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PROGRESS IN EXPERIMENTAL STUDIES ON THE THERMODYNAMIC AND ION EXCHANGE PROPERTIES OF CLINOPTILOLITE

Prepared for

Nuclear Regulatory Commission
Contract NRC-02-88-005

Prepared by

Center for Nuclear Waste Regulatory Analyses
San Antonio, Texas

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ABSTRACT

To support the Nuclear Regulatory Commission's high-level waste program, the Center for Nuclear Waste Regulatory Analyses is conducting experimental studies on the thermodynamic and ion exchange properties of clinoptilolite, which is the predominant zeolite mineral at the proposed repository site in Yucca Mountain, Nevada. These studies will provide data that are important in assessing the effectiveness of zeolitic tuffs as barriers to radionuclide migration. This document is a report of progress in Task 3 of the Geochemistry Research Project for the period May - October, 1989. It provides the theoretical bases for ion exchange and phase equilibrium studies, reviews experimental work reported in the literature on ion exchange between aqueous solutions and clinoptilolite, and presents the results of characterization work performed on experimental materials. Important factors that need to be considered or constrained in conducting ion exchange studies have been identified. Procedures for ion exchange experiments that take these factors into account were developed and are included in the appendices, together with other procedures relevant to the conduct of this work. Clinoptilolite specimens used in this study were obtained from zeolitized tuff localities in California, New Mexico, Idaho, and Texas. Characterization work performed on these specimens using X-ray diffraction, petrographic analysis, and scanning electron microscopy indicate that the samples contain mostly clinoptilolite which has replaced the glass in the poorly welded tuffs. The most common accessory minerals are quartz, mordenite, feldspars and clay. Specimens of the zeolite mineral analcime to be used in phase equilibrium experiments were obtained from Mt. St. Hilaire, Quebec. Considerations of published theoretical studies and experimental data indicate that the use of invariant retardation factors, K_d, in hydrologic models may not accurately model the transport behavior of radionuclides or other aqueous species in geologic environments where ion exchange behavior is the predominant sorption mechanism. The dependence of ion exchange selectivity on zeolite composition has important implications on the proposed waste repository because Yucca Mountain clinoptilolites show variations in composition (Broxton et al., 1986), grading laterally from sodic compositions on the western side of Yucca Mountain to calcic compositions on the eastern side, and to potassic compositions at the northern end.

PROGRESS IN EXPERIMENTAL STUDIES ON THE THERMODYNAMIC AND ION EXCHANGE PROPERTIES OF CLINOPTILOLITE

R. T. Pabalan
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January 1990

EXECUTIVE SUMMARY

A major technical consideration in evaluating Yucca Mountain, Nevada as a potential repository site for high-level nuclear wastes is the presence of thick lateral zones of zeolitic tuffs. Because of their sorptive properties, zeolites could provide important geologic barriers to migration of radionuclides away from the repository to the accessible environment. To support the Nuclear Regulatory Commission's high-level waste program, the Center for Nuclear Waste Regulatory Analyses is conducting experimental studies on the thermodynamic and ion exchange properties of zeolites under Task 3 of the Geochemistry Research Project. These studies are designed to generate data needed to evaluate the effectiveness of zeolitic tuffs as barriers to radionuclide migration. The initial work in this experimental program will focus on the mineral clinoptilolite, which is the predominant zeolite present at Yucca Mountain. This document is a report of progress in Task 3 for the period May - October, 1989. It provides the theoretical bases for ion exchange and phase equilibrium studies, reviews experimental work reported in the literature on ion exchange between aqueous solutions and clinoptilolite, and presents the results of characterization work performed on experimental materials.

Zeolites, which are crystalline, hydrated aluminosilicates of alkali and alkaline earth cations, are characterized by an ability to hydrate/dehydrate reversibly and to exchange some of their constituent cations with aqueous solutions, without a major change in structure. Studies reported in the literature show that their ion exchange behavior depends on several factors including: (1) charge density of the anionic crystal structure, (2) the mineral framework topology, (3) size and shape of the exchanging ions, (4) valence and charge of the ions, (5) composition and ionic strength of the external electrolyte solution, and (6) temperature.

One of the objectives of this study is to develop models that can be used in predicting ion exchange behavior in complex systems. Therefore it is necessary to apply thermodynamic principles to the study of ion exchange phenomena. The thermodynamics of ion exchange are discussed in this report.

A literature review of experiments on ion exchange between aqueous solutions and clinoptilolites is reported. Important factors that need to be considered or constrained in conducting ion exchange experiments have been identified. It is important that the exchange reactions be shown to be reversible if the data are to be subjected to thermodynamic treatment. The precision of parameters derived from thermodynamic models rely on the acquisition of accurate experimental data, particularly at the extrema of isotherms. Serious errors in derived thermodynamic parameters may result if hydronium ion participates in the exchange reaction or if dealumination and partial destruction of the zeolite framework takes place during the experiments, and no provision is made for these effects. For careful studies of ion exchange equilibria it is advisable to analyze for *each* exchanging ion in *both* the aqueous solution phase and the solid phase. This may be supplemented by controlling or monitoring the pH and other solution properties and by using other analytical techniques such as scanning electron microscopy.

Experimental studies on clinoptilolite present special problems because available clinoptilolite specimens are zeolitized tuffaceous samples. These commonly contain mineral impurities such as quartz, feldspar, clays, and volcanic glass. To minimize the problems associated with these impurities the clinoptilolite specimens must be carefully characterized, and steps must be taken to remove as much of the impurities as possible.

Based on these considerations, procedures were developed for conducting the ion exchange experiments. These are included in the appendices, including other procedures relevant to the conduct of this work.

The clinoptilolite specimens used in this study were obtained from localities in California, New Mexico, Idaho, and Texas. The materials were characterized by X-ray diffraction, petrographic analysis, and scanning electron microscopy. Results of the X-ray diffraction and petrographic analyses indicate that the samples contain mostly microcrystalline clinoptilolite, which has replaced the glass in the poorly welded tuffs. The most common accessory minerals are quartz, mordenite, feldspars, and clay. Specimens of the zeolite mineral analcime to be used in phase equilibrium experiments were obtained from Mt. St. Hilaire, Quebec and occur as large (1-6 cm) euhedral crystals.

Although standard state thermodynamic properties of clinoptilolite are required to predict its stability relative to other minerals and aqueous species, these data are poorly known. Consequently experiments were designed to assess standard-state thermodynamic properties of endmember zeolite minerals. These data will be coupled with solid solution properties generated in the ion exchange studies to give a fairly complete thermodynamic description of this mineral.

One implication of theoretical and experimental studies reviewed here is that the use of invariant retardation factors, K_d, in hydrologic models may not accurately model the transport behavior of radionuclides or other aqueous species in geologic environments where ion exchange is the predominant sorption mechanism. The assumption of linear isotherms inherent in the use of K_d's is valid only under restricted ranges of concentration. Furthermore, K_d's cannot adequately account for the complicated dependence of ion exchange equilibria on aqueous solution concentration and on the compositions of both the aqueous and zeolite phases.

The dependence of ion exchange selectivity on zeolite composition has important implications for Yucca Mountain. Clinoptilolite minerals at and below the water table grade laterally from sodic compositions on the western side of Yucca Mountain to calcic compositions on the eastern side, and potassium-rich clinoptilolite occur at the north end of Yucca Mountain. The study by Ames (1960) indicate the selectivity of clinoptilolite for various ions is $Cs > K > Sr > Na > Ca > Mg$. Thus, to a first approximation, Cs^{137} migration can be effectively retarded by ion exchange throughout the lateral extent of clinoptilolite-rich tuffs, but Sr^{90} may be less effectively retarded on the northern end of Yucca Mountain. The detailed ion exchange behavior is, of course, more complex because the geologic system is multicomponent in nature.

INTRODUCTION

A major technical consideration in selecting Yucca Mountain, Nevada as a potential repository site for high-level nuclear wastes is the presence of thick lateral zones of zeolitic tuffs. Because of their sorptive properties, zeolites could provide important geologic barriers to migration of radionuclides away from the repository, in case of leakage of the waste canisters. The presence of zeolitic tuffs in several stratigraphic units between the potential repository horizon, which is located in the unsaturated zone, and the water table could retard the downward movement of radionuclides, and additional zeolitic units below the water table could be potential barriers to lateral migration through the saturated zone.

To support the Nuclear Regulatory Commission's task of evaluating Yucca Mountain as a potential site for high-level nuclear wastes, the Center for Nuclear Waste Regulatory Analyses is conducting experimental studies on the thermodynamic and ion exchange properties of clinoptilolite, which is the predominant zeolite mineral at Yucca Mountain. These studies will provide critical data that are important in assessing the effectiveness of zeolitic tuffs as barriers to radionuclide migration.

This report discusses the theoretical bases for the performance of experimental work and the interpretation of experimental data, gives a review of experimental studies reported in the literature, and summarizes the results of laboratory work done to date.

ZEOLITE STRUCTURE AND CHEMISTRY

Zeolites are crystalline, hydrated aluminosilicates of alkali and alkaline earth cations that are characterized by an ability to hydrate/dehydrate reversibly and to exchange some of their constituent cations with aqueous solutions, both without a major change in structure. Natural zeolites commonly occur as fine crystals of hydrothermal origin in vugs and fissures of volcanic rocks and as micro-crystalline sedimentary masses formed by low temperature alteration of pre-existing volcanic tuffs.

Zeolites are classified as tektosilicates, i.e., they consist of three-dimensional frameworks of SiO_4^{4-} tetrahedra where all oxygen ions of each tetrahedron are shared with adjacent tetrahedra. This arrangement reduces the overall oxygen:silicon ratio to 2:1, and if each tetrahedron were to contain Si as its central cation, the structure would be electrically neutral as in quartz (SiO_2). In zeolite structures, however, some of the quadrivalent Si is replaced by trivalent Al, giving rise to a deficiency of positive charge in the framework. This charge is balanced by cations elsewhere in the structure, principally Na^+, K^+, Ca^{2+} and Mg^{2+}.

Gottardi (1978) proposed the following general formula for a zeolite:

$$(M_x^+ M_y^{2+})\ [Al_{(x+2y)}\ Si_{n-(x+2y)}O_{2n}] \cdot mH_2O$$

where M^+ and M^{2+} represent mono- and divalent cations, respectively. Cations within the first set of parentheses are called the exchangeable cations; those within the second set of parentheses are known as the structural cations because with oxygen they make up the framework of the structure. The (Si + Al) : O ratio of a zeolite is 1:2, and the number of tetrahedral Al ions is equal to the sum of positive charges of the exchangeable cations in the idealized formula. The symbol $\underline{m}$ represents the number of water molecules in the structure and gives an idea of the volume of the channels relative to the total volume. Normally this number does not exceed half the number of framework oxygens, and $n/2 < m < n$ (Gottardi, 1978).

A typical unit-cell formula for the (Na,K)-endmember clinoptilolite is given by:

$$(Na,K)_6(Al_6Si_{30}O_{72}) \cdot 24H_2O$$

A continuous isostructural solid solution exists between the alkali clinoptilolite given above and heulandite which is represented by the formula (Gottardi and Galli, 1985):

$$(Na,K)(Ca,Mg)_4(Al_9Si_{27}O_{72}) \cdot 24H_2O.$$

Small amounts of Fe^{3+} have also been reported to be present in clinoptilolites, presumably substituting for Si or Al in tetrahedral coordination. Thus the compositions of natural clinoptilolites (and heulandites) can be represented by the formula:

$$(Na,K)_x(Ca,Mg)_y(Al,Fe^{3+})_{x+2y}Si_{36-(x+2y)}O_{72} \cdot 19 \text{ to } 26\ H_2O$$

where x can take values between 0.3 and 6, y between 0.3 and 4, x+y lies between 4 and 7, and x+2y between 6 and 9 (Brindley and Brown, 1980). The variable number of water molecules reflects the ease with which clinoptilolite hydrates/dehydrates and the dependence of its water capacity to the volume of exchange ions (Barrer, 1978). Other alkali and alkaline earth ions may be present, such as Cs^+, Li^+, Ba^{2+}, and Sr^{2+}, due to exchange reactions with groundwater.

Subdivision into heulandite and clinoptilolite is arbitrary, but Mason and Sand (1960) proposed that minerals with (Na + K) > Ca be called clinoptilolite and those with (Na + K) < Ca be called heulandite. Mumpton (1960) suggested each zeolite of the heulandite group must be named clinoptilolite if its crystal structure survives an overnight heating at 450°C, otherwise, it is a heulandite. Boles (1972) also proposed naming these zeolites clinoptilolite if Si/Al > 4, and heulandite if Si/Al < 4. Gottardi and Galli (1978), adhering to common rules of mineralogical nomenclature, adopted Mason and Sand's nomenclature, naming those minerals with (Ca + Mg + Sr + Ba) > (Na + K) heulandite, and clinoptilolite the others. We will also adhere to this latter nomenclature.

In contrast to the three-dimensional framework structures of other tektosilicates such as quartz and feldspar, which are relatively dense and tightly packed, those of zeolite minerals are remarkably open and void volumes of dehydrated species as great as 50% are known. The structure of heulandite was determined by Merkle and Slaughter (1968), and Alberti (1975) confirmed the isostructural nature of clinoptilolite. The crystal structure of clinoptilolite (and heulandite) is shown in Fig. 1. A major feature of the structure is a tight network of interlinked 4- and 5-member rings of tetrahedra in the ac-plane, which accounts for the excellent cleavage of the mineral. Between these layers are open 10- and 8-member ring channels parallel to the c-axis (A and B in Fig. 1), with approximate free dimensions of 0.79 x 0.35 nm and 0.44 x 0.30 nm, respectively. There are also channels parallel to the a-axis formed by eight-member rings, but the exchange sites are mainly located in the channels parallel to the c-axis. Two cation sites are present in each of these two channels parallel to c (M_1 and M_2 in Fig. 1), and both coordinate water molecules and framework oxygens on one side only (Merkle and Slaughter, 1968; Alberti, 1972; Alberti, 1975). The presence of these two cation sites only in heulandites was confirmed by Bresciani-Pahor et al. (1980) and by Alberti and Vezzalini (1983). For clinoptilolite Alberti (1975) found a third site at the crossing of the two main channels, but Koyama and Takeuchi (1977) neglected this site and identified two additional cation sites, one of which is in the minor channel parallel to the a-axis (M_3) and the other (M_4) is in the 10-ring main channel and surrounded by water molecules only.

ION EXCHANGE IN ZEOLITES

There is an extensive body of literature on ion exchange processes between aqueous solutions and various materials such as layered silicates and synthetic resins. A number of papers were published in the

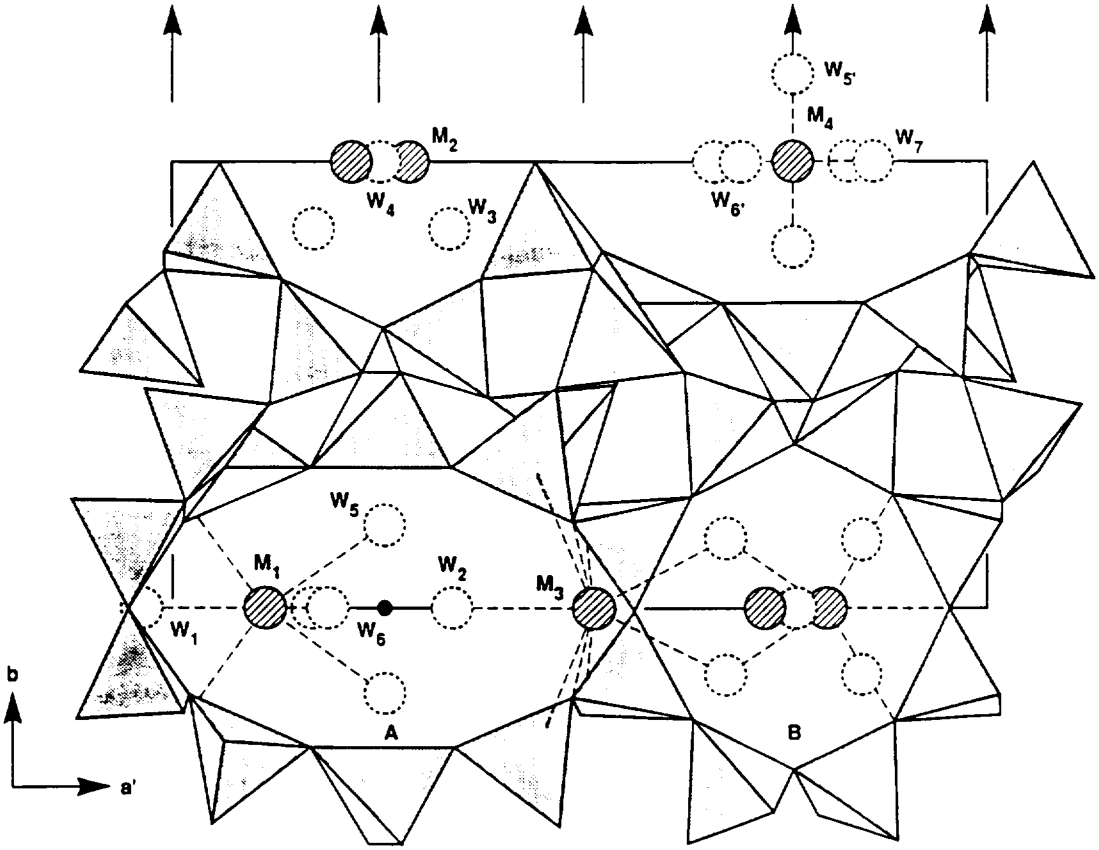

FIGURE 1. The crystal structure of clinoptilolite viewed along the c-axis showing 10-member and 8-member ring channels (A and B, respectively). M's represent cation sites and W's represent water sites. To avoid confusion, only part of equivalent atoms are shown, particularly in channel A (adapted from Koyama and Takeuchi, 1977).

period 1960-1970 in which zeolites were used to study some of the more fundamental aspects of cation exchange, and reviews of these papers have been published by Sherry (1971) and Breck (1974). It was assumed in early studies that zeolites, because of their crystallinity and well-defined anionic frameworks, would behave as ideal exchangers. However, these various studies brought to light many problems which showed that zeolite exchangers are not ideal.

The exchangeable cations of a zeolite are only loosely held in the anionic framework, and, to a first approximation, can be removed or exchanged easily by washing the zeolite with a concentrated solution of another cation. The cation exchange capacity (CEC) is primarily a function of the charge density of the anionic structure, i.e., the degree of substitution of Al^{3+} (and Fe^{3+}) for Si^{4+} in its tetrahedral framework. The greater the Al substitution, the more alkali or alkaline earth cations are needed to maintain electrical neutrality and, hence, the higher the CEC.

In practice, the ion exchange behavior of zeolites also depends on other factors, including: (1) framework topology (channel configuration and dimensions), (2) ion size and shape (polarizability), (3) valence and charge density of the ion(s), and (4) composition and concentration of the external electrolyte solution (Barrer, 1978). The diffusion character of a zeolite depends on the number of channels and their spatial configuration. All other factors remaining equal, cations diffuse faster through zeolites with three-dimensional channel systems than those with one- or two-dimensional systems. The size of the ion, as well as the channel dimensions, determine whether or not a given cation will fit into a particular framework. For example, analcime, which has an effective channel diameter of about 0.28 nm, will almost completely exchange its Na^+ for Rb^+ (ionic radius = 0.149 nm), but not at all for Cs^+ (ionic radius = 0.165 nm) (Breck, 1974). To some extent, high temperatures can offset the effect of larger ionic radius. Thus, at approximately 200°C, Cs^+ begins to migrate in analcime.

