it is difficult or impossible to reverse reactions or recognize equilibrium between silicate phases at these temperatures. However, some kinetic parameters of prograde
reaction may be obtainable by further careful laboratory study and should be useful if repository design temperatures approach zeolite reaction temperatures. Despite some uncertainty, there appears to be sufficient information on temperatures and conditions of reactions to constrain temperature maxima in zeolitic horizons.

CONSTRAINTS ON REPOSITORY CONDITIONS

Dehydration Reactions.—Although emplacing radioactive waste directly into zeolite horizons is not currently contemplated, rocks containing major amounts of clinoptilolite and mordenite surround potential repository horizons at Yucca Mountain, Nevada. Also, zeolites are important fracture-filling minerals which may control permeability in basalts of the Columbia River Plateau. Simple dehydration of natural clinoptilolite and mordenite is viewed as being of secondary importance to repository design relative to the mineralogical reactions discussed below. However, these reactions may cause degradation of mine tunnels and pillars, or they may open fractures. Some simple experiments were carried out by Smyth and Caporuscio (1981) to delineate or bound dehydration reaction conditions.

Smyth and Caporuscio (1981) reported preliminary data outlining potential effects of dehydration reactions in clinoptilolite and analcime tuffs. They concluded that a major dehydration (loss of >3 wt % water) does not occur at temperatures less than 100°C if the zeolite remains equilibrated with liquid water. However, minor dehydration (loss of 2% or less water by weight) may occur and be of some significance. For example, if clinoptilolite is under an external water pressure of 30 bar (= 300 m water head) and the temperature is raised from 35 to 85°C, the “fullyhydrated” state at the higher temperature may contain less water than at the lower temperature. Within the limits of current knowledge, this amount could be as much as 1 or 2 wt %, and if so, pressures in excess of the hydrostatic head could develop in and around the heated, saturated zeolitic horizon. This could have a significant effect on the hydrology of the repository site. To evaluate such effects, it will be necessary to undertake careful differential thermal analysis of the dehydration process and to measure the water contents of clinoptilolite as a function water pressure at various temperatures.

Smyth and Caporuscio (1981) also concluded that major dehydration (greater than 3 wt % water) of clinoptilolite would only occur in a repository at mine tunnel surfaces if liquid water were not present or in rock masses if boiling should occur. If temperatures in the repository do not exceed 100°C, the latter should not be a problem. If heated mine tunnels are cooled by surface air, the former could become a problem; however, it could easily be avoided by wetting tunnel surfaces. If boiling should occur in rock masses by some accident or severe miscalculation, dehydration or clinoptilolite with decrease in volume, propagation of fractures, and evolution of large amounts of water could become a severe problem.

Mineralogical Reactions.—As pointed out, clinoptilolite and mordenite have a somewhat limited thermal stability and react to form denser, less hydrous phases (analcime and albite, progressively) at temperatures below 150°C under conditions which could conceivably be achieved in the rock volume surrounding a waste repository. Although the reactions might possibly result in more inherently stable rocks, and the recrystallization might fix migrating radionuclides, potential negative effects are currently unknown and unpredictable. The reactions have the potential to release large amounts of water, to cause significant volume decreases with development and propagation of fractures, and to completely alter the physical and chemical properties of the rock.

Because kinetic and other thermodynamic parameters of these reactions were unknown, it is currently impossible to accurately model or predict the effects. It therefore seems advisable to avoid conditions which might induce such reactions. This may place a significant constraint on waste emplacement densities (thermal loading) in any repository at Yucca Mountain. The reaction of clinoptilolite to analcime is the one which appears to take place at the lowest temperatures and, hence, has the greatest potential to constrain thermal loadings. This reaction has been observed in the laboratory in pore fluids moderately concentrated in sodium (approximately
5000 ppm at pH 11) at 100°C in as little as 21 days (Boles 1971). Also, analcime is reported to be forming in the field at temperatures as low as 85°C in slightly more concentrated sodic pore fluids (approx. 10,000 ppm at pH 8.5) (fig. 2).

