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# Evaluation of Clays and Clay Minerals for Application to Repository Sealing

## Technical Report

July 1983

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of

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Material Research Laboratory  
The Pennsylvania State University

prepared for

Office of Nuclear Waste Isolation  
Battelle Memorial Institute  
Columbus, OH 43201

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BATTELLE Project Management Division

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## PREFACE

This report has been prepared by combining reports submitted independently to the Office of Nuclear Waste Isolation by D'Appolonia Consulting Engineers, Inc. (D'Appolonia) and the Materials Research Laboratory at The Pennsylvania State University (MRL). Contributors include W. E. Coons, P. C. Kelsall, and D. Meyer of D'Appolonia and J. J. Howard and D. M. Roy of MRL. The combined report has been edited by D. Meyer of D'Appolonia and J. J. Howard of MRL, and reflects the opinions of both. Final compilation was made by D'Appolonia.

## ABSTRACT

Clays (i.e. fine-grained, earthen mixtures containing a substantial proportion of clay minerals) are promising candidate materials for use in sealing nuclear waste repositories. Clay seals can be constructed with internal hydraulic conductivities lower than  $10^{-9}$  cm/sec, approaching conductivities of candidate repository host rocks. Other favorable properties of clays include high sorptivity, high compressibility, and in some cases, high swelling capacity. Although not all clay stability issues are resolved, the potential of clays and clay minerals for long-term sealing is inferred from their geologic persistence, their low solubility in repository-like environments and their slow reaction kinetics. Moreover, expectations of long-term seal performance can be enhanced by prudent selection of clay mineralogy, clay content, moisture content, and emplacement technique. Techniques for emplacing clay-rich barriers include in-place compaction, emplacement in precompacted form, and slurry injection. Technologies for most of these techniques already exist.

The sorptivity of clays with respect to radionuclides may be closely related to the cation exchange capacity of the constituent clay minerals. The sorptive capacity of a material may be gauged also by reference to a sorption coefficient (Kd). Laboratory studies have shown clays to be efficient sorbers of selected radionuclides although performance depends on radionuclide concentration, temperature, Eh, pH, fluid composition, and clay mineralogy.

Outstanding issues exist for all of the performance areas identified above, and are considered to be high priority research items within the sealing program. Issues include: 1) thermodynamic properties of clays, and their thermal stabilities and phase transformations, bearing on longevity; 2) seal-rock interface permeability, and permeability at extended times and elevated temperatures, bearing on performance of clay as a barrier to ground water movement; 3) sorptivity under realistic repository conditions, bearing on performance as a chemical barrier.

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## EXECUTIVE SUMMARY

Clays are candidate materials for use in sealing or backfilling penetrations such as shafts, tunnels, and boreholes associated with mined nuclear waste repositories. Clays may be used to achieve low permeability barriers to fluid flow, or to provide media capable of limiting radionuclide migration chemically by sorption of dissolved species. As used in this report, "clay" refers to any fine-grained, earthen, generally plastic material containing a substantial proportion of clay minerals. Candidate clay seal materials include processed soils, shale, and bentonite as well as synthetic mixtures of clays and other minerals, and individual clay minerals; i.e., any of a group of granular materials in which the clay minerals control the physical behavior of the material.

The specific application of clays as either fluid flow or chemical barriers depends in part on the properties of the clay mineral to be used. These properties, in turn, are related to the mineralogic structure of the clay mineral. Among the major clay mineral groups are kaolinites, illites, and smectites. The minerals in the various groups share structural and behavioral characteristics. For example, smectites, which include the mineral montmorillonite, have the most significant swelling capabilities. Consequently, smectites and bentonite, which is a natural material usually containing large proportions of smectite, are considered good candidates for constructing fluid flow barriers.

#### Permeability and Mechanical Properties

Low permeability is achieved in clays by increasing compaction (decreasing void ratio), and/or by increasing the clay mineral content. Smectite is particularly effective in reducing the permeability of granular materials, partly because of its fine grained mineral habit which enables it to fill pore spaces, and partly because of its tendency to swell into void spaces upon contact with water.

Permeability is also affected by the intrinsic water content of the clay and by the emplacement and compaction methods employed to establish the barrier. These relationships arise because both the initial water content and the engineering or construction techniques affect the density of the emplaced body and its fabric. Fabric is important because it may impart tortuosity to the water flow path or otherwise affect internal permeability. For example, the breakdown of flocculated fabrics increases the disorder among the clay particles and tends to decrease permeability. In contrast, barriers in which clay mineral platelets are aligned may develop preferential water flow paths and be somewhat more permeable in directions parallel to the crystallographic alignments. Depending on factors such as these, hydraulic conductivities may be as low as  $10^{-8}$  cm/sec in kaolinites, as low as  $10^{-9}$  cm/sec in illites, and as low as  $10^{-12}$  cm/sec in smectites.