Size considerations and the effect of the rigid nature of the zeolite framework, hence the nearly fixed pore volumes, can also explain the steric limitations and ion sieve properties exhibited by zeolites, such as those observed by Barrer et al. (1967) in their exchange studies between Na-clinoptilolite and various alkyl-ammonium cations. Ions that are small enough to enter the two main channels of clinoptilolite exchange completely with Na^+ [e.g., NH_4^+, $CH_3NH_3^+$, $C_2H_5NH_3^+$, $(CH_3)_2NH_2^+$, and n–$C_3H_7NH_3^+$]; those small enough to enter the 10-ring channel but too large to penetrate the 8-ring channel are only partially exchanged [e.g., $(CH_3)_3NH^+$ and iso-$C_3H_7NH_3^+$], while the largest ions [e.g$(CH_3)_4N^+$ and tert-$C_4H_9NH_3^+$] are totally excluded.

For exchange reactions in which the exchange ions have equal charges, the concentration of the aqueous solution need not have a large effect on the selectivity or preference of the zeolite for a particular ion. However, when the exchange ions have different valences, the ion exchange behavior of the system depends strongly on the total concentration of the external electrolyte, and the selectivity of the zeolite for the ion of high valence becomes progressively greater with increasing dilution. This concentration-valency effect which can arise universally from high dilution of the electrolyte solution, independently of the exchanger phase, has been studied quantitatively by Barrer and Klinowski (1974).

As in the case of clinoptilolite, many zeolites contain several crystallographically distinct sets of sites which can be occupied by exchangeable ions. These sets of sites are intimately mixed with one another throughout the crystal, and each may exhibit different selectivities and ion exchange behavior. The number of available exchange sites commonly exceeds the number of negative charges to be neutralized. Hence, the anionic charge of the framework may be neutralized when only some of the sites are occupied, and the occupancy factors may vary with the nature of the neutralizing cation (Barrer, 1980; 1984). In addition, the entering ion does not necessarily take the position of the leaving ion (Sherry, 1971; Cremers, 1977). Thus the zeolites may exhibit a high degree of cationic disorder, both in terms of unoccupied sites and in terms of different distributions of cations of different kinds among the site groups.

This site heterogeneity in the zeolite is likely to manifest itself in the compositional variations of the selectivities and activity coefficients of the zeolite components. As a consequence it is difficult to predict multicomponent equilibrium exchange relations from binary data alone (Fletcher et al., 1984). Although it is theoretically possible to evaluate the contribution of the component site groups to the overall thermodynamics of exchange and to the overall equilibrium constant (Barrer, 1978), it is questionable whether one should use measurements of exchange equilibria to infer details of a particular heterogeneous site model for the exchanger, unless independent measurements that provide information on the structure and site heterogeneity are also applied to the material (e.g., X-ray diffraction, neutron diffraction, nuclear magnetic resonance, electron microscopy) (Townsend, 1984). These thermodynamic measurements are concerned with changes in macroscopic physical properties of the system under study, and it is difficult to infer from these thermodynamic data alone the fundamental mechanisms which underlie the observed behavior. Nevertheless, thermodynamic formulations, if properly conceived, provide firm and systematic structures for understanding ion exchange behavior and its dependence on various parameters, and serve as tools for predicting exchange equilibria under conditions not previously studied. The basic thermodynamic formulations for ion exchange are based on principles developed long ago by researchers on inorganic exchange materials, especially clays (Vanselow, 1932; Gapon, 1933; Kielland, 1935; Gaines and

Thomas, 1953). These formulations are still widely used in current ion exchange literature, irrespective of the nature of the exchanger under study. A brief review of the thermodynamics of ion exchange is given below.

THERMODYNAMICS OF ION EXCHANGE

Ion Exchange Isotherm

For a binary exchange involving ions A^{z_A+} and B^{z_B+} initially in solution and zeolite, respectively, the basic reaction may be written as

$$z_B A^{z_A+} + z_A \overline{B}^{z_B+} \Leftrightarrow z_B \overline{A}^{z_A+} + z_A B^{z_B+} \tag{1}$$

where z_A and z_B refer to the valences of the ions $A^{z_A+}$and B^{z_B+}, respectively, and the superscripted bar refers to the exchanger phase (Dyer et al., 1981). Co-anions, X, are also present in the aqueous solution and maintain electroneutrality in that phase.

The binary exchange equilibrium can be described conveniently by the ion exchange isotherm, which is a plot of the equilibrium concentration of an exchanging ion in solution against the equilibrium concentration of that same ion in the zeolite at constant temperature and solution concentration. The isotherm is usually plotted in terms of the equivalent cation fraction of the ion in solution (A_s) against that in the solid (A_c) (Dyer et al., 1981). The equivalent cation fraction of A^{z_A+} in solution is given by:

$$A_s = z_A m_A/(z_A m_A + z_B m_B) \tag{2}$$

where m_A and m_B are the molalities of the respective ions in solution. An analogous expression can be written for the zeolite phase:

$$A_c = z_A \overline{m}_A /(z_A \overline{m}_A + z_B \overline{m}_B) \tag{3}$$

where $\overline{m}_A$ and $\overline{m}_B$ are the concentrations (mol/kg) of the respective ions in the zeolite.

The ion exchange isotherm can then be plotted from the equilibrium values of A_s and A_c. For the binary exchange reaction (1),

$$1 - A_s = B_s \tag{4}$$

and

$$1 - A_c = B_c \tag{5}$$

Therefore, the isotherm plots fully define the equilibrium at a specified temperature and solution concentration.

The selectivity or preference of a zeolite for the ion A^{z_A+} can be conveniently defined by a selectivity coefficient α which is defined as:

$$\alpha = A_C m_B / B_C m_A. \tag{6}$$

Because $m_A = (z_A m_A + z_B m_B)A_S/z_A$ and $m_B = (z_A m_A + z_B m_B)B_S/z_B$, it follows that

$$\alpha = (z_A/z_B)\ A_C B_S / B_C A_S \tag{7}$$

or, from Fig. 2 (Dyer et al., 1981):

$$\alpha = (z_A/z_B)\text{Area I/Area II.} \tag{8}$$

It is apparent from Fig. 2 that α generally varies with the level of exchange (A_C). The conditions for selectivity at a specified A_C are:

$\alpha > (z_A/z_B)$, zeolite selective for A^{z_A+}

$\alpha = (z_A/z_B)$, zeolite exhibits no preference

$\alpha < (z_A/z_B)$, zeolite selective for B^{z_B+}

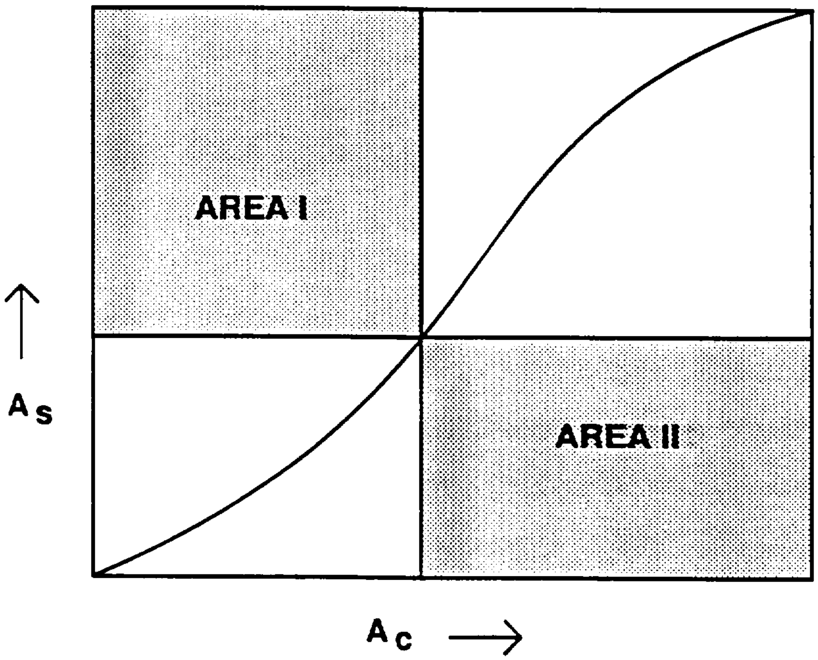

FIGURE 2. Generic isotherm plot for the exchange reaction given by Eqn. (1) showing equivalent cation fraction of ion $A^{z_A^+}$ in solution (A_s) versus its equivalent cation fraction in the exchanger phase (A_c)

The Thermodynamic Equilibrium Constant

The mass action quotient (K_m) for the ion exchange reaction given by Eqn. (1) is:

$$K_m = A_c^{z_B} m_B^{z_A} / B_c^{z_A} m_A^{z_B} \tag{9}$$

which is related to the selectivity coefficient, α, by (Barrer and Klinowski, 1974):

$$\alpha = K_m^{(1/z_A)} (A_c/m_A)^{(z_A - z_B)/z_A} \tag{10}$$

Because α varies with A_c, the same will be true for K_m. The variation in K_m is a reflection of the degree of departure from ideality of the system for a given value of A_c. The non-ideality of the system comprises non-ideal behavior in the aqueous solution phase and in the exchanger phase.

The thermodynamic equilibrium constant is defined as:

$$K_a = a_{\bar{A}}^{z_B} a_B^{z_A} / a_{\bar{B}}^{z_A} a_A^{z_B} \tag{11}$$

where <u>a</u> stands for activity. This may be expanded to give:

$$K_a = A_c^{z_B} f_A^{z_B} m_B^{z_A} \gamma_B^{z_A} / B_c^{z_A} f_B^{z_A} m_A^{z_B} \gamma_A^{z_B} \tag{12}$$

or,

$$K_a = K_m \Gamma (f_A^{z_B} / f_B^{z_A}) \tag{13}$$

where $\Gamma = (\gamma_B^{z_A}/\gamma_A^{z_B})$, γ_A and γ_B are the single ion activity coefficients in the solution of the ions A^{z_A+} and B^{z_B+}, and f_A, f_B are the activity coefficients for ions A^{z_A+} and B^{z_B+} in the zeolite phase associated with their equivalents of zeolite anionic framework. The function Γ is a non-ideality correction for the aqueous solution phase, while $(f_A^{z_B}/f_B^{z_A})$ is a correction term for the non-ideal behavior in the zeolite phase. It is apparent that an evaluation of K_a involves activity correction for both solution phase and exchanger phase.

It is necessary to define the standard states of the various components to allow the evaluation of K_a, f_A and f_B from experimental data using the Gibbs-Duhem relation. For the aqueous electrolyte solution external to the zeolite phase, it has been common practice to adopt the standard state of a hypothetical ideal one molal solution of the appropriate species in which the ion is regarded as behaving in the one molal solution (1 mol/kg solvent) as it does when it is infinitely diluted with solvent. (Note that other units such as molarity, mol/liter solution, can be used provided the choice is clearly specified.) For the exchanger phase it has been normal practice to follow Gaines and Thomas (1953) and make the standard state for each exchanging cation the appropriate homo-ionic form of the zeolite in equilibrium with an infinitely dilute solution of the same cation (Sposito, 1981). Thus the thermodynamic equilibrium constant is a measure of the relative affinity between the zeolite and the two cations involved in the exchange (Helfferrich, 1962).

The non-ideal behavior in the aqueous solution is accounted for by the ratio Γ. Although this correction term is defined in terms of single ion activity coefficients, γ_A and γ_B cannot be evaluated separately by experiments due to electroneutrality constraints. Thus Γ is evaluated in terms of the mean molal stoichiometric activity coefficients $\gamma_\pm$.

For a given mixture of electrolytes A_mX_n and B_pX_q where m,n and p,q refer to the salt stoichiometries, A and B are cations and X is the anion, the mean molal stoichiometric activity coefficient of A_mX_n can be defined as:

$$\gamma_{\pm(A_mX_n)} = (\gamma_A^{z_X} \cdot \gamma_X^{z_A})^{(1/(z_A + z_X))} \tag{14}$$

and Γ can be rewritten as

$$\Gamma = (\gamma_B^{z_A}/\gamma_A^{z_B}) = [\gamma_{\pm,B_pX_q}]^{z_A(z_B + z_X)/z_X}[\gamma_{\pm,A_mX_n}]^{-z_B(z_A + z_X)/z_X} \tag{15}$$

where z_A, z_B, and z_X are the valences of the ions A, B, and X, respectively.

Because $\gamma_\pm$ depends on the ionic strength and composition of the solution, the mean activity coefficients should be calculated for the mixed electrolyte solution at the experimental ionic strength (Dyer et al., 1981). For binary mixtures of two electrolytes with a common anion, these values can be calculated using the model of Glueckauf (1949), while values for multicomponent cation-anion systems can be determined from the models by Fletcher and Townsend (1981) and Pitzer (1973, 1979). The ion exchange studies by Fletcher and Townsend (1985) on systems with mixed background anions have shown the critical importance of evaluating correctly the solution phase non-ideality term Γ for accurate interpretation, as well as prediction of exchange equilibria.

It is now convenient to define a new function, the so-called Kielland or corrected selectivity quotient, K_c (Dyer et al., 1981), where

$$K_c = K_m \Gamma , \tag{16}$$

and from Eqn. (13) and (16),

$$K_a = K_c (f_A^{z_B} / f_B^{z_A}) . \tag{17}$$

In order to evaluate both the equilibrium constant and the zeolite phase activity coefficients, Gaines and Thomas (1953), using the Gibbs-Duhem relation, derived the following:

$$\ln K_a = (z_B - z_A) + \int_0^1 \ln K_c \, d\, A_c . \tag{18}$$

The zeolite phase activity coefficients f_A and f_B (at any zeolite composition A_c, B_c) are given by:

$$\ln f_A^{z_B} = (z_B - z_A) B_c - \ln K_{c(A_c)} + A_c \ln K_{c(A_c)} + \int_{A_c}^1 \ln K_c \, d\, A_c \tag{19}$$

and

$$\ln f_B^{z_A} = -(z_B - z_A) A_c + A_c \ln K_{c(A_c)} - \int_0^{A_c} \ln K_c \, d\, A_c . \tag{20}$$

Equation (18) enables the calculation of K_a from isotherm data to which the solution activity coefficient corrections have been applied. K_a may be determined by graphical integration of the plot of $\ln K_c$ versus A_c, or analytically by integrating a polynomial fit to the experimental data.

The standard free energy per equivalent of exchange (ΔG°) can then be calculated from

$$\Delta G^{\circ} = -(RT \ln K_a)/z_A z_B \tag{21}$$

Systems That Exhibit Incomplete Exchange

In some zeolites and for certain entering ions, A^{z_A+}, the exchange reactions reach a limit before all the B^{z_B+} ions initially present are replaced. Thus it is not always possible to produce the homoionic A-zeolite, and it is necessary to 'normalize' the isotherm (Barrer et al., 1973). This involves dividing all values of A_c by the maximal value observed experimentally to give normalized A_c values:

$$A_c^N = A_c/A_c(\max) \,. \tag{22}$$

This procedure does not affect the solution activity correction, but does affect the Gaines and Thomas treatment. A normalized Kielland selectivity quotient, K_c^N, is expressed in terms of the normalized equivalent cation fractions, and the essential step in obtaining the thermodynamic equilibrium constant then involves evaluating (Barrer et al., 1973):

$$\int_0^1 \ln K_c^N \, d\, A_c^N .$$

The equations derived above are still applicable, but normalized parameters must be used throughout. For example, Eqn. (19) becomes:

$$\ln f_A^{z_B} = (z_B - z_A)B_c^N - \ln K_{c(A_c)}^N + A_c^N \ln K_{c(A_c)}^N + \int_{A_c^N}^1 \ln K_c^N \, d\, A_c^N \,. \tag{23}$$

The superscript N refers to normalized values.

This procedure is necessary to conform to the definition of the exchanger phase standard state given previously. In effect, normalization results in the B^{z_B+} ions that are not involved in exchange being regarded as part of the exchanger framework (Dyer et al., 1981). These ions can still affect the ion exchange equilibrium, of course, but these effects are accounted for in f_A and f_B.

Limitations

The thermodynamic formulations given above are valid under conditions where imbibition of neutral electrolyte is negligible, which for zeolites is at solution concentrations <0.5 m (Barrer and Walker, 1964). Ion exchange studies at high ionic strengths may need to utilize the more rigorous thermodynamic treatment initially derived by Gaines and Thomas (1953), which encompassed the effects of either sorbed or imbibed solvent, and of imbibed salts. The formulations given above also assume that the effects of water activity changes in the zeolite are negligible, and the study by Barrer and Klinowski (1974) has shown that this is correct in most cases.

ION EXCHANGE STUDIES ON CLINOPTILOLITE

A number of ion exchange studies have been performed on clinoptilolite, primarily because of its ability to extract Cs^{137} from radioactive waste solutions and ammonium ion from municipal wastewater streams. The initial investigations into the selectivity of clinoptilolite for inorganic ions were conducted by Ames who demonstrated its high selectivity for Cs^+ (Ames, 1960; 1961; 1962) and established the selectivity series:

$$Cs > Rb > K > NH_4 > Ba > Sr > Na > Ca > Fe > Al > Mg > Li$$

for the zeolite material from Hector, California on the basis of the power of the different cations to compete with Cs (Ames, 1960). Other studies were reported at that time evaluating the use of clinoptilolite in extracting Cs^{137} and Sr^{90} from radioactive wastes (Mercer, 1960; Mathers and Watson, 1962; Tomlinson, 1962; Nelson et al., 1960). Because clinoptilolite also exhibits relatively high selectivity for NH_4^+, a number of studies have also evaluated the use of that mineral in the treatment of municipal wastewater (Ames, 1967; Mercer et al., 1970; Mercer and Ames, 1978).

Studies of a more quantitative nature were initiated by Ames (1963) on clinoptilolite-cesium and -strontium exchange in the presence of high concentrations of competing cations K^+, Na^+, Rb^+ and Ca^{2+}. Later on, Ames (1964a,b) published exchange isotherms for the couples Na $\Leftrightarrow$ K, Na $\Leftrightarrow$ Sr, Na $\Leftrightarrow$ Ca, and Ca ⇔ Sr, which are shown in Fig. 3, and values of thermodynamic constants relative to these experiments.

A study on exchange equilibria between Na-clinoptilolite and various alkyl-ammonium cations was conducted by Barrer et al. (1967) which revealed interesting steric and ion sieve effects that can be readily explained on the basis of the clinoptilolite-heulandite structure determined by Merkle and Slaughter (1968).

More recent studies on clinoptilolite ion exchange were conducted by Townsend and co-workers, using zeolite materials from Hector, California. Barrer and Townsend (1976b) studied the exchange equilibria between the ammonium form of clinoptilolite and copperammine and zincammine metal complexes. The exchange isotherms (Fig. 4) indicate maximum exchange limits of 88% and 73% for the copper and zinc, respectively. Reversibility tests showed good reversibility for the copperammine + clinoptilolite system, but not for zincammine + clinoptilolite. In the latter case, the conventional method used to test for reversibility involved drying the zeolite sample at 80°C before measuring the reverse isotherm points, and this apparently allowed the zinc ions to enter exchange sites not accessible to the complexed species at ambient temperatures (Barrer and Townsend, 1976a). Thus the reverse isotherm points were at higher values of Zn_c than for the forward isotherm points. The results of Barrer and Townsend (1976b) also showed that ammination improves the selectivity of clinoptilolite for copper and zinc, and that the zeolite shows increasing selectivity for the complexed transition metal ion with decreasing concentration.

Townsend and Loizidou (1984) published an isotherm for the Na^+/NH_4^+ exchange in clinoptilolite (Fig. 5), and compared their derived thermodynamic constants for the exchange to those determined by other workers. Their results showed that clinoptilolite exhibits high preference for NH_4^+ over Na^+, but that it only shows partial exchange with ammonium ions, indicating that the theoretical exchange capacity estimated from the chemical analysis of the zeolite cannot be attained with ammonium. Also, the range in standard free energy values obtained by different workers for the Na^+/NH_4^+ exchange on different clinoptilolite samples emphasizes the importance of complete characterization of specimens used in the experiments.