Ground water at Yucca Mountain is of substantially lower sodium concentrations and pH. Water from well J-13 in western Jackass Flat has sodium ion concentrations of approximately 200 ppm and a pH of 7.8 to 8.2 (Schoff and Moore 1964; Young 1972). This water comes from fracture permeability in the densely welded, non-zeolitized Topopah Springs member of the Paintbrush Tuff and may not be representative of pore water in zeolitized horizons. However, it is not expected that such waters will exceed 1000 ppm sodium. It is known that sufficient sodium concentrations did exist in the past for the reaction to proceed at depths greater than 3500 feet in drill hole USW-G1 (Bish et al. 1981).

Plotting the sodium concentrations observed in ground water at Yucca Mountain, Nevada in figure 2, I predict that the reaction of clinoptilolite to analcime will begin at about 105°C. However, Boles (1971) did not do experiments below 100°C, so his work does not provide a firm lower temperature bound for the reaction. Also, sodium concentrations in situ could be as high as 1000 ppm, so a safe lower bound for the beginning of the reaction could be set at about 95°C. Translation of this lower bound into a design criterion for a radioactive waste repository is certainly open to some discussion. However, for any given thermal loading, it should be required to show that temperatures cannot approach the lower bound in zeolithic horizons by any plausible heat transfer mechanism, including vapor transport in fractures. For safety, it may be deemed advisable to constrain design temperature maxima by at least a further 10° to 85°C.

Figure 3 is a plot of the observed geothermal gradient in USW-G1. Also plotted are the maximum paleogeothermal gradient as inferred from the first appearance of analcime and albitionized tuffs in USW-G1 and the temperature of the Zone II - Zone III (clinoptilolite - analcime) transition. Potential repository horizons are zones of dense welding and primary devitrification with little or no zeolite content. Three such zones exist at the Yucca Mountain site and vary in thickness from about 30 to about 90 m. It appears from this figure that maximum temperature rises in zeolithic zones adjacent to these potential repository horizons will be limited to about 50°C. Possible alternatives to these horizons might be to emplace the wastes much deeper, in Zones III or IV (Bish et al. 1981), or above the water table in the densely welded Topopah Springs Member of the Paintbrush Tuff.

Preliminary thermal conduction models for a repository located at 800-m depths in tuff or Yucca Mountain indicate that temperatures in clinoptilolite zones will not exceed 85°C if reprocessed high level waste is emplaced at a gross thermal loading of 75 KW/acre (Tyler and Langkopf 1980). However, calculations for spent fuel emplaced at the same loading indicate that temperatures in zeolithic zones
may reach 110° to 120°C. Any potential problem can be avoided by reducing the gross thermal loading for spent fuel. More precise thermal models will, of course, be required to estimate maximum allowable thermal loadings. Also, other plausible heat transfer mechanisms will need to be evaluated.

CONCLUSIONS

Review of the literature shows that the instability of clinoptilolite may constrain heat loadings in possible radioactive waste repositories in zeolite-bearing volcanic rocks. To prevent dehydration of clinoptilolite, wetting of mine tunnel and shaft surfaces may be required if dry air is used to cool heated geologic formations during the active life of the repository. Otherwise, major dehydration of clinoptilolite should not become a problem unless boiling of interstitial water should occur. Boiling should not occur if thermal constraints imposed by potential mineralogical reactions are observed. It is possible that minor dehydration (less than 2 wt % water loss) could occur in the temperature range 20 to 85°C and at water pressures greater than one atmosphere and affect local hydrology. These effects should be evaluated by measurement of water content as a function of water pressure and temperature.

It is possible to place a firm constraint on the maximum temperature of clinoptilolite horizons based on mineralogical reactions. There is substantial evidence to suggest that in environments similar to Yucca Mountain, Nevada, clinoptilolite and mordenite break down at temperatures above 95°C. To avoid consequences of these reactions, temperatures in zeolitic horizons should not exceed about 85°C. This will limit temperature rises in rocks 20 to 50 m above potential emplacement horizons to about 50°C. If this constraint is exceeded, the reactions may provide both a pathway (shrinkage fractures) and driving force (evolved fluid) for release of radionuclides.

ACKNOWLEDGMENT.—This work was supported by the U.S. Department of Energy through its Nevada Operations Office as part of the Nevada Nuclear Waste Storage Investigations. The work was performed at Los Alamos National Laboratory which is operated by the University of California under contract W-7405-ENG-36. Helpful reviews of the manuscript were received from D. Hoover, A. Waters, J. Whetten, and B. Crowe.

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