Isotherms for the exchange of cadmium into the sodium and ammonium forms of clinoptilolite were published by Loizidou and Townsend (1987). Their results (shown in Fig. 6) indicated that the ion exchange is reversible for the $Na^+ \Leftrightarrow Cd^{2+}$ couple within experimental uncertainty, but not for the

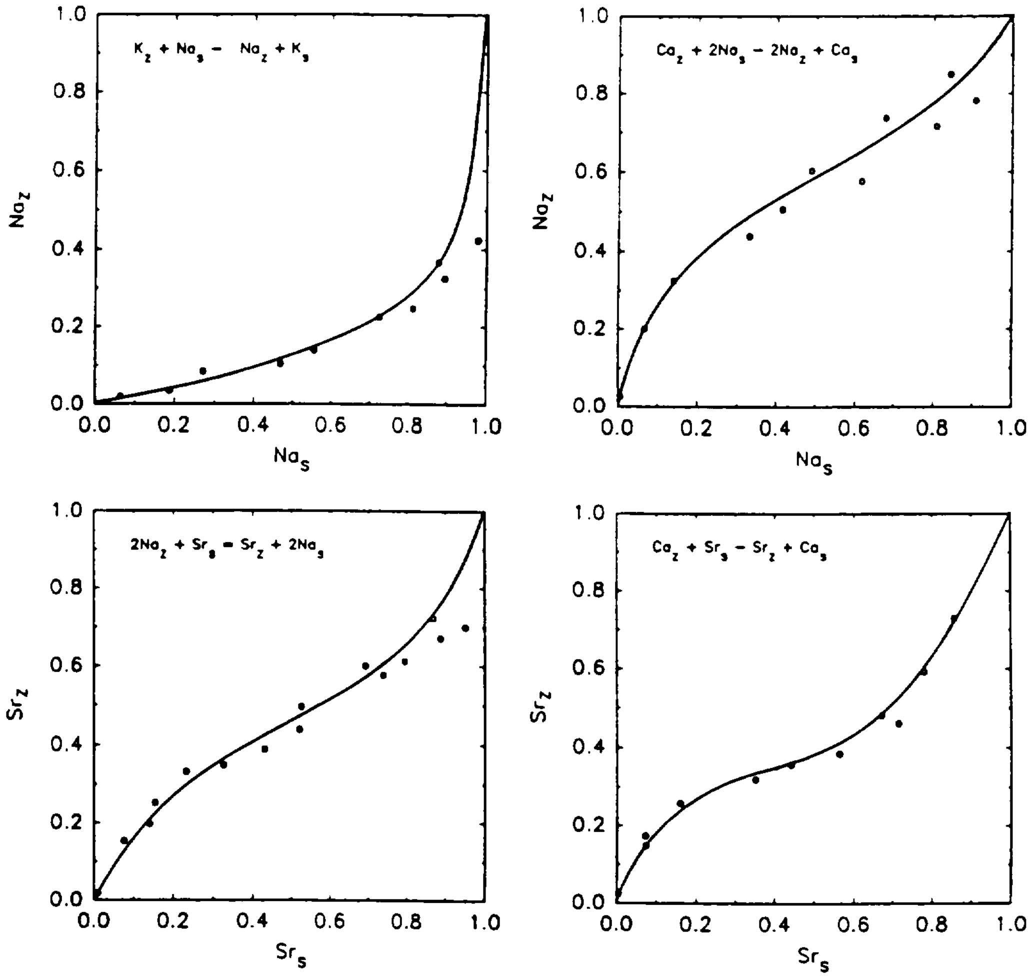

FIGURE 3. Ion exchange isotherms of clinoptilolite from Hector, California, at 25°C, 1N total normality: a) Na ⇔ K, b) Na ⇔ Ca, c) Na ⇔ Sr, d) Ca ⇔ Sr (Ames, 1964 a,b). Subscripts s and z denote equivalent cation fractions in the aqueous solution and zeolite phase, repsectively.

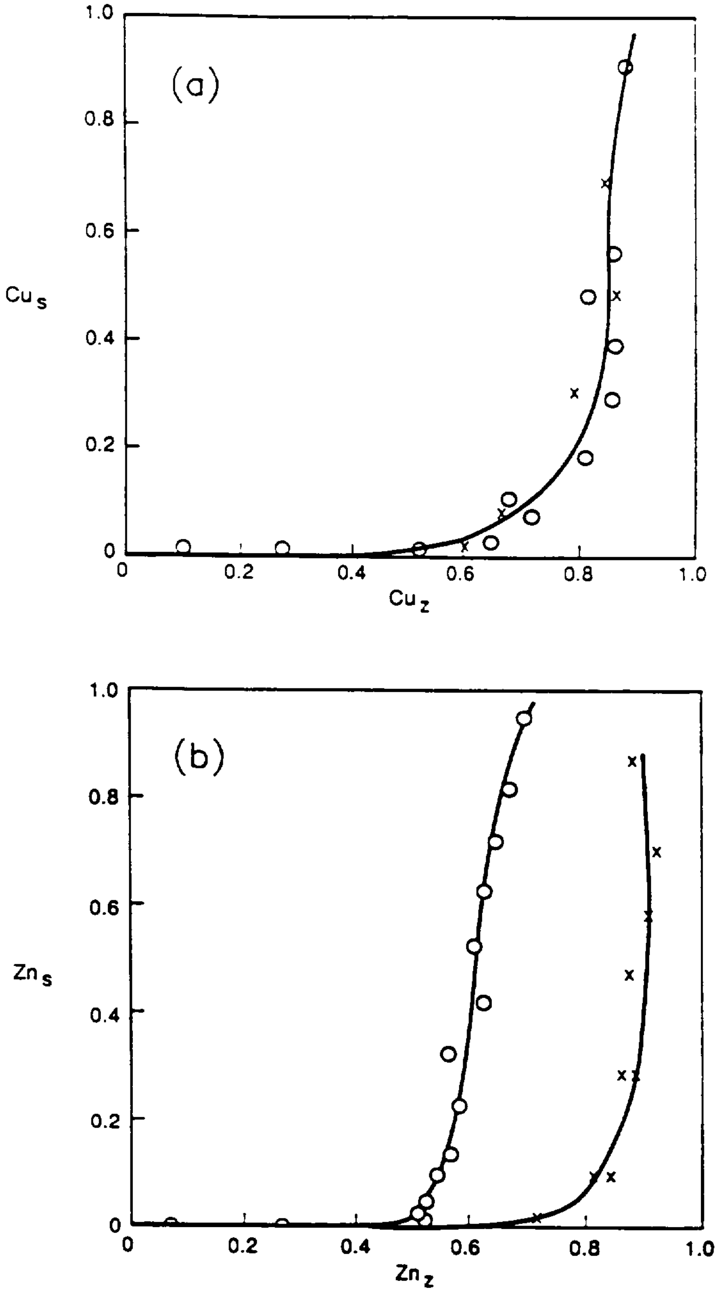

FIGURE 4. Experimental isotherms for ion exchange at 25°C of: a) copperammine and b) zincammine in ammonium forms of clinoptilolite (from Barrer and Townsend, 1976). Circles are forward isotherm points; crosses are reverse points.

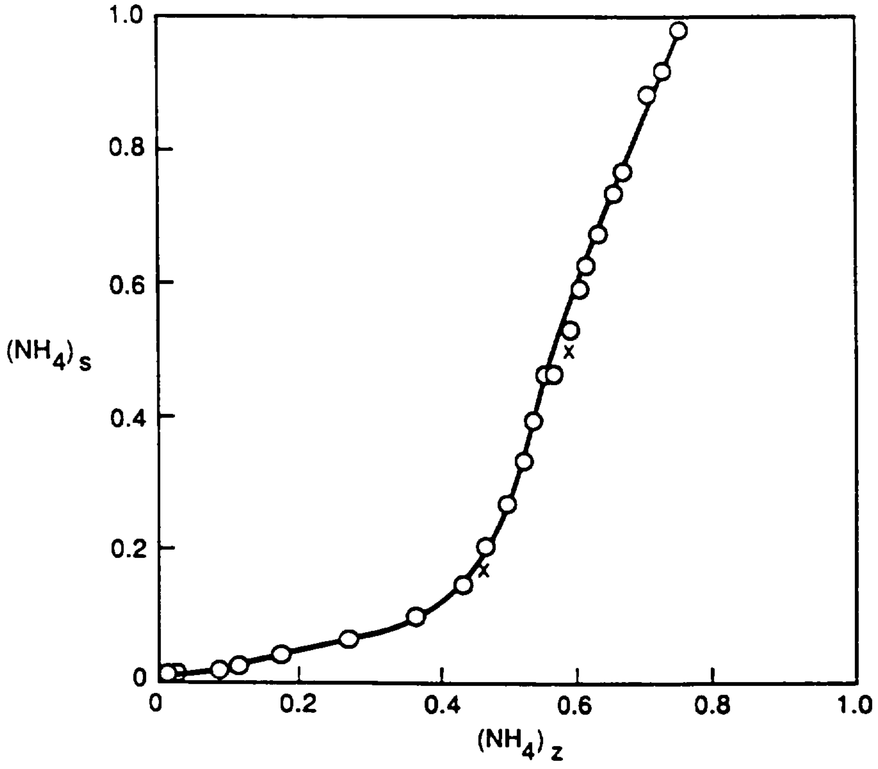

FIGURE 5. Ion exchange isotherm obtained at 25°C for the sodium-ammonium exchange in clinoptilolite (from Townsend and Loizidou, 1984). Circles represent forward isotherm points; crosses are reverse points.

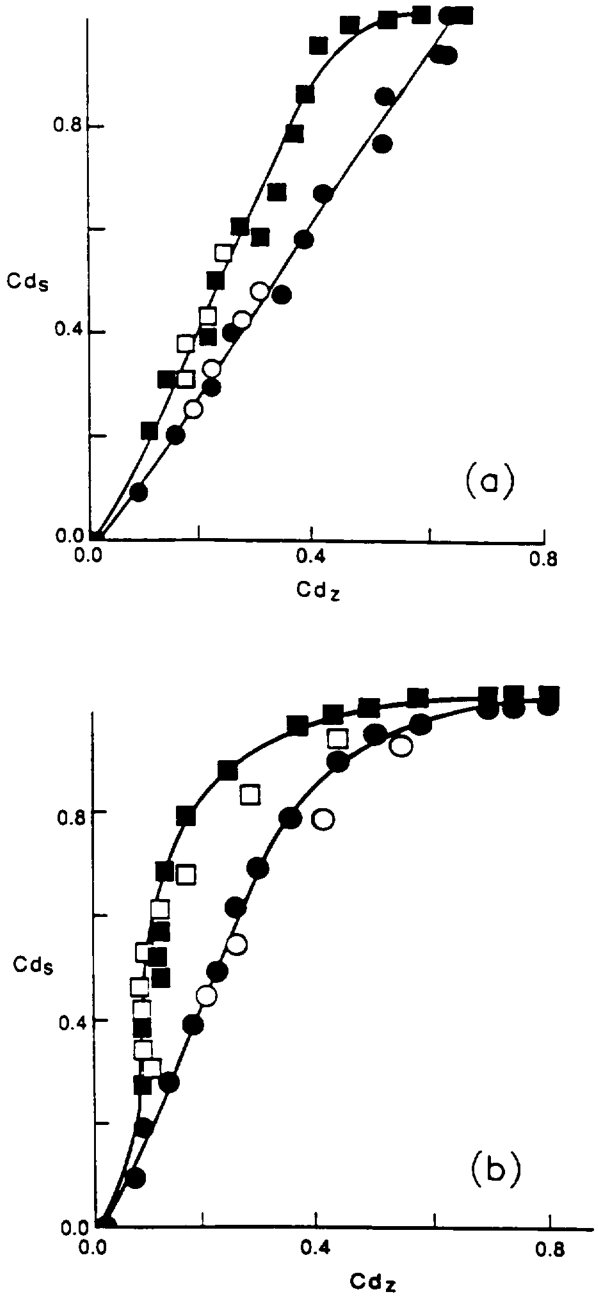

FIGURE 6. Isotherms at 25°C for the exchange of sodium by cadmium (a) and of ammonium by cadmium (b) in clinoptilolite (from Loisidou and Townsend, 1987), in the presence of either chloride (square symbols) or nitrate (circles). Filled symbols represent forward isotherm points; open symbols, reverse points.

$Cd^{2+} \Leftrightarrow NH_4^+$ couple. It was shown in their study that overexchange phenomena, which were observed to occur in exchange studies of bivalent metal ions and clays (Sposito et al., 1981) due to a partial exchange of metal complexes with sodium ions at the edges and dislocations of smectite layers, are not significant for clinoptilolite. However, because of the tendency of cadmium to associate strongly with some anions in solution, the selectivity of clinoptilolite for cadmium is strongly dependent on the nature of the co-anion.

Additional isotherms were published by Semmens and Seyfarth (1978) on exchange equilibria between Na-clinoptilolite and the heavy metal ions Ba^{2+}, Cd^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+}, using zeolite material from Buckhorn, New Mexico. They reported good reversibilities for the exchange couples Na ⇔ Ba, Na ⇔ Cd, and Na ⇔ Cu, but not for Na ⇔ Pb and Na ⇔ Zn. They showed that heavy metals are concentrated well by clinoptilolite at low solution fractions of the heavy metals, and established the selectivity sequence Pb ≈ Ba >> Cu, Zn, Cd > Na. More importantly, their results indicated that the ion exchange capacity of clinoptilolite depends significantly on the method used to pretreat the samples. For example, the exchange capacity tends to increase with repeated capacity determinations on the same zeolite sample. This has important implications on the manner in which ion exchange experiments on clinoptilolite are conducted if reproducible results are to be achieved and if valid extrapolation of experimental data to other clinoptilolite samples is desired.

CONSTRAINTS ON ION EXCHANGE EXPERIMENTS

A quantitative understanding of exchange processes requires corrections for non-ideal behavior in both the aqueous solution and the exchanger phase (Fletcher et al., 1984; Fletcher and Townsend, 1985). Although activity coefficients for a wide variety of aqueous species can be successfully modeled by various techniques (Pitzer, 1973, 1979; Helgeson et al., 1981; Fletcher and Townsend, 1981), activity coefficients for the exchanger phase, particularly for natural zeolites like clinoptilolite, have received relatively little attention. Extensive experimental work needs to be done to define solid solution properties for minerals of interest to the high-level waste program.

Before ion exchange experimental data can be subjected to thermodynamic treatment, it is important that the exchange be shown to be reversible. In early ion exchange work on clinoptilolite this has not been the case. For example, Ames (1964a,b), while providing important isotherms for the couples Na ⇔ K, Na ⇔ Ca, Na ⇔ Sr, and Ca ⇔ Sr, demonstrated reversibility only for the Na ⇔ Sr pair.

The thermodynamic models used in evaluating exchanger phase activity coefficients essentially involve integrating Gibbs-Duhem type equations [e.g., Eqns. (18)-(20) given above]. The precision of parameters derived from such models relies on the acquisition of accurate experimental data. Thus, Rees (1980) emphasized the importance of accuracy in analysis, particularly at the extrema of the isotherm plot. Small errors in the analysis of low concentrations of an ion can have a dramatic effect on the shapes of plots of the quantity ln K_c versus composition. This is undoubtedly the primary explanation for the many discrepant results in the literature for a given system (Townsend, 1986). It also has important implications to the development of isotherms relevant to the high-level waste program because of the expected low concentrations of radioactive species.

However, this is likely not the only cause of discrepant data being obtained for different studies on a given exchange. It was common practice in past binary exchange measurements to analyze both phases for one ion only, and to infer the concentrations of the other ion by differences (e.g., Ames, 1964a,b). For some zeolites, however, hydronium exchange also takes place concomitant with the other exchange reaction (Drummond et al., 1983). When this occurs the exchange becomes a ternary exchange equilibria, and serious errors may result in the calculation of selectivity coefficients, especially at the extrema of isotherms. In addition, particularly those with low Si/Al ratios, hydronium exchange is accompanied by dealumination and partial destruction of the zeolite framework. For high framework Si/Al zeolites like clinoptilolite, however, dealumination may not be as important (Townsend et al., 1984).

A similar problem may occur for systems that exhibit incomplete exchange relative to a certain cation. During the course of an experiment the cation remaining in the solid phase may eventually exchange out, changing the nature of the exchange to a ternary reaction. For example, in Townsend and Loizidou's (1984) study on Na-NH_4 equilibria, clinoptilolite which had already been maximally exchanged for Na^+ released traces of K^+ when equilibrated with the mixed sodium/ammonium solutions. Thus, a third component was added to the exchange. In this particular case, however, the K^+ concentration was low enough that the reaction remained essentially binary (Townsend and Loizidou, 1984).

Thus for careful studies of ion exchange equilibria it is advisable to analyze for *each* exchanging ion in *both* the aqueous solution phase and the solid phase. This may be supplemented for systems that exhibit incomplete exchange by analysis of other cations in both phases. In cases where there is potential dealumination of the solid, aluminum in both phases may be analyzed. The pH of the aqueous solution may also be controlled or monitored and other analytical techniques may be used. For example, scanning electron microscopy may be used to assess any visible crystal damage.

Ion exchange studies on clinoptilolites present special problems. Clinoptilolite materials used in ion exchange experiments are essentially zeolitized tuff specimens. These commonly contain mineral impurities such as quartz, feldspar, clays and unaltered volcanic glass, and in some cases, halite and calcite. Soluble salts and carbonate minerals, if not eliminated before conducting the experiments, can later dissolve and invalidate the assumption of binary exchange reaction. In addition, thermodynamic treatment requires that the cation exchange capacity (CEC) be known. Previous studies have estimated the CEC from the Al concentration in the zeolite determined by chemical analysis (e.g., Townsend and Loizidou, 1984), from the concentration of exchangeable cation(s) in the zeolite determined by chemical analysis (e.g., Barrer and Townsend, 1976), or from the observed maximum levels of exchange (e.g., Ames, 1964a,b). Each of these methods has drawbacks due to impurities in clinoptilolite samples. If the first method is used, chemical analysis of clinoptilolite will overestimate CEC in cases where feldspars or other aluminosilicate minerals are present and result in higher Al content. If the second method is used, chemical analysis will overestimate the amount of exchangeable cations Na, Mg, and Ca, hence CEC, in cases where impurities such as halite or carbonate minerals are present. On the other hand, CEC's determined by the third method are sensitive to the method of pretreatment used (Semmens and Seyfarth, 1978).

These problems can be minimized by careful characterization (e.g., analysis of mineralogical composition) or pretreatment (e.g., dissolution of soluble minerals or physical separation/purification) of clinoptilolite specimens. Unfortunately, little attention has been given in many ion exchange studies to the methods used in the preparation of the materials, or, in some cases, to their mineralogical and chemical composition. Thus comparisons of experimental results and related thermodynamic quantities derived by various investigators can be complicated. Townsend (1984) suggested that a fundamental re-examination of much of the data already published on ion exchange in zeolites appears necessary.

Procedures for planned zeolite ion exchange experiments which describe the methods and equipment to be used in the Center's conduct of ion exchange experiments are attached in Appendix 1. Other pertinent technical operating procedures (e.g., X-ray diffraction analysis, thin-section preparation) are also included in Appendix 1.

THEORETICAL BASIS FOR PHASE EQUILIBRIUM EXPERIMENTS

The standard state thermodynamic properties of clinoptilolite are required to make predictions of its solubility and stability relative to other minerals as a function of temperature and aqueous solution composition. These data also permit theoretically based modeling of the geochemical evolution of the proposed repository at Yucca Mountain. However, these properties are poorly known. The values presently used in repository related calculations have been estimated by Daniels et al. (1982) and Kerrisk (1983), who state: "The data generated in this review are not adequate for accurate chemical-equilibrium calculations" (Daniels et al. p. 224). Consequently, experiments are being designed in the CNWRA's Geochemistry Research Project to assess standard-state thermodynamic properties of endmember zeolite minerals. These data will be coupled with solid solution properties being generated in the ion exchange studies to give a fairly complete thermodynamic description of this mineral.

Phase equilibrium experiments will be used to derive the standard state Gibbs free energy ($\Delta G^{o}_{(rxn)}$) for the reaction:

$$\underset{\text{Na-clinoptilolite}}{Na_2Al_2Si_{10}O_{24} \cdot 8H_2O} \Leftrightarrow \underset{\text{analcime}}{2\ NaAlSi_2O_6 \cdot H_2O} + \underset{\text{aqueous silica}}{6\ SiO_2} + 6\ H_2O\ . \tag{24}$$

For reaction (24),

$$\Delta G^{o}_{(rxn)} = 2\Delta G^{o}_{(anal)} + 6\Delta G^{o}_{(SiO_2)} + 6\Delta G^{o}_{(H_2O)} - \Delta G^{o}_{(Na-clin)} \tag{25}$$

$$= -RT \ln K_{(rxn)}.$$

For the case in which the clinoptilolite, analcime and water are in their standard states with unit activities, the equilibrium constant ($K_{(rxn)}$) in equation (25) is given by

$$K_{(rxn)} = a^{6}_{SiO_2}. \tag{26}$$

It follows that measurement of the aqueous silica activity in a solution that is in equilibrium with both analcime and Na-clinoptilolite allows calculation of the equilibrium constant and the standard state free energy for reaction (24). In turn, knowledge of the standard state free energies of analcime, aqueous silica, and water, together with that for reaction (24), enable calculation of the standard state free energy of Na-clinoptilolite according to equation (25).

Phase relations involved in this study are illustrated in Fig. 7, which was generated using the law of mass action for dissolution reactions such as that for Na-clinoptilolite:

$$Na_2Al_2Si_{10}O_{24} \cdot 8H_2O \Leftrightarrow 2Na^+ + 2Al(OH)_4^- + 10SiO_2 + 4H_2O\,. \tag{27}$$

Equilibrium for this reaction is represented by

$$\log K_{Na-clin} = \log a^2_{Na+} + \log a_{Al(OH)_4^-} + \log a^{10}_{SiO_2} \tag{28}$$

which can be rewritten as

$$\log\,[(a_{Al(OH)_4^-})(a_{Na+})] = 0.5 \log K_{Na-clin} - 5 \log\,(a_{SiO_2}). \tag{29}$$

This is the equation for the straight line in Fig. 7 labelled clinoptilolite. Aqueous solutions with compositions represented to the upper right of this line are supersaturated with respect to Na-clinoptilolite, and solutions with compositions to the lower left of this line are undersaturated with respect to Na-clinoptilolite. Saturation lines for analcime and albite are plotted in a similar manner. The unconventional axes in Fig. 7 are particularly useful for this system because Na-clinoptilolite, analcime, and albite all have the same Na to Al ratio in their stoichiometric formulas. Because kaolinite does not contain sodium, it is possible to plot its solubility limit in Fig. 7 only by specifying values for the pH and sodium activity. Also plotted in the figure are solubility limits for quartz and cristobalite, which depend only on the aqueous silica activity.

Equilibrium constant data at 95°C used to generate Fig. 7 were taken from the EQ3/6 data base (e.g. Wolery, 1986). For all minerals except clinoptilolite, these data are from the work of Helgeson and others (e.g. Helgeson et al., 1978; 1981). The clinoptilolite data are those estimated by Kerrisk (1983).

The equilibrium boundary between analcime and clinoptilolite is represented in Fig. 7 by the intersection of their solubility lines. The unique value of the activity of silica corresponding to this intersection is the equilibrium value in equation (27). Note that this activity falls between the solubility limits for quartz and cristobalite. This observation is consistent with the negative correlation between the occurrences of clinoptilolite and cristobalite in core samples from Yucca Mountain (e.g. Bish, 1989). The field

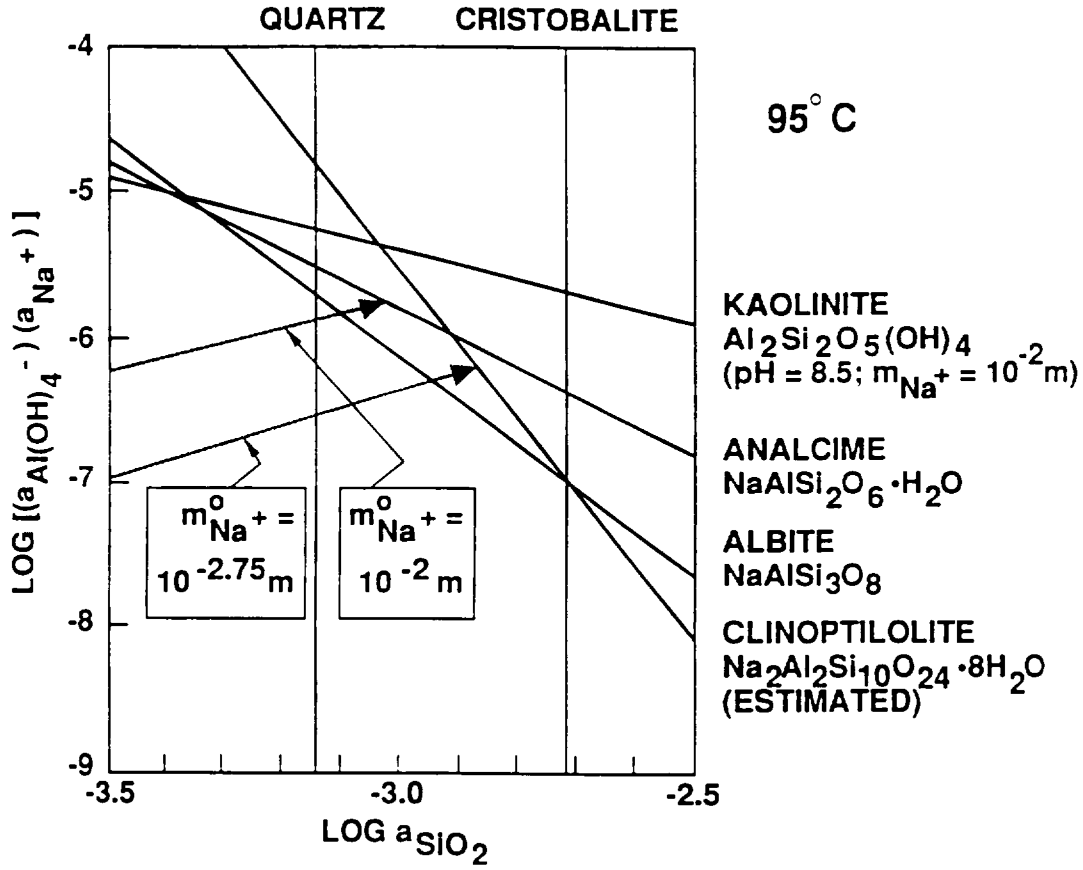

FIGURE 7. Phase relations involved in the study of clinoptilolite-analcime equilibrium. The intersection of the solid lines representing Na-clinoptilolite and analcime solubility limits indicates the aqueous silica activity for the equilibrium coexistence of the two minerals. The stippled vectors represent paths for the reaction of Na-clinoptilolite and analcime with the aqueous phase for different initial Na^+ concentrations. The equilibrium state can be reversed by approaching it from two directions.

observations also suggest that the stability of clinoptilolite relative to analcime is controlled in nature by the aqueous silica activity as represented in Fig. 7.

The experimental technique to be utilized in the phase equilibrium experiments comprises two steps. First, it is necessary to obtain or synthesize pure endmember samples of clinoptilolite and analcime. Homo-ionic Na-clinoptilolite is being synthesized in the experimental program devoted to ion exchange equilibria. Pure analcime from the Mt. St. Hilaire locality in Quebec has been acquired commercially from Ward's Scientific.

The second step is to react a mixture of these minerals with solutions of known and monitored composition to achieve the composition of the solution in equilibrium with both of them. Initial solutions will be dilute sodium bicarbonate/chloride solutions to minimize ambiguities with regard to activity coefficients of aqueous species. Vectors representing reaction paths for dissolution of analcime and Na-clinoptilolite are represented in Fig. 7 for initial solutions of pH 8.5 and initial sodium molalities of 10^{-2} and $10^{-2.75}$ m. These paths were calculated using EQ6 (e.g. Wolery, 1986). The former solution impinges on analcime saturation at a silica activity for which analcime is calculated to be stable relative to clinoptilolite. The latter solution impinges on the solubility limit for Na-clinoptilolite at a greater silica activity for which Na-clinoptilolite is stable relative to analcime. After hitting the solubility limits, each of these solutions is predicted to migrate toward the equilibrium silica value. Hence, in the two experiments equilibrium is approached from two directions, and the equilibrium determination can be reversed. The pH and sodium activities corresponding to these reaction paths are also chosen so that secondary precipitation of kaolinite should not interfere with the equilibrium determination, as indicated by the relation between the solubility line for kaolinite in Fig. 7 and the reaction path vectors. It is anticipated that slow nucleation kinetics for quartz and albite will inhibit their precipitation, even though the analcime-Na-clinoptilolite equilibrium is predicted to be metastable with respect to both albite and quartz as indicated in Fig. 7. Slow nucleation of quartz and albite, and low temperature solutions that are supersaturated with respect to these minerals are common in nature. Preliminary kinetic calculations corresponding to the reactions represented by vectors in Fig. 7 indicate that equilibrium between Na-clinoptilolite and analcime can be closely approached in a few days or less at 95°C. Experiments at other temperatures (e.g. 55° and 25°C) will enable derivation of the standard state enthalpies of reaction and of the Na-clinoptilolite mineral.

Aside from the ion exchange equilibrium studies reviewed in another section, the only experimental thermodynamic study of clinoptilolite in the literature are calorimetric heat capacity measurements by Hemingway and Robie (1984). Data were collected between 15° and 305°C. The clinoptilolite was of mixed composition: $(Na_{0.56}K_{0.98}Ca_{1.50}Mg_{1.23})(Al_{6.7}FeV_{0.3})Si_{29}O_{72} \cdot 22H_2O$. Hence, its properties are expected to differ from that of the homoionic species to be used in the phase equilibrium studies described above. Nevertheless, these data could be useful in calibrating heat capacity estimations for a variety of clinoptilolite species. Fairly accurate techniques for estimating heat capacities of minerals are reported in the literature (e.g. Helgeson, 1978).

CHARACTERIZATION OF ZEOLITE SAMPLES

The absence of sufficient amounts of macroscopic crystals of clinoptilolite has made experimental studies on clinoptilolite problematical. In fact, due to the microscopic size of commonly available clinoptilolite, no refinement on its structure was done until Alberti (1975) performed detailed X-ray diffraction analyses on two macrocystalline clinoptilolites which occur in vugs of volcanic rocks in Agoura, California and Alpe di Siusi, Bolzano, Italy. Thus, all previously published studies of ion exchange in clinoptilolite have been done using zeolitized tuff specimens. The detailed mineralogy of samples from different localities will be different, and even samples from different outcrops in one locality may show variations in mineralogical composition. Because mineralogical and chemical composition can influence the results of ion exchange and phase equilibrium studies, it is essential to characterize the clinoptilolite materials that will be used for the experiments. Characterization is also important in identifying methods that will eliminate some, if not all, of the impurities.

In connection with the Center's experimental studies on clinoptilolite, specimens from four localities were obtained from Minerals Research (P.O. Box 591, Clarkson, N.Y. 14430), namely: 1) Hector, California, 2) Barstow, California, 3) Death Valley Junction, California, and 4) Castle Creek, Idaho. Samples from two additional localities, Tilden, Texas and Buckhorn, Grant County, New Mexico, were obtained from Zeotech Corp. (3224 Candelaria N.E., Albuquerque, N.M. 87107).

Initial characterization of these samples was done using X-ray diffraction analysis, petrographic (thin section) analysis, and scanning electron microscopy. Results of the X-ray diffraction and petrographic analyses indicate that the samples contain mostly well-crystallized clinoptilolite, which has completely replaced all the glass in the poorly welded tuffs. The most common accessory minerals are quartz, mordenite, feldspars, and clay. X-ray diffraction patterns for the clinoptilolite samples are given in Appendix 2, and results of detailed petrographic analyses are given in Appendix 3.

Scanning electron microscope images of clinoptilolite from Hector, California and Death Valley Junction, California are given in Appendix 4.

Additional petrographic and X-ray diffraction work will be done to determine variability in modal composition within each batch of samples received. These will be supplemented by wet chemical analysis to determine the composition of clinoptilolite materials to be used for the experiments.

In contrast to clinoptilolite, the zeolite analcime commonly occurs as large euhedral crystals of hydrothermal origin. Analcime crystals 1-6 cm. in diameter were obtained from Ward's Natural Science Establishment. These samples are from Mt. St. Hilaire, Quebec where the analcime occurs in late-stage coarsely crystalline pegmatites in nepheline syenite. Accessory minerals, including K-feldspar, hornblende, and muscovite, occur with the analcime samples, but these were easily separated by crushing the samples and selecting pure mineral phases by hand-picking. The X-ray diffraction pattern of the analcime sample is also shown in Appendix 2.

CONCLUSIONS

It is apparent from the literature review that ion exchange processes are functions of various parameters including: (1) charge density of the anionic crystal structure, (2) the mineral framework topology, (3) size and shape of the exchanging ions, (4) valence and charge of the ions, (5) composition and ionic strength of the external electrolyte solution, and (6) temperature. Therefore, an adequate understanding of exchange processes, particularly in geologic systems where physico-chemical conditions can vary widely, relies on both theoretical and experimental studies. A knowledge of the crystal chemistry of zeolites and the thermodynamic principles of ion exchange provides the basic tools necessary for a quantitative understanding of ion exchange behavior. Thermodynamic models also form rigorous bases for predicting ion exchange behavior in multicomponent systems and under conditions not studied previously.

For geologic systems, one implication of theoretical and experimental studies reviewed in this report is that the use of invariant retardation factors, K_d, in hydrologic models may not accurately model the transport behavior of radionuclides or other aqueous species for environments where ion exchange is the predominant retardation mechanism. The assumption of linear isotherms inherent in the use of K_d's is valid only under restricted ranges of concentration. This is apparent from ion exchange experiments that have been done on clinoptilolite and other zeolites.

The simple treatment offered by K_d's also cannot adequately account for the complicated dependence of ion exchange equilibria on aqueous solution concentrations and on the compositions of both the aqueous and zeolite phases. For example, the observed concentration-valency effect on ion exchange equilibria, in which cations of higher charge are preferred by the zeolite over cations of lesser charge as the aqueous solution becomes more dilute, not only negates the assumption of isotherm linearity in the dilute range for exchanges involving cations of unequal charges, but also requires K_d parameters that are strongly dependent on the composition of the exchanger phase.

This dependence of ion exchange selectivity on zeolite composition has important implications for Yucca Mountain. Studies on the chemistry of diagenetically altered tuffs at Yucca Mountain (Broxton et al., 1986) show that clinoptilolite minerals at and below the water table grade laterally from sodic compositions on the western side of Yucca Mountain to calcic compositions on the eastern side, and that potassium-rich clinoptilolite occur at the north end of Yucca Mountain. The study by Ames (1960) indicate that the selectivity of clinoptilolite for various ions is Cs > K > Sr > Na > Ca > Mg. Therefore, to a first approximation, Cs^{137} migration can be effectively retarded by ion exchange throughout the lateral extent of clinoptilolite-rich tuffs, but Sr^{90} may not be so effectively retarded on the northern end of Yucca Mountain. The detailed ion exchange behavior is, of course, more complex because the geologic system is multicomponent in nature.

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APPENDIX 1.

CNWRA TECHNICAL OPERATING PROCEDURES PERTINENT TO THE GEOCHEMISTRY RESEARCH PROJECT.

UNCONTROLLED

CENTER FOR NUCLEAR WASTE REGULATORY ANALYSES

TECHNICAL OPERATING PROCEDURE

Proc. TOP-004

Revision 0

Page 1 of 6

Title PROCEDURE FOR CONTROL, PREPARATION AND CHARACTERIZATION OF GEOLOGIC MATERIALS

EFFECTIVITY AND APPROVAL

Revision 0 of this procedure became effective on 6/1/89. This procedure consists of the pages and changes listed below.

Page No.	Change	Date Effective
All	-	June 1, 1989

UNCONTROLLED

Supersedes Procedure No. None.

Approvals

Written By Roberto T. Pabalan	Date 5/31/89	Technical Review John L Russell	Date 5/31/89
Quality Assurance	Date 6/1/89	Cognizant Director Allen R. Whiting	Date 6/1/89

CNWRA Form TOP-1

PROCEDURE FOR CONTROL, PREPARATION AND CHARACTERIZATION OF GEOLOGICAL MATERIALS

1. Purpose

The purpose of this procedure is to describe the requirements for controlling, preparing, and characterizing geological materials to be used in geochemistry research.

2. Scope and Application

This procedure describes the equipment and methods which may be utilized for specimen preparation and characterization, and specimen identification, records keeping and storage requirements.

2.1 Applicable Documents

The following documents form a part of this procedure, as applicable:

(1) Center Technical Operating Procedures

(2) Center Quality Assurance Manual

(3) U.S. Environmental Protection Agency "Test Methods for Evaluating Solid Waste"

(4) U.S. Environmental Protection Agency "Test Methods for Chemical Analysis of Water and Wastes"

3. Responsibility

(1) The cognizant principal investigator of the project shall be directly responsible for the implementation of this procedure. In cases where the principal investigator is not a member of the CNWRA, the Project/Element Manager shall retain this responsibility.

(2) The cognizant principal investigator shall be

responsible for the compilation, storage, and retrieval of records prepared in response to this procedure.

(3) The Center Director of Quality Assurance is responsible for providing independent surveillance, review or audits to verify implementation of this procedure.

4. Equipment

Listed below are pieces of equipment that may be utilized in the preparation and characterization of geological materials, as required:

(1) Mortar and pestle

(2) Stainless steel sieves

(3) Ro-Tap sieve shaker

(4) Thin-section equipment (rock saws, grinders, etc.)

(5) Petrographic microscope

(6) Stereo microscope

(7) X-ray diffraction equipment

(8) X-ray fluorescence equipment

(9) Scanning electron microscope

(10) Energy dispersive spectrometer

(11) Surface area analyzer

(12) Atomic absorption spectrometer

(13) Plasma emission spectrometer

(14) Ion-chromatograph

(15) and other specialized equipment which may be required in the preparation and characterization of geological materials.

5. Procedure

(1) Specific characterization methods will be described in the Center Technical Operating Procedures.

(2) Test specimens analyzed using non-destructive methods shall be returned to their respective containers with proper identification.

(3) Duplicate test specimens prepared from the same material shall be properly identified and stored in separate containers/bags.

(4) Records of the results of characterization studies, the methods used, and the person(s) who performed the work are to be kept at the Center.

(5) There are no special environmental controls to be applied to this procedure.

6. Identification and Storage

(1) The geological material shall be stored in canvas bags, plastic jars/bags, glass jars, or other suitable containers.

(2) Identification numbers or labels shall be marked on the container or, when appropriate, on the sample itself.

(3) Records of identification numbers or labels and source locality of the geological material are to be kept at the Center.

7. Control of Samples

Geological samples under the control of the Center shall be kept in a cabinet if not being utilized in a project or being characterized. The cabinet in which geological samples are stored shall be locked during non-business hours. Only the principal investigator, his Project/Element Manager, or their designee will have key or codes to the storage cabinet or container.

8. Deviation from Procedures

Although Center Technical Operating Procedures and other Center-prescribed procedures will be utilized and the characterizations documented, deviation from established and controlled procedures may be necessary. In such cases, no deviation and nonconformance report is required. Instead, the description of the procedure deviation will be properly recorded in the laboratory notebook.

9. Records

9.1 The laboratory notebook or other device used to record the results of geological characterizations shall contain the following information:

(1) Date

(2) Full name, initials or assigned stamp of individual(s) performing the characterization work

(3) Method of characterization utilized, including any deviation from established procedures

(4) Equipment used

(5) Results

9.2 Each laboratory project task will have its own lab notebook with bound and numbered pages, or another method to capture the results of the work. The lab notebook is the responsibility of the principal investigator until project completion or termination. At that point, the project lab notebook(s) are retained as are other results, in appropriate Center files as primary evidence of work accomplishment. Copies of lab notebook pages may be made, but the lab notebook remains Center property.

UNCONTROLLED

CENTER FOR NUCLEAR WASTE REGULATORY ANALYSES **TECHNICAL OPERATING PROCEDURE**	Proc. TOP 004-01 Revision 0 Page 1 of 10

Title

TOP 004-01
PROCEDURE FOR PREPARATION OF THIN SECTIONS
OF GEOLOGICAL MATERIALS

EFFECTIVITY AND APPROVAL

Revision 0 of this procedure became effective on June 27, 1989. This procedure consists of the pages and changes listed below.

Page No.	Change	Date Effective
All	----	6/27/89

UNCONTROLLED

Supersedes Procedure No. None

Approvals

Written By Robert T Patelson	Date 6/19/89	Technical Review John Russell	Date 6/23/89
Quality Assurance Bruce Mabrito	Date 6/24/89	Cognizant Director Allen R. Whiting	Date 6/27/89

CNWRA Form TOP-1

PROCEDURE FOR PREPARATION OF THIN SECTIONS OF GEOLOGICAL MATERIALS

1. Purpose

The purpose of this procedure is to describe the methods, equipment, and supplies to be used in making thin sections of geological materials.

2. Scope and Application

This procedure describes the techniques, equipment, and materials which may be utilized in the preparation of thin sections of rock and mineral specimens. The thin sections prepared using this procedure may be used for petrographic analyses of the geological materials using transmitted light, reflected light, and/or electron microscopy.

2.1 Applicable Documents

The following documents form a part of this procedure, as applicable:

(1) Center Technical Operating Procedures
(2) Center Quality Assurance Manual
(3) Operating Manual for Rock Saw/Grinder
(4) Operating Manual for Grinding/Polishing Lapidary Wheel
(5) Epoxy Material Data Sheet

3. Responsibility

(1) The cognizant Principal Investigator of the project shall be directly responsible for the implementation of this procedure and for determining acceptability of thin sections prepared using this procedure. In cases where the Principal Investigator is not a member of the Center, the Project/Element Manager shall retain this responsibility.

(2) The Center Director of Quality Assurance is responsible for providing independent surveillance, review or audits to verify implementation of this procedure.

4. Equipment and Supplies

Listed below are pieces of equipment and supplies that may be utilized in the preparation of thin sections:

(1) Rock saw/grinder

(2) Grinding/polishing lapidary wheel

(3) Convection oven

(4) Vacuum bell jar

(5) Vacuum pump

(6) Vacuum/pressure chamber

(7) Ultrasonic cleaner

(8) Petrographic microscope

(9) Binocular microscope

(10) Nitrogen tank with pressure regulator

(11) Epoxy

(12) Silica Carbide grit #220, 400, and 600

(13) Corundum grit #1000 or 1500

(14) Plastic embedding mold

(15) Petroleum jelly

(16) Metal clamp

(17) Glass plate

(18) Glass petrographic microscope slide and cover slip

(19) Glass beaker

(20) Wash bottle

(21) Ethyl Alcohol

(22) Razor blade

5. Procedures

A. Rock Preparation

1. If a rock is cohesive and firm, saw it with a diamond saw into a chip approximately 3-10 mm thick depending upon rock type, i.e. hardness and friability, and trim it square to approximately 24 x 24 mm; a larger specimen may be cut as a rectangle of approximately 24 x 34 mm, while a smaller sample may be left untrimmed. A width of 24 mm and length of 34 mm are upper limits due to the size of the glass slides.

2. A large-diameter diamond blade may be used initially for sawing large hand specimens into smaller slabs. Final trimming should be done with a thinner blade, such as a 127x 0.38 mm or similar sized diamond saw blade. The thinner blade is desirable because the cut is considerably smoother and it also conserves material.

3. If the rock is extremely porous or friable, the rock should be epoxy impregnated to bind the rock together (see Part B of this procedure). For hydrous rock or mineral specimens, special procedures are required (see Section 6. Special Procedures for Hydrous Rocks and Minerals).

4. Make sure the sample is properly labeled with its identification number(s) and/or letter(s). If necessary, the sample should be marked or labeled to indicate its orientation with respect to bedding planes, structures, or other suitable reference criteria.

B. Impregnation of a Porous or Friable Rock

1. The rock is cut to the smallest dimension possible while retaining cohesion. The rock is then dried for at least 12 hours at approximately 75°C in a convection oven.

2. In a glass beaker of suitable size, mix an appropriate epoxy designed for impregnation. The epoxy may be mixed with an appropriate epoxy dye to facilitate porosity recognition. Follow the protocol for the particular epoxy recommended by the manufacturer in the epoxy material data sheet. Line the bell jar with petroleum jelly to aid in epoxy removal should spillage occur. Place the beaker in a vacuum bell jar for about 15 minutes until the frothing ceases. Break and restore the vacuum several times. A vapor trap must be present between the bell jar and the vacuum line to trap any gas or moisture coming from the bell jar.

3. Using plastic breakaway embedding molds, immerse the rock chip in the epoxy. Label each mold with the respective sample number and, if necessary, sample orientation. Place the specimen in the vacuum bell jar for about 10 minutes until frothing ceases. Then transfer the specimen into a vacuum/pressure chamber. Line the chamber with petroleum jelly to aid clean-up should spillage occur. Evacuate the pressure chamber for about 30 minutes. Then slowly bleed nitrogen from a nitrogen gas tank into the chamber over a ten minute interval until the pressure in the chamber reaches approximately 1500 psi. After 45 minutes shut off nitrogen supply. Leave specimen under pressure in the chamber until epoxy cures, usually 24-48 hours. The curing time is given in the epoxy material data sheet.

   Note: This protocol for impregnation may be modified depending on the type of epoxy used and its respective curing time.

4. After epoxy has cured, slowly vent the nitrogen gas from the chamber. Remove the specimen from the mold.

Trim the specimen to the proper dimensions recommended in Section A above.

C. Mounting the Specimen.

1. Use a petrographic microscope frosted-glass slide approximately 26 X 50 mm in size to mount the rock specimen.

2. The specimen surface to be mounted is ground on a cast-iron lap wheel or a glass plate. First, in a water slurry of #220 silica carbide grit, the sample is ground until all saw marks, pits, and imperfections which are visible to the naked eye or with the aid of a 10X lens are removed and a smooth flat surface is obtained. The sample is then rinsed, cleaned in an ultrasonic bath for about 1 minute, and reground in a water slurry of #400 silica carbide grit until a smooth finish is reached, confirming surface finish with the use of at least a 10X lens. Again the sample is rinsed, ultrasonically cleaned for about 1 minute, and reground in a water slurry of #600 silica carbide grit until a polished surface is obtained. Rinse and clean the specimen in an ultrasonic bath and then check it under the binocular microscope to assure that the specimen is polished and contains no imperfections.

3. The thoroughly washed sample is placed, polished surface upward, on a tray to dry. Allow time for sample to dry completely (24-48 hours). Sample may be placed in a dessicator or oven (approximately 25^{o}C) to facilitate drying.

4. In a small beaker, mix an appropriate amount of mounting epoxy. Allow epoxy to set for approximately 5 minutes. An epoxy with a refractive index of 1.55 is advantageous for the distinction of common rock-forming minerals--quartz, alkali feldspar and plagioclase.

5. A thin even coat of the epoxy is spread on the polished side of the sample. Lay the sample on a flat surface. The glass slide, frosted side down, is then slowly pressed against the specimen, starting at one end from

an angle of approximately 45 degrees. Pressure is applied to the surface of the slide to remove any trapped air bubbles. The glass slide is pressed against the sample for about one minute. Using the metal clamp, carefully clamp the glass slide and sample together to allow the epoxy to cure under pressure.

Note: For specimens containing no quartz or feldspar, judging the thickness of the thin section is difficult; therefore, quartz grains can be added to the mounting epoxy at each corner of the glass slide. This method helps keep the thin section level during grinding, and allows the thin section thickness to be checked based on the interference colors of quartz.

6. After epoxy has cured completely, remove metal clamp. Any traces of epoxy on the glass can be removed gently with a razor blade.

D. Sawing and Grinding

The procedure for sawing and grinding the slide-mounted specimen, whether performed manually or by machine, is as follows:

1. Saw the mounted chip with a diamond saw 0.38 mm thick to a thickness of approximately 0.5 mm if an automated machine is used or to a final thickness of approximately 1-2 mm if held by hand. The section should be fed slowly through the saw to prevent plucking the chip from the glass slide.

2. The section is further reduced either on an automatic machine, or hand-held on a lap wheel or glass plate. A diamond impregnated wheel is recommended. If a machine is used, the microscrew adjustment is positioned so that the chip barely touches the grinding wheel. The sample is slowly advanced against the wheel. From time to time the sample is removed and examined with a petrographic microscope under crossed polars for thickness. When the specimen is about 40 microns (.04 mm) thick, grinding ceases. At this point quartz should show first-order yellow-to-orange birefringence.

3. After ultrasonic cleaning, further grinding is done by hand on a glass slide with #600 silica carbide in a water slurry. Grind the sample applying light even pressure. After 15 to 20 seconds the slide is rinsed with clear water and examined under the petrographic microscope for thickness. This process continues until the proper thickness is obtained (i.e., when quartz exhibits first-order gray birefringence).

4. The final step is done on a glass plate with #1000 or #1500 corundum grit in a water slurry after cleaning the samples from Step 3 in an ultrasonic bath for about 1 minute. This hand grinding provides good control over the final thickness which should be approximately 30 microns (.03mm), as indicated by birefringence colors. Also, hand grinding practically eliminates plucking.

5. The use of a cover slip is optional and depends upon the intended uses of the specimen. If the slide is to be stained for mineral identification, to be used for the study of opaque minerals under reflected light, or to be examined in the electron microscope, a cover slip should <u>not</u> be used. If the specimen is for normal petrographic work, then a cover slip is desirable.

6. <u>Special Procedures for Hydrous Rocks and Minerals</u>

A. Rock Preparation

1. Special procedures are required to make thin sections of hydrous geological materials such as zeolites. The zeolites are soft rocks, thus the initial chip cut for a thin section with a diamond saw should be approximately 8-10mm thick. After trimming the chip, it should be placed in an oven (at approximately 25°C) or dessicator to dry. The dry chip is then ready to be impregnated (Section 5.B) or to be ground for mounting.

2. If impregnation is not desired, the protocol is as follows: The chip is first ground in a slurry of ethyl alcohol and #220 silica carbide grit. The sample is ground until all saw marks, pits, and imperfections

which are visible to the naked eye or with the aid of a 10X lens are removed and a smooth flat surface is obtained. The sample is then rinsed, cleaned in an ultrasonic bath of ethyl alcohol for about 1 minute, and reground in an ethyl alcohol slurry of #400 silica carbide grit until a smooth finish is reached, confirming surface finish with the use of at least a 10X lens. Again the sample is rinsed with ethyl alcohol, ultrasonically cleaned for about 1 minute, and reground in an ethyl alcohol slurry of #600 silica carbide grit until a polished surface is obtained. The specimen is rinsed and cleaned in an ultrasonic bath, then checked under the binocular microscope to assure that the sample is polished and contains no imperfections.

3. The thoroughly washed sample is placed, polished surface upward, on a tray to dry. Allow time for sample to completely dehydrate (24-48 hours). Sample may be placed in a dessicator or oven (approximately 25°C) to facilitate dehydration.

4. After sample is completely dry, check again to ensure the the surface is flat. The sample is now ready to mount to a thin section slide. The protocol to follow is the same as described in Section 5.C.

5. If the thin section is to be impregnated, follow procedures described above in Sections 5.B and 5.C.

6. The protocol to follow to finish the impregnated sample is given below.

B. Sawing and Grinding

The procedure for sawing and grinding the slide-mounted specimen, whether performed manually or by machine, is as follows:

1. Follow the steps given in 5.D.1.

2. Follow the steps given in 5.D.2.

3. After ultrasonic cleaning allow the thin section to dry. Further grinding is done by hand on a glass slide with #600 silica carbide in an ethyl alcohol slurry. Grind the sample applying light even pressure. After 10 to 15 seconds the slide is rinsed with ethyl alcohol and examined under the binocular microscope for thickness. This process continues until the proper thickness is obtained (e.g., quartz exhibits first-order gray birefringence).

4. The final step is done on a glass plate with #1000 or #1500 corundum grit in an ethyl alcohol slurry after cleaning the samples from Step 3 in an ultrasonic bath of ethyl alcohol for about 1 minute.

7. <u>Identification and Storage</u>

1. The prepared thin sections shall be stored in a glass slide tray or cabinet or other appropriate container. Each slide will be properly labeled using a diamond-tipped stylus, or other suitable material.

2. Records of identification numbers or labels and source locality of the geological material, the name of the individual(s) who prepared the thin section, and the date it was prepared, are to be kept at the Center in the project files.

8. <u>Records</u>

No records other than sample identification and source locality are required to be generated or maintained regarding preparation of thin sections of geological materials. The thin sections are either acceptable for characterization work (e.g., petrographic analysis, porosity studies, etc.), or not acceptable, and will be utilized only if acceptable as determined by the cognizant Principal Investigator or his Project/Element Manager.

9. <u>Reference</u>

The above procedures are based on the techniques given in <u>Laboratory Handbook of Petrographic Techniques</u> by C.S. Hutchison (1974, Wiley and Sons, New York, pp. 1-9).

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CENTER FOR NUCLEAR WASTE REGULATORY ANALYSES

TECHNICAL OPERATING PROCEDURE

Proc. TOP-004-02

Revision 0

Page 1 of 12

Title

PROCEDURE FOR QUALITATIVE X-RAY POWDER DIFFRACTION ANALYSIS OF GEOLOGICAL MATERIALS

EFFECTIVITY AND APPROVAL

Revision 0 of this procedure became effective on June 27, 1989. This procedure consists of the pages and changes listed below.

Page No.	Change	Date Effective
All	-	6/27/89

UNCONTROLLED

Supersedes Procedure No. **None**

Approvals

Written By Roberto T. Pabalan	Date 6/22/89	Technical Review J. Russell	Date 6/23/89
Quality Assurance	Date 6/26/89	Cognizant Director Allen R. Whiting	Date 6/27/89

CNWRA Form TOP-1

PROCEDURE FOR QUALITATIVE X-RAY POWDER DIFFRACTION
ANALYSIS OF GEOLOGICAL MATERIALS

1. Purpose

The purpose of this procedure is to describe the methods and equipment to be used in conducting qualitative X-ray powder diffraction analysis of geological materials.

2. Scope and Application

This procedure describes the equipment and techniques which may be utilized in determining the major mineralogic constituents of geological specimens by X-ray powder diffraction methods. The specimen can be a whole rock or mineral sample, an insoluble residue, a heavy mineral separate or a size fraction of any of these materials. This procedure does not apply to detailed clay mineral analysis which involves treatment of the sample to allow dispersion and concentration of the clay mineral fraction, although qualitative information on clay minerals may be derived by this procedure. Methods to analyze clay mineralogy are covered under a separate procedure. Detailed procedures for calibrating, adjusting and operating the X-ray diffractometer are given in the Operating Instructions for Siemens D-500 Diffractometer and Kristalloflex 800 X-Ray Generator. The procedures described here may vary slightly if another make or model of diffractometer is used.

2.1 Applicable Documents

The following documents form a part of this procedure, as applicable:

(1) Center Technical Operating Procedures

(2) Center Quality Assurance Manual

(3) Operating Instructions for Siemens D-500 X-ray Diffractometer

(4) Operating Instructions for Siemens Kristalloflex 800 X-Ray Generator

(5) Joint Committee on Powder Diffraction Standards

(J.C.P.D.S.) Search Manuals

(6) Joint Committee on Powder Diffraction Standards (J.C.P.D.S.) Powder Data File

3\. Responsibility

(1) The cognizant Principal Investigator of the project shall be directly responsible for the implementation of this procedure. In cases where the Principal Investigator is not a member of the Center, the Project/Element Manager shall retain this responsibility.

(2) The Center Director of Quality Assurance is responsible for providing independent surveillance. review or audits to verify implementation of this procedure.

4\. Equipment and Supplies

Listed below are pieces of equipment and supplies that may be utilized in the preparation of powder samples and in conducting the X-ray powder diffraction analysis.

(1) Siemens D-500 X-ray diffractometer

(2) Siemens Kristalloflex 800 X-ray generator

(3) Agate mortar and pestle

(4) Glass slide or cover glass

(5) Aluminum specimen holder

(6) Wash bottle

(7) Acetone or alcohol

5\. Procedures

A. Sample Preparation and Mounting

Method A:

(1) If the sample is not already pulverized, put a few crystals

or fragments of the specimen to be analyzed in a clean agate mortar and grind with an agate pestle until all of the powdered sample passes through a 325 mesh sieve.

(2) Invert an aluminum specimen holder (Figure 1) and place it in contact with a glass slide so that its well is sealed by the glass. The glass slide may be temporarily taped onto the aluminum holder.

(3) Fill the hole with the powdered specimen by gently tapping in the powder from a spatula or from the sample container, and pressing it gently with a flat spatula blade or with another glass slide. Smooth off any excess powder with the edge of the blade or slide.

(4) A second glass slide or a thin cover glass is taped on top of the powder to cover the specimen well completely.

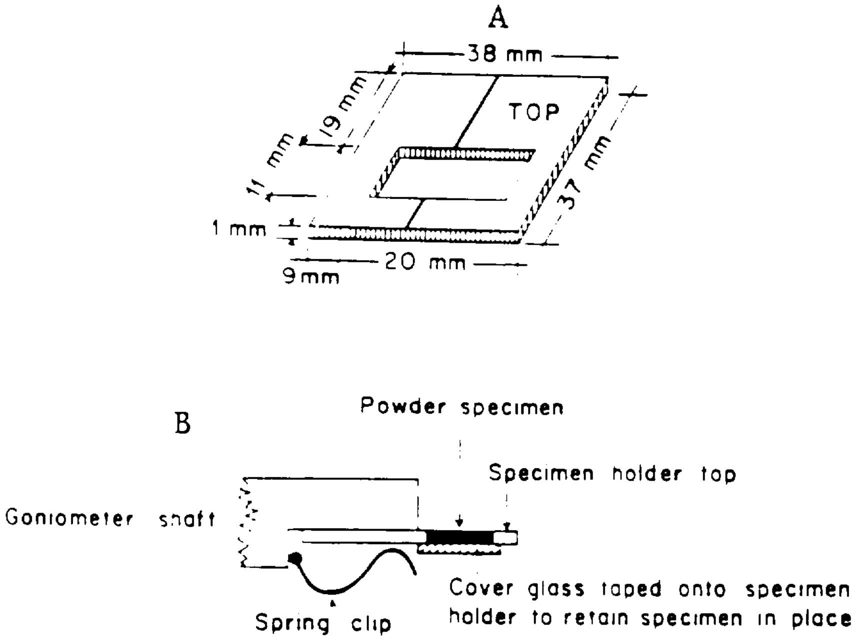

Figure 1. A - aluminum specimen holder; B - specimen mounted flat against the goniometer shaft of the diffractometer in correct position (side view). Dimensions are approximate.

(5) The specimen holder, together with the glass plates, is inverted right-side-up so that the free surface of the specimen powder is exposed on top after removal of the first glass slide from the specimen holder. If the specimen surface has retained its flat smooth surface parallel to the aluminum surface, it is ready for use. The specimen powder surface may be smoothed flat if necessary by pressing the glass slide onto it before final removal. The aluminum sample holder can be labeled with the specimen name and/or number.

Method B:

A simpler and more convenient method is to smear the fine mineral powder on a glass slide and slurry it with acetone.

(1) Prepare the specimen as in Method A, Step (1), above.

(2) Scatter a thin layer of the powder on one-half of one surface of a glass slide.

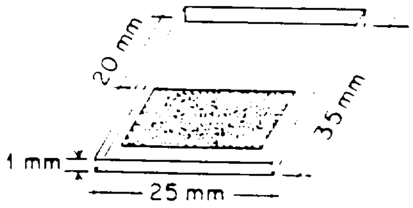

Figure 2. Mineral powder slurry on a glass slide. Dimensions are approximate.

(3) From a wash bottle add enough acetone to the powder to produce a thin slurry. The powder will smear evenly and spread. Spreading may be assisted by a spatula blade. The amount of powder and acetone added should produce a layer of approximately even thickness.

(4) Once the acetone has evaporated the powder layer will cohere. An area approximately 20 mm wide on the end of the slide surface should be wiped free of powder. The final appearance of the preparation is shown in Figure 2.

3. Running the X-ray Diffractogram

(1) Turn on the cooling water supply, the goniometer, the X-ray generator, and the detector according to the Operating Instructions. Make sure the K-beta filter appropriate to the particular type of X-ray tube is inserted, e.g. for a Cu tube, use a Ni filter.

(2) Make sure the shutter is closed. Then open the lead-glass window of the radiation protection housing.

(3) Mount the specimen on the specimen shaft of the goniometer, and firmly hold in place with the spring-loaded clip. Make sure that the space between the clip and specimen shaft is clean and free of specimen powder. Close the shield door, then open the shutter.

(4) Turn the strip chart recorder power on. Determine the optimum chart scale according to the Operating Instructions.

(5) Set the speed selector dial on the control panel to the desired rotational direction and to the most appropriate scanning rate. If a rapid record of low angular resolution for identification purposes is desired, a fast scanning rate of 1° or 2° 2-theta per minute may be selected. If, on the other hand, high 2-theta precision is desired, a slow scanning rate of $1/2^\circ$, $1/4^\circ$, or even $1/8^\circ$ 2-theta per minute may be chosen.

(6) Choose an appropriate strip chart recorder speed to suit the scanning speed of the goniometer. A slow goniometer scanning speed should always be combined with a slow recorder speed and a fast goniometer speed with a fast recorder speed. A useful goal is to achieve 2 cm per degree 2-theta (or 1 inch per degree) for moderately slow scans of 1/2° or 1/4° 2-theta per minute, so that peak centers can be accurately located with the eye. There is no virtue in having a long chart distance per degree; indeed 1 inch per degree (or 2 cm per degree) is normal practice at the U.S. Geological Survey and the Carnegie Institute in Washington for high-precision lattice parameter refinement. The following combinations give ideal diffractogram scales of 2 cm/1° 2-theta:

Goniometer speed, $^{\circ}$ 2-theta/min	1/8	1/4	1/2	1
Recorder speed, cm/min	0.25	0.5	1	2

The slowest scanning rates of 1/8° 2-theta per minute should be reserved for highest 2-theta precision determinations, whereas the fast rate of 1° per minute would be used for normal identification purposes requiring less precision. An even faster scan of 2° 2-theta per minute is possible, and this may be combined with 2 cm/min giving 1° 2-theta/cm on the diffractogram, which is perfectly adequate for rapid identification purposes.

(7) Select the appropriate time constant according to the scanning rate selected; for example, a scanning speed of 1° 2-theta per minute should normally be combined with a 2 second time constant. For slower rate of 1/2° or 1/4° 2-theta per minute a longer time constant of 4 seconds may be preferable. For a 2° 2-theta per minute rate the time constant would have to be 1 second. A longer time constant gives a smoother, more easily read diffractogram. Too short a time constant of less than 1 second will show too many random changes in the detector response; hence the diffractogram will not be smooth.

(8) Rotate the 2-theta setting of the goniometer a few degrees below the starting value required on the diffractogram, then slowly come up to the starting

2-theta value. The initial 2-theta value should be a whole number, for example, 27.00°.

(9) Advance the strip chart recorder so that the pen rests exactly on one of the chart lines.

(10) Record on the strip chart the following information:

a) Date

b) Name(s) of the operator(s)

c) Sample identification

d) Starting 2-theta value

e) Type of X-ray tube and K-beta filter used

f) Operating voltage and current

g) Time constant and chart scale

h) Scan rate

i) Other pertinent information, e.g. type of specimen holder used.

(11) Push the scan button, then the start button on the goniometer. This will start the goniometer scan and the strip chart recorder simultaneously.

(12) After having passed the desired angular range push the stop button, or let the goniometer run to the maximum 2-theta set on the instrument (determined by multiplying the values of 'step size' and 'step number' on the scan control panel). Rotate the goniometer back to the starting 2-theta value.

(13) If any of the peaks are offscale, the diffractogram may be rerun on a larger chart scale to identify their exact positions.

C. Calibration of X-ray Diffractometer Using Standard Substances

To check the calibration of a diffractometer, a diffractogram may be taken of a pure standard substance of known and highly refined structure and lacking in isomorphic substitution and lattice vibration. Pure quartz or silicon powder is the most commonly used standard, but other substances such as $KBrO_3$, high purity aluminum powder, tungsten powder, silver powder, and cadmium oxide powder may be used. Their respective diffraction lines are tabulated in the Joint Committee on Powder Diffraction Standards (J.C.P.D.S.) powder data file. The calibration will be conducted either before analyzing the unknown samples using Method A, or simultaneously with the unknown samples using Method B.

Method A:

(1) Prepare a powder specimen and make a diffractogram of pure silicon or other standard substance using procedures described above. A quartz standard provided by the instrument manufacturer may be used in lieu of a silicon powder specimen.

(2) After the X-ray diffraction scan of the standard has been completed, the recorded 2-theta positions of the 5 most intense peaks are compared with theoretical positions given in the J.C.P.D.S. powder data file. Any systematic error, either positive or negative, is noted and used to correct the 2-theta readings on any subsequent experiment, provided that the alignment of the goniometer has not been changed and the same specimen preparation technique is used for both standard and unknown.

(3) If the difference between the recorded 2-theta of the standard substance differs too much from the ideal value (e.g., by as much as 0.10° or 0.20° 2-theta), the 2-theta drum of the goniometer shall be adjusted following the Operating Instructions for the X-ray diffractometer.

(4) Both standard specimen and subsequent unknown should be run with 2-theta progressing in the same direction, both from low to high or both from high to low. The goniometer may not reproduce exactly the same angles for both directions of scan because of backlash. Preferably the unknown and standard should be scanned at the same speed as well as in the same direction.

(5) The angular error in 2-theta becomes less as 2-theta

approaches 180°; therefore any error detected in a particular 2-theta position must be used to correct only the lines in its vicinity. For example, any error found in the 2-theta position of silicon 111 peak at Cu K-alpha 28.467° 2-theta should be used subsequently to correct only the lines in this 2-theta neighborhood. Likewise, silicon peak 422 should be used for correction in the 88.124° 2-theta neighborhood. It may well be found that the errors in these two neighborhoods are not identical.

Method B:

An alternative would be to mix weighed amounts of an unknown specimen and weighed amounts of an internal standard to achieve approximately a 10:1 sample:standard ratio. The diffractogram will then contain the lines of both the standard and the unknown. Each standard line should be clearly labeled. This labeling may be facilitated by indexing the mixture by comparing it with a diffractogram of the pure standard, previouly taken and kept in the laboratory for quick reference. Any systematic error in the position of the standard line may then be used to correct the 2-theta values of neighboring lines of the unknown. The standard so mixed should have been chosen to prevent its peaks from overlapping with those of the unknown. Some of the peaks may overlap, but it is important that the peaks of particular interest be distinctly resolved from the standard peaks.

D. Identification of Specimen Mineralogy

(1) Mineralogical composition of geological samples will be identified by comparison of observed X-ray diffraction patterns to standard patterns of reference substances determined by the Center, and/or by comparison to the powder diffraction data file published by the Joint Committee on Powder Diffraction Standards (J.C.P.D.S.). The reference material diffractograms produced by the Center shall have been previously compared with the J.C.P.D.S. powder data file and the diffraction lines properly labeled with their respective hkl planes.

(2) For comparison with the J.C.P.D.S. powder data file, the 2-theta peak positions and intensities are read off the strip chart or other recording device. The 2-theta values are converted to d-spacing values using the Bragg equation:

$$d_{hkl} = \text{lambda}/(2\ \sin(\text{theta}_{hkl})$$

where d_{hkl} is the interplanar spacing between hkl planes, lambda is the wavelength of X-rays giving rise to the reflection, and theta is the angle measured from the diffractogram (=2-theta/2). If a Cu X-ray source is used, lambda equals 1.541 angstroms for K-alpha$_1$, 1.544 angstroms for K-alpha$_2$, and 1.542 angstroms for K-alpha (weighted average). If the peak is not resolved into a K-alpha$_1$ and K-alpha$_2$ doublet, lambda is taken as the value for K-alpha. If the peak is resolved into a K-alpha$_1$ and K-alpha$_2$ doublet, particularly at high 2-theta values, the 2-theta position of K-alpha$_1$ is used and converted to d_{hkl} using the value for K-alpha$_1$.

(3) The measured intensities are converted to relative intensities by

$$I_r = I/I_o$$

where I is the measured intensity, I_o is the highest measured intensity, and I_r is the relative intensity.

(4) After the experimental values of d_{hkl} and I_r are tabulated, the unknown will be identified using the Hanawalt method or the Fink method. These methods are discussed in detail in the J.C.P.D.S. Search Manuals.

Note: Every mineral and crystalline substance, whether organic or inorganic, has a unique powder diffraction pattern. Minerals and other crystalline substances of fixed chemistry which are not characterized by chemical substitution and isomorphism, such as quartz and fluorite, can be readily identified by their X-ray powder patterns because of the rather constant nature of their crystal structure. Nevertheless this should not be taken to mean that any single mineral can be identified solely on the basis of its powder pattern. Isostructural compounds may have identical diffraction patterns except for intensities; the CaF_2 pattern, for example, is nearly identical to that obtained from HoF_2. In addition many minerals have no fixed chemistry; for example, olivine, which may range from forsterite to fayalite. Each member of the olivine series has its own particular diffraction pattern, although there are certain similarities between all olivine diffractograms. Feldspars also present difficulties because of their complex structural variation.

Accordingly, for many minerals it will not always be possible to obtain a perfect match between the X-ray pattern of the unknown and one of the powder data file cards. Interpretations and judgements will be necessary and the data file should not be used blindly. Other additional data may be sought, for example, using petrographic thin section analysis or microscopic immersion methods to complement the X-ray diffraction analysis.

The analysis of mixtures of mineral components may be complex. Interpretations of such mixtures approaches an art rather than a science and requires comparison of all the lines of the mixtures with lines of each of the assumed separate phases. If the individual phases are known, then a comparison of the mixture pattern with patterns taken of individual separate phases helps a great deal. Tentative hypotheses about the components may have to be made and confirmed or rejected by identifying all the lines of each component in the mixture. To aid in identifying the mineral components of a mixture, computerized peak matching methods may be employed.

6. Identification and Storage
According to TOP-004.

7. Control of Samples
According to TOP-004.

8. Deviation from Procedures
According to TOP-004.

9. Records
According to TOP-004 or Item 5.B.10 above.

10. References

Hutchison C.S. (1974) Laboratory Handbook of Petrographic Techniques, John Wiley, New York, p.132-179.

Cullity B.D. (1978) Elements of X-ray Diffraction, Addison-Wesley, Reading, Massachusetts, 555p.

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CENTER FOR NUCLEAR WASTE REGULATORY ANALYSES **TECHNICAL OPERATING PROCEDURE**	Proc. TOP-005 Revision 0 Page 1 of 9

Title

PROCEDURE FOR ZEOLITE ION EXCHANGE EXPERIMENTS

EFFECTIVITY AND APPROVAL

Revision 0 of this procedure became effective on August 21, 1989. This procedure consists of the pages and changes listed below.

Page No.	Change	Date Effective
ALL	-	8/21/89

UNCONTROLLED

Supersedes Procedure No. None

Approvals

Written By R T Pabalan	Date 8/17/89	Technical Review John L Russell	Date 8/17/89
Quality Assurance	Date 8/18/89	Cognizant Director Wesley Patrick	Date 8/21/89

CNWRA Form TOP-1

PROCEDURE FOR ZEOLITE ION EXCHANGE EXPERIMENTS

1. Purpose

The purpose of this procedure is to describe the methods, equipment and supplies to be used in conducting ion exchange experiments with zeolites.

2. Scope and Application

This procedure describes the techniques, equipment and supplies which may be utilized in performing zeolite ion exchange experiments. The experiments are designed to help understand the distribution of ions between a zeolite phase and an aqueous solution as a function of certain parameters. These parameters may include zeolite structure and composition, aqueous solution composition and ionic strength, temperature, time and other variables. The zeolite material to be used in this procedure shall be characterized using X-ray diffraction, scanning electron microscopy, energy dispersive spectrometry, transmitted light microscopy, wet chemical analysis, or some other appropriate methods.

2.1 Applicable Documents

The following documents form a part of this procedure, as applicable:

(1) Center Technical Operating Procedures
(2) Center Quality Assurance Manual
(3) U.S. Environmental Protection Agency "Test Methods for Evaluating Solid Waste"
(4) U.S. Environmental Protection Agency "Test Methods for Chemical Analysis of Water and Wastes"

3. Responsibility

(1) The cognizant principal investigator of the project shall be directly responsible for the implementation of this procedure. In cases where the principal investigator is not a member of the CNWRA, the Project/Element Manager shall retain this responsibility.
(2) The Center Director of Quality Assurance is responsible for providing independent surveillance, review or audits to verify implementation of this procedure.

4. Equipment and Supplies

Listed below are pieces of equipment and supplies that may be utilized in the preparation of zeolite materials and in the conduct of the experiment:

(1) Constant temperature water bath
(2) Convection oven
(3) Grinder/mixer
(4) Sieve shaker
(5) Analytical balance
(6) Ultrasonic cleaner
(7) Centrifuge
(8) Vacuum dessicator
(9) Mortar and pestle
(10) Stainless steel sieves
(11) Thermometer
(12) Polyethylene bottles
(13) Volumetric flask, beaker, and other necessary glassware
(14) Reagent grade NaCl, $AgNO_3$, $BaCl_2$ and other chemicals
(15) and other necessary equipment and supplies.

5. Procedures

5.1 Purification of zeolite material

(1) If the zeolite material is not already pulverized, then lightly crush and gently grind the sample to pass a 35-mesh (500 microns) sieve.

(2) Using the stainless steel sieves with either the automatic sieve shaker or by manual hand-sieving, divide the zeolite powder into four size ranges: 35-100 mesh (500-150 microns), 100-200 mesh (150-75 microns), 200-450 mesh (75-32 microns), and <450 mesh (<32 microns). Other size ranges may be used when appropriate.

(3) If the presence of soluble chloride and sulfate salts were indicated by previous characterization work, repeatedly reflux the material to be used in the experiments with deionized water in an erlenmeyer flask (about 400 ml of water per 50 g of sample) for about 5 minutes to remove soluble salts. Decant approximately 50 ml portions of the washing into two beakers and discard the remaining portion. Test for the presence of dissolved Cl^- by adding a few drops of 0.1 M $AgNO_3$ solution to one beaker. The presence of Cl^- in solution is indicated by turbidity due to the formation

of colloidal AgCl. Test for the presence of SO_4^{2-} by adding a few drops of 0.1 M $BaCl_2$ solution to the other beaker. The presence of dissolved SO_4^{2-} is indicated by turbidity due to the formation of colloidal $BaSO_4$. Repeat this procedure until no Cl^- and SO_4^{2-} is detected.

(4) If calcite or other carbonate minerals appear to be present based on previous characterization work, then add to the sample 1 M NaOAc buffer of pH 5 (prepared using 82 g of sodium acetate and 27 ml of glacial acetic acid per liter of solution, and adjusted to pH 5) and digest the mixture in a near-boiling water bath for about 30 minutes with intermittent stirring. Use approximately 400 ml of solution per 50 g of zeolite. Dissolution of the carbonate mineral is evidenced by evolution of CO_2 gas bubbles. Apply two additional washings with the 1 M NaOAc buffer. Repeat this procedure if necessary until no CO_2 gas evolution is evident. Then rinse ten times with deionized water using about 400 ml of water per 50 g of zeolite.

(5) If necessary, other mineral separation methods may be employed to remove impurities, such as density separation using heavy liquids, magnetic separation, or dissolution of organic matter and Mn and Fe oxides.

(6) Remove fine particles clinging to the zeolite surfaces by immersing the sample flask (containing about 400 ml of deionized water per 50 g of zeolite) in an ultrasonic bath for about 3 minutes. Decant and repeat at least five times.

5.2 Preparation of Homoionic Zeolites

(1) To prepare homoionic Na-zeolites, equilibrate approximately 50 g of the zeolite material prepared above with about 400 ml aliquots of 1 m sodium chloride solution in a 500 ml polyethylene bottle immersed in a constant temperature shaker bath. Do this 5 times at 25°C and 2 times at 70°C, each equilibration lasting about one day.

(2) Wash the sample thoroughly with deionized water until no Cl^- can be detected with 0.1 M $AgNO_3$ solution. Then equilibrate with 400 ml deionized water for about two days at 25°C in the shaker bath, decant and test the water for Cl^-. Repeat this last step if necessary until no Cl^- is detected, then dry overnight at approximately 80°C. Equilibrate the dry sample with water vapor over saturated sodium chloride solution in a dessicator at room temperature for at least one week to ensure an equilibrium uptake of

water into the zeolite. The mass of the zeolite may be weighed periodically to monitor its uptake of water.

(3) Characterize the zeolite material using X-ray diffraction, scanning electron microscopy, and/or other appropriate techniques.

(4) Determine the chemical composition of the zeolite using wet chemical, spectroscopic and/or other appropriate methods.

(5) To prepare other homoionic forms of the zeolite (e.g. Cs-zeolite, Ca-zeolite), follow the same procedures given in steps (1) to (4) using the chloride salt of the cation of interest.

(6) When appropriate, metal salts other than chloride forms (e.g., metal nitrate, metal sulfate) may be used in the preparation of homoionic zeolites. If other than chloride forms are used, the detection method given in step (2) shall be modified accordingly.

5.3 Preparation of Binary Isotherm Solutions

(1) Only reagent grade chemicals shall be used in preparing solutions for ion exchange experiments.

(2) Mixtures containing different ratios of the two competing cations of interest, but at a constant total normality or at a constant ionic strength, are prepared by dissolving the required weights of the two salts in deionized water.

(3) The solutions prepared above are stored in polyethylene bottles previously washed with 4% nitric acid for at least 24 hours and rinsed at least ten times with deionized water.

(4) The pH values of these stock solutions are measured after preparation, and are monitored on a periodic basis until the completion of the ion exchange experiments. Their compositions may be analyzed together with the experimental solutions at the conclusion of each experiment.

5.4 Kinetic Experiments

(1) To demonstrate that the isotherms obtained from the ion exchange experiments represent equilibrium conditions, kinetic experiments are to be performed. A salt solution of the competing cation and of known concentration is equilibrated with the initially homoionic zeolite. Samples of the solution are withdrawn at intervals, centrifuged and analyzed for its cation composition by flame photometry, atomic absorption spectrometry, or other appropriate methods. When appropriate, ion selective electrodes may

also be utilized to monitor the changes in the isotherm solutions as well as in reference solutions.

(2) Equilibrium will also be demonstrated by procedures described in Section 5.6.

5.5 Ion Exchange Experiments

All equilibria are measured with solutions of known constant normality or constant ionic strength. The temperature is kept constant and the solutions agitated by using a constant temperature shaker bath. 1.0 g of the homoionic zeolite is equilibrated in capped 60 ml polyethylene bottles with known volumes of the solutions containing known proportions of the competing ions. The amount of zeolite and the ratio of zeolite to solution may be varied when necessary, e.g., in order to obtain points at the isotherm extrema. The experiments are run for at least 5 days or longer, depending on the results of the kinetic experiments. After equilibration the phases are separated by centrifugation and/or filtration. The resulting solution phases, as well as the corresponding original isotherm solutions, are analyzed for their cation compositions by flame photometry, atomic absorption spectrometry, ion chromatography, or some other appropriate method. The solution pH's may also be measured using a glass pH electrode. The solid phases are washed (briefly) three times with about 100 ml of deionized water and analyzed for their composition using a suitable method of sample digestion and analysis. The solid phases may also be analyzed using X-ray diffraction analysis, scanning electron microscopy, or other suitable methods.

5.6 Reversibility

Method A:

In order to establish reversibility of the exchange isotherms the following method may be employed. Samples of the zeolite are equilibrated with solutions to obtain forward isotherm points as discussed in Section 5.5. After equilibration, the suspensions are centrifuged and exactly 25 ml of solution are removed for chemical analysis. This gives the forward isotherm point. Then to the remaining zeolite and solution is added a known volume of another solution of equal total normality or equal ionic strength but having a larger proportion of the ion originally present in the zeolite. The resulting solution is re-equilibrated, centrifuged, and analyzed. These data, together with a forward isotherm to the latter point, enables reverse isotherm points to be calculated.

Method B:
An alternate and conventionally used method may be used. For an exchange reaction involving A^+ in the zeolite phase and B^+ in solution, forward isotherm points are determined by equilibrating homoionic A-zeolite with solutions of known A^+/B^+ ratios, as discussed in Section 5.5. The reverse isotherm points are determined by equilibrating homoionic B-zeolite with solutions of known B^+/A^+ ratios, in manner discussed in Section 5.5.
This alternate method, however, may result in consistently higher values of zeolite A^+/B^+ ratio for the reverse isotherms than for the forward isotherm points. This effect has been suggested by Barrer and Townsend (1976) to be due to a redistribution of ions having occurred at the drying stage during the preparation of the metal-exchanged zeolites. They suggested that drying of the zeolites enables the cations to enter crystallographic sites which are not normally accessible to the hydrated species at ambient temperatures. Thus Townsend and coworkers recommended against using this method. However, other investigators, particularly L.L. Ames (1964a,b), appears to have used this method successfully.

6. Identification and Storage

(1) The zeolite samples will be stored in canvas bags, plastic jars/bags, glass jars, or other suitable containers.
(2) Reagent chemicals in their respective containers will be kept in appropriate storage cabinets.
(3) Identification numbers or labels shall be marked on the containers of zeolite samples and experimental solutions.

7. Control of Samples

Experimental samples under the control of the Center shall be kept in a cabinet if not being utilized in the project or being analyzed. The cabinet in which these samples are stored shall be locked during non-business hours. Only the Principal Investigator, his Project/Element Manager, or their designee will have key or codes to the storage cabinet.

8. Modification of the Procedures

Although Center Technical Operating Procedures and other Center-prescribed procedures will be utilized, modification of established and controlled procedures may be necessary to successfully complete the experiment. In such cases, no Deviation and Nonconformance Report (DNR) is required. Instead, the description of the procedure modification will be properly recorded in the laboratory notebook, from which the final report is written.

9. Records

9.1 The laboratory notebook or other device used to record the results of the experiment shall contain the following information:
- (1) Date of activity
- (2) Full name, initials or assigned stamp of individual(s) performing the work
- (3) Description of work to be performed, e.g., preparation of isotherm solutions
- (4) Equipment and/or materials to be used
- (5) Methods or procedures used, including any modification of established procedures
- (6) Results.

9.2 Further guidance is available from Center Quality Assurance Procedure-001, Scientific and Laboratory Notebooks.

10. References

Ames L.L. Jr. (1964a) Some zeolite equilibria with alkali metal cations, American Mineralogist, v.49, 127-145.

Ames L.L. Jr. (1964b) Some zeolite equilibria with alkaline earth metal cations, American Mineralogist, v.49, 1099-1110.

Barrer R.M. and Townsend R.P. (1976) Transition metal ion exchange in zeolites, Part 1. - Thermodynamics of exchange of hydrated Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} ions in ammonium mordenite, J. Chem. Soc. Faraday Trans. 1, v.72, 661-673.

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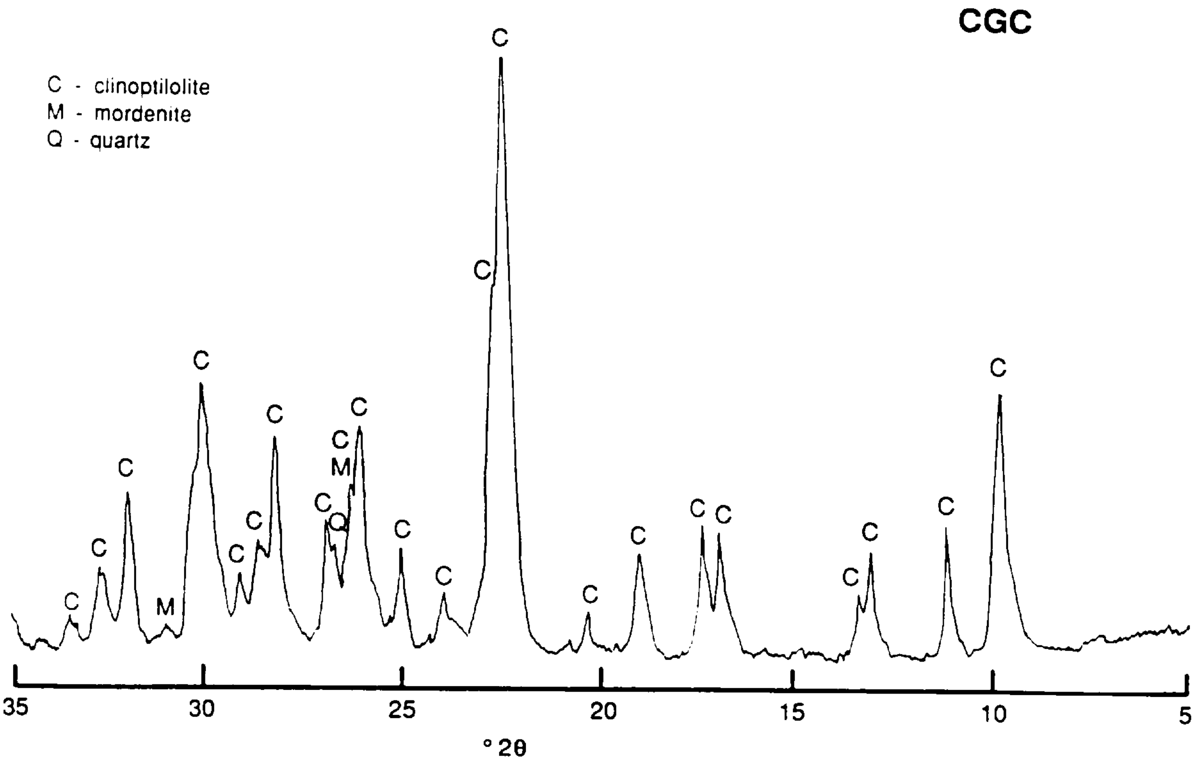
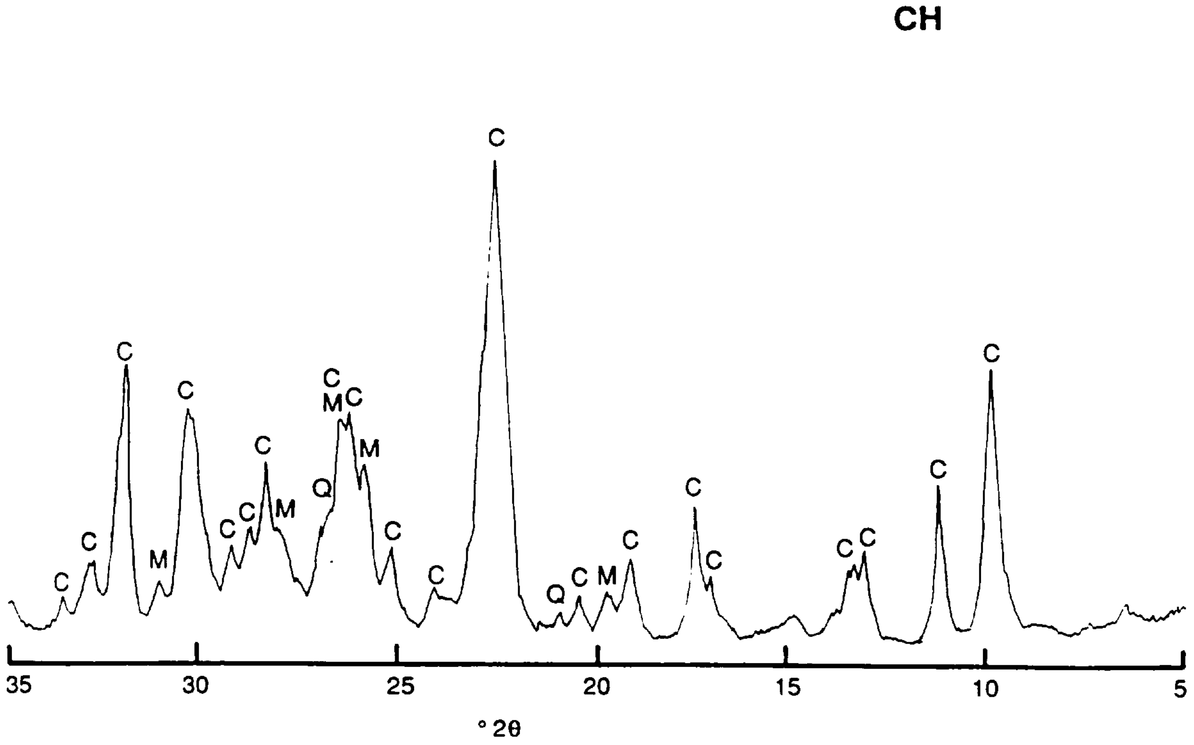
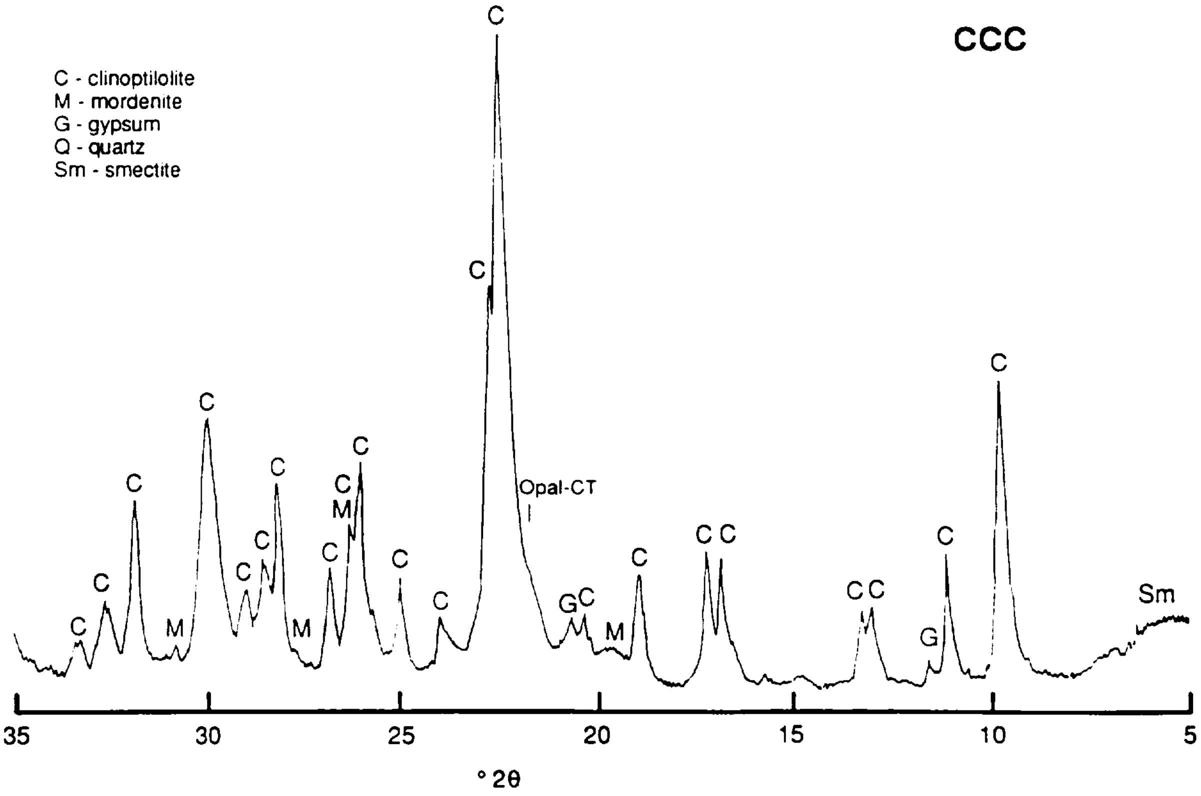
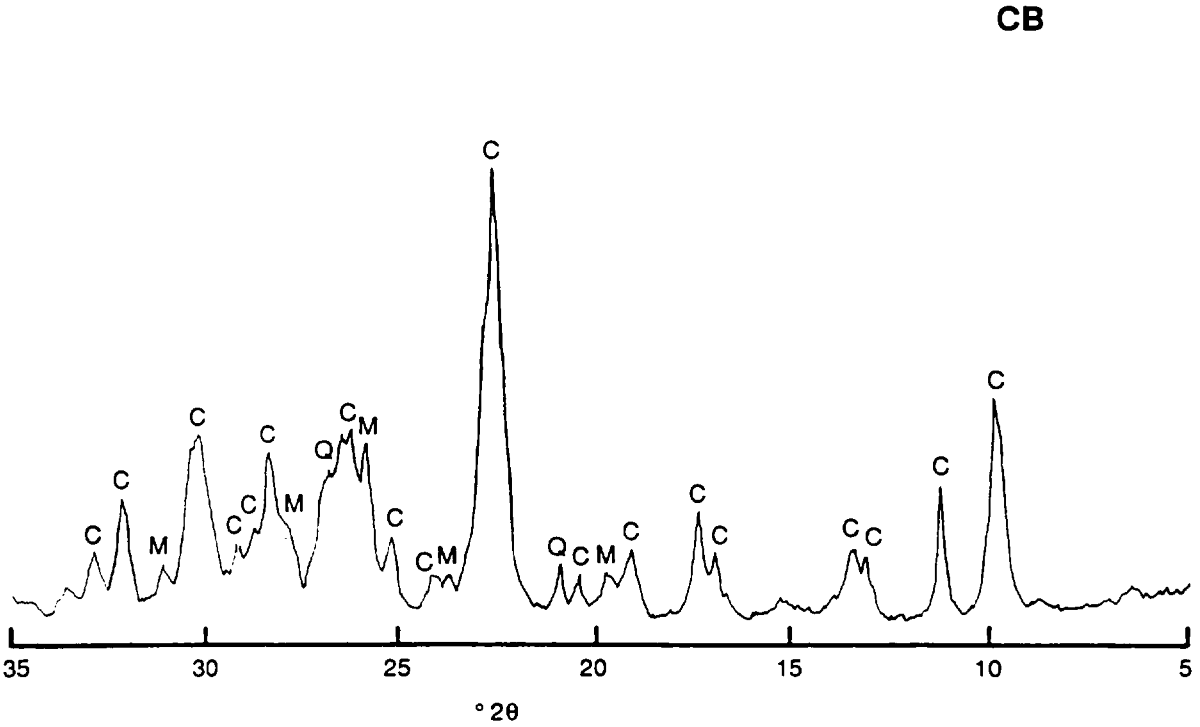
APPENDIX 2.

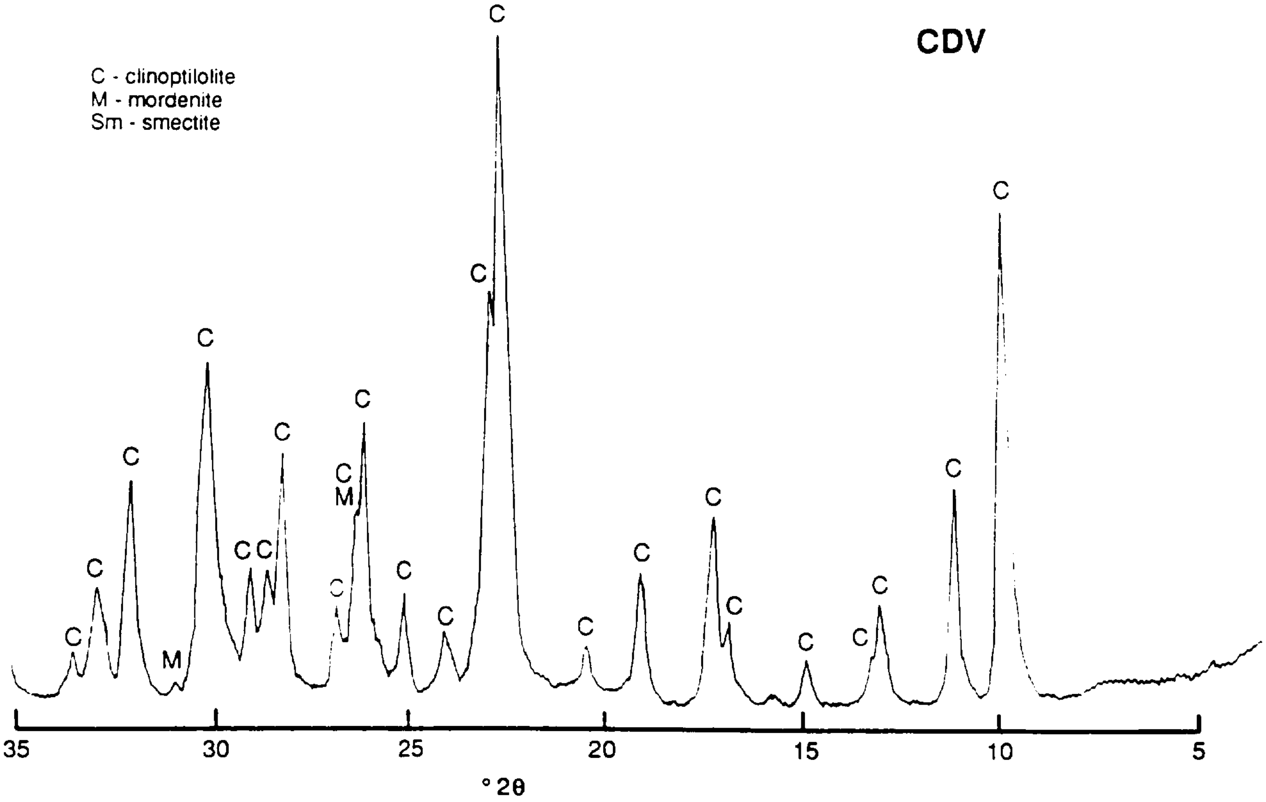
X-RAY DIFFRACTION PATTERNS OF AN ANALCIME SAMPLE FROM MT. ST. HILAIRE, QUEBEC (ASH), AND CLINOPTILOLITE SAMPLES FROM HECTOR, CALIFORNIA (CH); BUCKHORN, GRANT COUNTY, NEW MEXICO (CGC); BARSTOW, CALIFORNIA (CB); DEATH VALLEY JUNCTION, CALIFORNIA (CDV); CASTLE CREEK, IDAHO (CCC); AND TILDEN, TEXAS (CT).

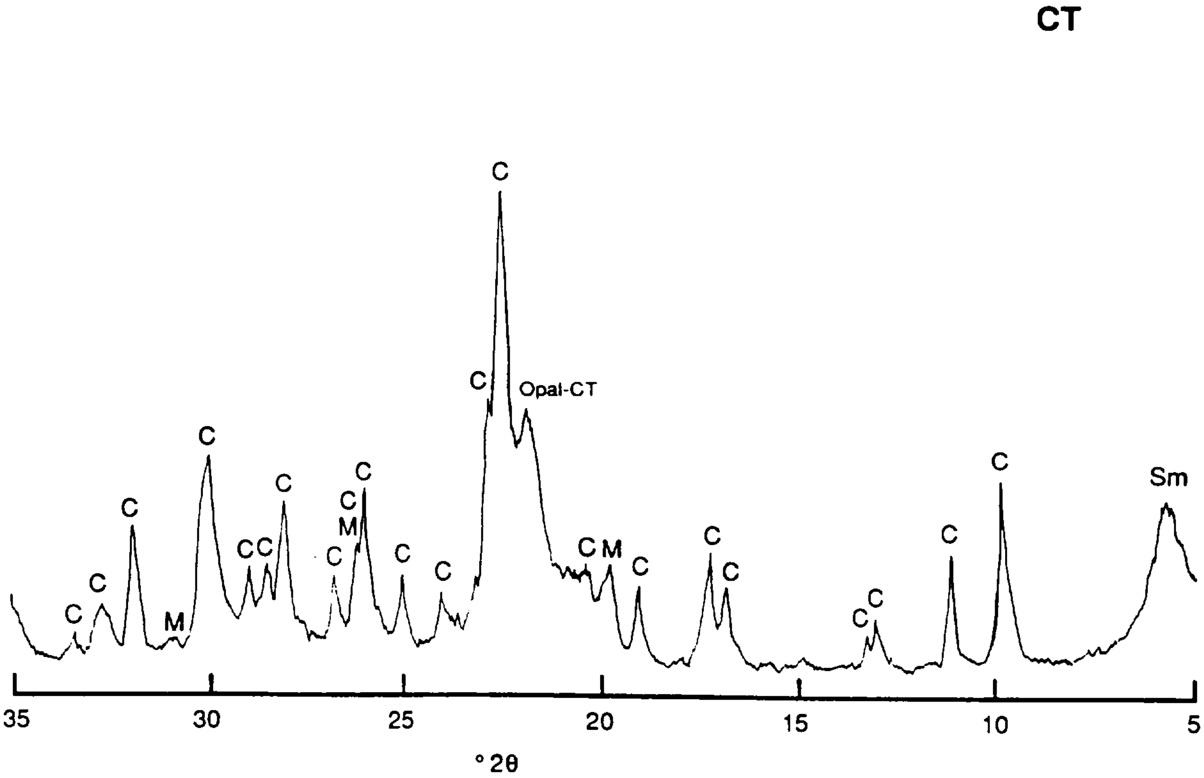

CGC
C - clinoptilolite
M - mordenite
Q - quartz
C
C
C
C
C
C
C
C
C
M
C
Q
C
C
C
C
C
C
C
C
C
C
M
C
35
30
25
20
15
10
5
° 2θ

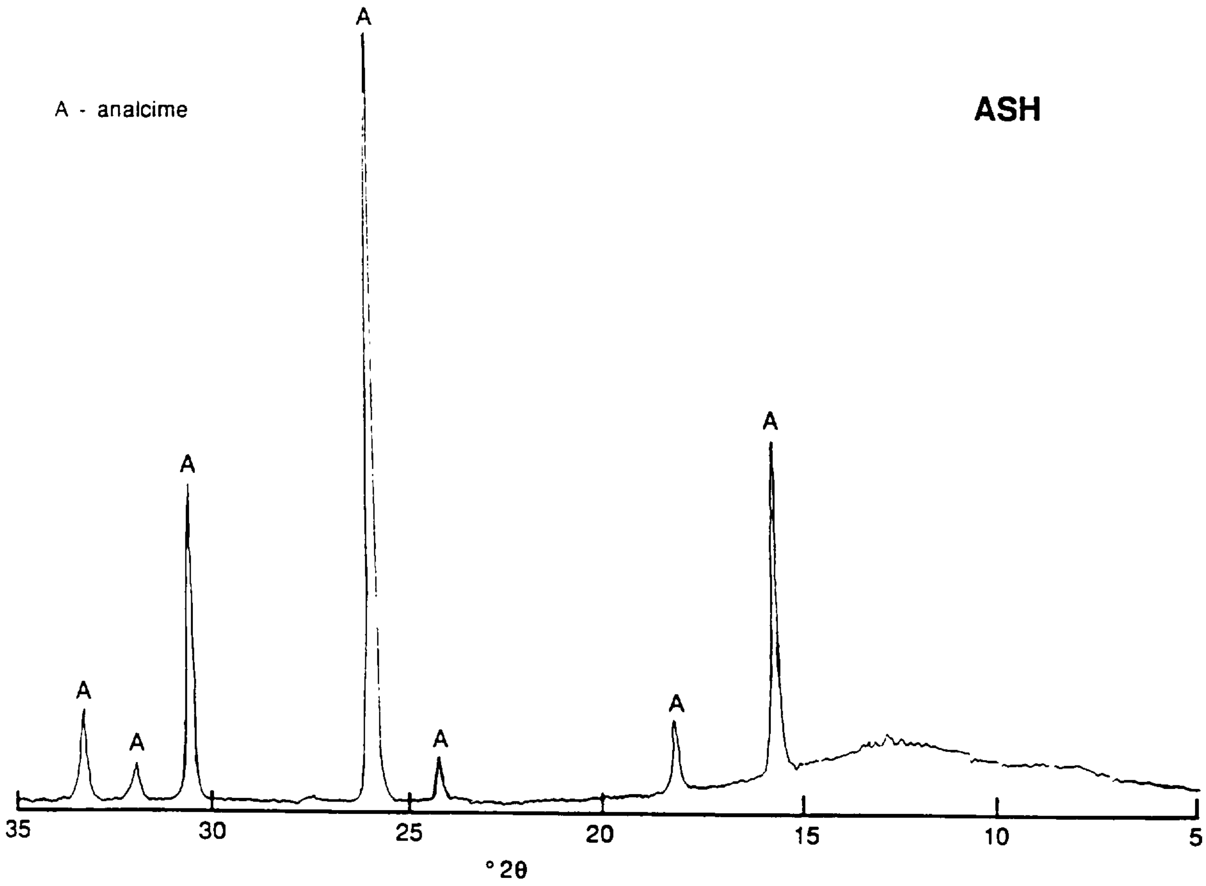

CH
C
C
C
C
C
M
C
M
C
M
Q
C
C
C
C
C
C
M
C
Q
C
M
C
C
C
C
35
30
25
20
15
10
5
° 2θ


CCC
C - clinoptilolite
M - mordenite
G - gypsum
Q - quartz
Sm - smectite
C
C
C
C
C
C
C
C
M
C
C
C
C
M
M
C
Opal-CT
G
C
M
C
C C
C C
C
G
Sm
35
30
25
20
15
10
5
° 2θ


CB
C
C
C
C
C
C
Q
C
M
M
C
C
M
C
M
Q
C
M
C
C
C
C C
C
C
35
30
25
20
15
10
5
° 2θ


CDV
C - clinoptilolite
M - mordenite
Sm - smectite
C
C
C
M
C
C
C C
C
C
C
M
C
C
C
C
C
C
C
C
C
C
C
C
35
30
25
20
15
10
5
° 2θ


CT
C
C
Opal-CT
C
C
C
C
C
M
C C
C
C
C
M
C
C M
C
C
C
C
C
C
C
Sm
35
30
25
20
15
10
5
° 2θ


A - analcime
ASH
A
A
A
A
A
A
A
A
35
30
25
20
15
10
5
° 2θ

APPENDIX 3.

PETROGRAPHIC ANALYSES OF CLINOPTILOLITE SAMPLES.

SAMPLE NAME: CH

LOCALITY: Hector, California

TYPE OF ROCK: Quartz Latite or Dacite Tuff

MATRIX: 85-90%
Zeolitized glass with some relict shards (0-40%)
Non-descript opaque (10-20%)

GRAINS:
Phenocrysts:
Quartz and feldspars 10-15%
Biotite 1-2%
Clinopyroxene trace

TEXTURE:

Poorly welded, very fine grained - largest are 75 microns.

Graded laminations, exhibiting symmetric grading from one lamination which is entirely without relict shards or phenocrysts.

ALTERATION/MINERALIZATION:

All glass has altered to zeolites.

Veins of non-descript opaque, same mineral has also replaced some of the shards. This opaque mineral may be ultra-fine clinoptilolite or else, an amorphous clay.

DEPOSITIONAL ORIGIN:

Fallout tuff or possibly, surge deposit

SAMPLE NAME: CGC

LOCALITY: Buckhorn, Grant County, New Mexico

TYPE OF ROCK: Quartz Latite or Dacite Tuff

MATRIX: 90%
Zeolitized glass shards (70-90%)
Some round bubble shards
Brownish opaque around shards

GRAINS: 10%
Phenocrysts:
Quartz 1-2%
Feldspars 5-8%
Biotite 1-2%
Clinopyroxene 2%
Hornblende trace
Magnetite or ilmenite trace

Lithoclasts:
A few glassy lithic fragments with plagioclase microlites
Some detrital iron-titanium oxide

TEXTURE:

Poorly welded, no compaction or deformation of shards and very little glassy matrix around shards.

Phenocryst fragments are very fine grained about 100 microns in size. Relict shards are slightly larger at about 200 microns in length.

Abundant shards; many plucked from thin-section, rest are bordered with a high birefringent mineral (possibly sericite), and rimmed and replaced with zeolites.

Clinoptilolite appears better crystallized than in other samples.

ALTERATION/MINERALIZATION:

Many of the plagioclase phenocrysts are altered to sericite.

Some of the magnetite is altered to hematite.

Many of relict shards appear to be rimmed; perhaps the shards were dissolved out and then infilled with zeolites. Many of the shard borders are outlined with a high birefringent mineral, possibly sericite although the XRD analysis only indicates 1-2% illite and mica.

Grungy brown opaque could be an amorphous clay (it does not have the high birefringence or relief of leucoxene/sphene).

DEPOSITIONAL ORIGIN:

Fallout tuff

SAMPLE NAME: CB

LOCALITY: Barstow, California

TYPE OF ROCK: Quartz Latite or Dacite Tuff

MATRIX: 75-85%
Zeolitized glass with relict shards (30-60%)
Dendritic Manganese-iron oxide (goethite?)
Many round bubble shards

GRAINS: 15-25%
Phenocrysts:
Quartz and feldspars
Biotite 4%
Hornblende 1%

TEXTURE:
Thinly laminated, one lamination of coarser grains, both quartz and relict shards up to 300 microns.
Average grain size about 100 microns.
Poorly welded, some uncompacted relict shards visible especially in the coarser lamination.
Dendritic manganese-iron oxide extends from the coarser lamination.

ALTERATION/MINERALIZATION:
All glass has altered to zeolites.
Rare detrital ferromagnesian mineral (pyroxene or amphibole) is altered to hematite.
Some plagioclase phenocrysts altered to sericite.
Bubble shards are partially infilled with a brownish-green clay (possibly smectite?),

DEPOSITIONAL ORIGIN:
Fallout tuff

SAMPLE NAME: CDV

LOCALITY: Death Valley Junction, California

TYPE OF ROCK: Quartz Latite or Dacite Tuff

MATRIX: 95%
    Zeolitized glass shards (70%)

GRAINS: 5%
    Phenocrysts:
        Quartz Tr
        Plagioclase 2%
        K-feldspar (sanidine) Tr
        Biotite Tr
        Hornblende Tr
    Lithoclasts: 1%
        A few devitrified volcanic fragments (possibly from another tuff)
        pumice - one with biotite, 1 mm long bone fragments
        one sandstone fragment

TEXTURE:

Poorly welded, well-preserved shard texture.
Many bubble shards.
Average shard size is about 250 microns.
Subhedral to rounded and abraded feldspar phenocrysts (about 1 mm in size). Other (hornblende) phenocrysts are euhedral to subhedral and average 100 microns in size.

ALTERATION/MINERALIZATION:

The glassy groundmass is altered to zeolites. Zeolites also replaced the hydrated rinds of the shards. In many of the shards, the remaining glass was dissolved out and the void partially infilled with internal rims of large (30 microns) euhedral clinoptilolite crystals. There are a few glass shards left in the sample but many of the (also still glass ?) shards are plucked from the slide. (The presence of glass shards could account for 5% amorphous content in the XRD analysis.

Patches of bladed to dendritic iron oxide (goethite) are present and may be spatially associated with the more mafic xenoliths or xenocrysts.

A trace amount of smectite or chlorite-smectite is present in some lithic fragments as a replacement of a mafic mineral, possibly a pyroxene. This replacement probably occurred before deposition of the ash flow tuff because the hornblende phenocrysts in the sample are complete unaltered.

This sample is very porous. The porosity is both primary (in bubbles) and secondary (a result of dissolution of glass shards).

DEPOSITIONAL ORIGIN:

Fallout tuff

SAMPLE NAME: CT

LOCALITY: Tilden, Texas

TYPE OF ROCK: Quartz Latite or Dacite Tuff

MATRIX: 95%
Glass altered to a mixture of zeolites, smectite, and opal-CT.

GRAINS: 5%
Phenocrysts:
Quartz and feldspars 3%
Biotite 2%

TEXTURE:

Poorly welded with little to no recognizable shard texture (may be obscured by zeolites and clays).

Very fine-grained phenocrysts; average size of the biotite grains is about 30 microns, a couple are up to 100 microns in length.

ALTERATION/MINERALIZATION:

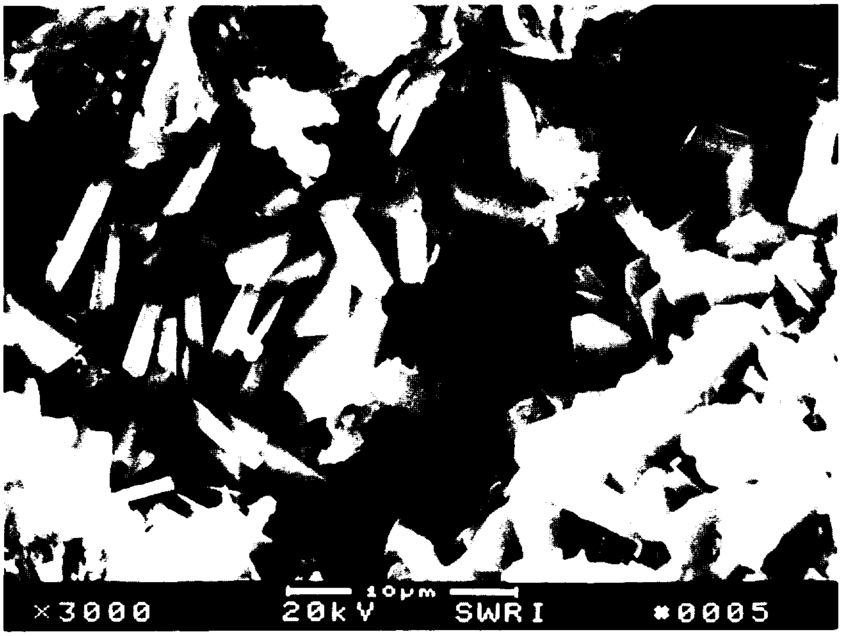
Smectite and clinoptilolite almost completely obscure the very fine phenocrysts, hence the phenocryst content listed above may be an underestimate. There are some rounded to elongate clumps of opal (up to a millimeter in size) without smectite which may have been larger shards in the generally shard-poor ash flow tuff. The fine ash groundmass is completely altered to clinoptilolite, smectite and iron oxides.

DEPOSITIONAL ORIGIN:

Fallout tuff

APPENDIX 4.

SCANNING ELECTRON MICROSCOPE IMAGES OF CLINOPTILOLITE FROM HECTOR, CALIFORNIA (CH) AND DEATH VALLEY JUNCTION, CALIFORNIA (CDV).



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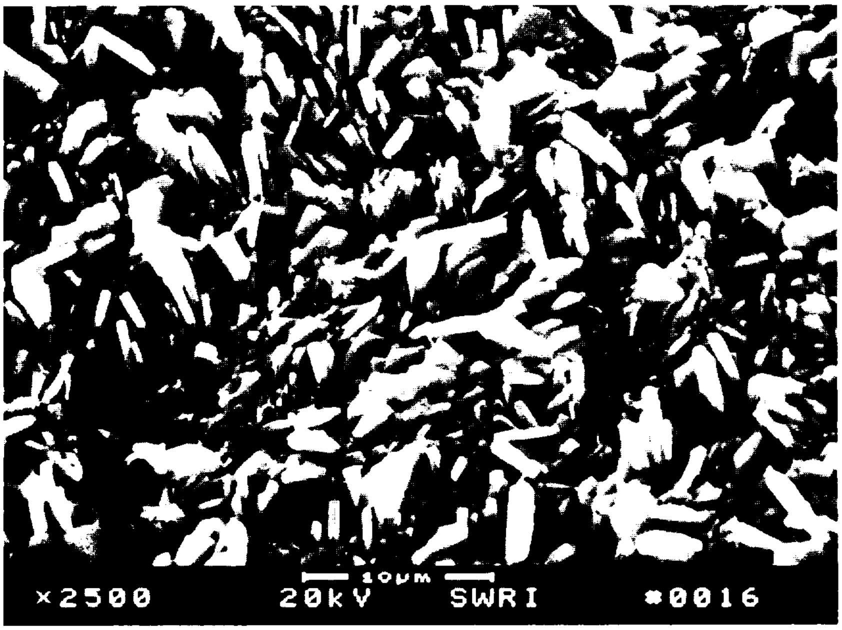
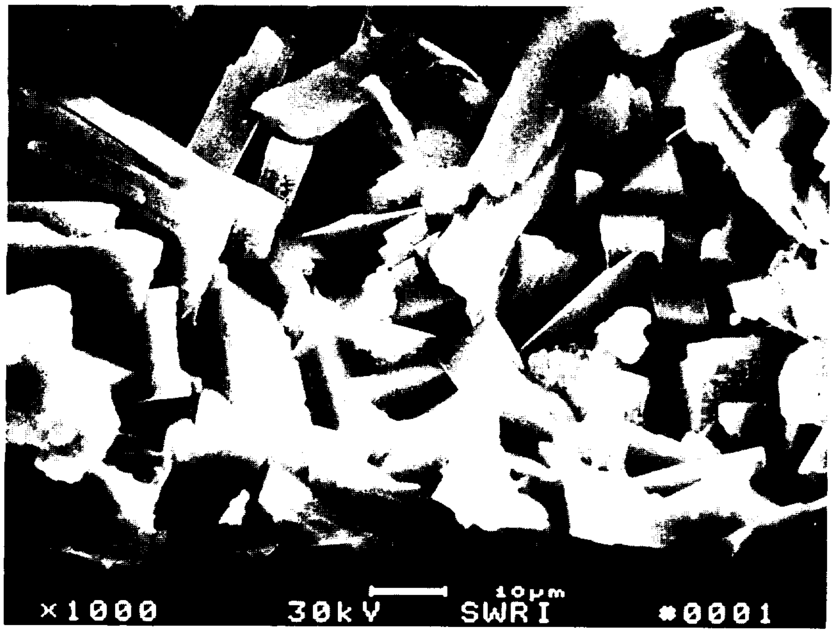
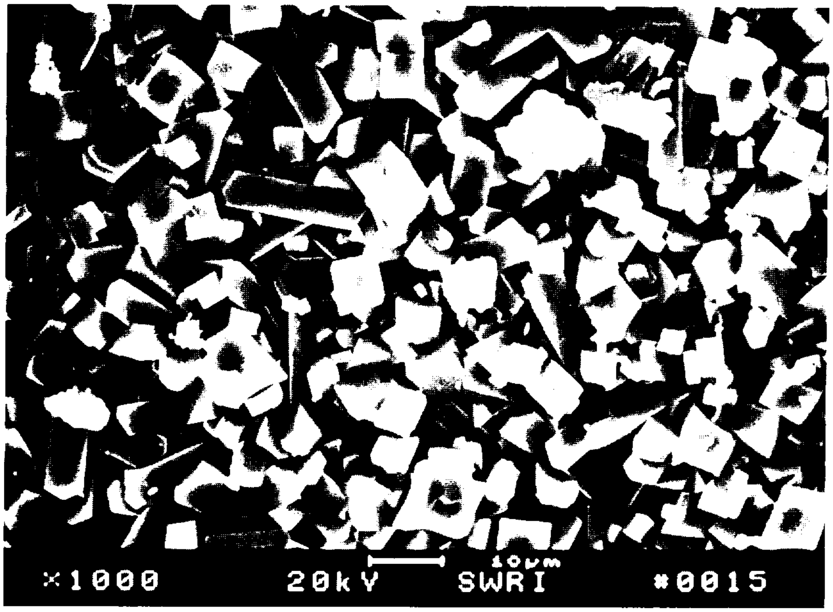


CH



CDV



CDV