The plastic behavior of a material under stress may be significant in preventing fracture development and subsequent failure of the fluid flow barrier. Plasticity in a granular material increases with the clay mineral content, and is greatest for materials containing smectite clays. Water content is also a major control on the response of a clay material to stress by a degree dependent on clay mineral content and species.

Shear strength of a granular material may also be significant in assessing the ability of the material to resist fracturing under stress. Clay mineral type is a major control on shear strength; for example, a granular material containing illite or kaolinite will display greater shear strength than a material containing an equivalent smectite component. Shear strength is also affected by clay mineral content, stress history, temperature, confining pressure, cementation, and fabric.

Shrinkage and swelling may be significant to clay seal permeability. Shrinkage usually occurs in clays upon desiccation, with the loss of absorbed and pore water. Shrinkage is most marked in plastic clays. Upon rehydration, clays may or may not be restored to their original volume. The rate and degree of rehydration and volume recovery may vary

due to mineralogy, fabric, or degree of compaction. Dehydration can be caused by increased temperature, or by chemical desiccation. If dehydration is accompanied by phase transformations or dehydroxylation of the clay mineral, then the change may be irreversible. As a result, dehydration of some clay minerals may have permanent consequences for seal integrity, such as a loss of swelling capacity, plasticity, or sorptive capacity. Theoretical studies, as well as natural occurrences of clay minerals, suggest that under near field repository pressure and temperature conditions, dehydroxylation would occur very slowly, if at all. Dehydroxylation of clay minerals in shaft seals is not expected because shafts should not experience temperatures much above ambient after decommissioning of the facility.

Swelling in a closed volume results in development of swelling pressure. Such swelling occurs in smectite clays upon absorption of water and may be a significant property in achieving a low-permeability seal-host interface in moist environments. The swelling pressure that can be generated by a material is a common measure of its ability to form an hydraulically tight seal. The maximum pressure that can be generated increases with density and smectite content of the seal. Conversely, the maximum pressure decreases with increasing total seal volume and ionic strength of the water being absorbed.

Thermal properties of clay-bearing materials are difficult to generalize because they are greatly influenced by factors such as water content and compaction density. Fabric anisotropy may also affect thermal properties of granular materials to some degree.

Model tests have been used to evaluate the behavior of clay-bearing seals in the laboratory. Studies have included natural shales, natural bentonites, and synthetic mixtures of clay and non-clay materials, compacted by different methods. One of the major results of model tests of clay seal materials is evidence for preferential fluid flow at interfaces between the seal and the model host material.

Perhaps the most intensively studied candidate seal material is bentonite. Studies in Sweden have shown that the permeability of highly compacted bentonite is directly related to bulk density. Permeability increases as the bentonite is permitted to swell in an unconfined volume. Furthermore, the swelling capacity, swell pressure, and permeability of compacted bentonite are functions of the composition of the associated water, with more saline solutions reducing swelling and increasing permeability. Studies in the U.S. and Sweden define the permeability of bentonite-sand mixtures, showing that low values are achieved provided that the bentonite content is greater than about 25%.

### Sorption

Many clays, particularly those containing smectites, have favorable sorptive properties for many cations. The sorptivity of a clay mineral with respect to dissolved radionuclides is indicated to some degree by its cation exchange capacity. Generally, cation exchange capacities of smectite clays tend to be greater than other major clay mineral groups. Sorptivity is difficult to quantify and, as measured experimentally, is strongly influenced by environmental factors as well as by mineralogy. These environmental factors include: pH, Eh, temperature, radionuclide concentration, fluid composition, and the solid (sorber) to fluid ratio.

Future sorption research must incorporate close control of all experimental parameters. Experimental conditions must reflect actual repository conditions, or encompass a range of conditions which realistically may be expected to prevail in a given repository. Experiments may require simplification, for example by selecting particular radionuclides (especially hazardous species) for initial study.

Clays and clay minerals do not appear to be efficient sorbers of anions. Consequently, the retardation of anionic species by clay barriers will require the study and development of non-clay additives, such as transition metals, in order to maximize barrier performance.

### Longevity

Clay minerals occur in all geologic periods and under a wide range of physiochemical conditions in the earth's crust. In light of this evidence, the incorporation of at least some select species of clay minerals has been proposed as one means to achieve chemical stability and long-term performance in repository seals. Nonetheless, attention must be given to factors such as solubility, thermal stability, phase transformations, and possible effects of radiation, which may lead to decreases in the operational efficiency of clay seals.

Clay solubility in distilled water or ground water is evident to some degree at elevated temperatures. Dissolution of clay minerals is incongruent and controlled by intermediate silica-rich phases. Besides temperature, the pH of the fluid and the mineralogy of the clay are additional controls on the degree of clay solubility. Depending on these parameters, as well as the rate of fluid movement and the duration of dissolution, the chemical degradation of clay-rich barriers may or may not be significant.

The stability of clays at elevated temperatures is also a longevity issue. Some clays (e.g., chlorite and kaolinite) display little dehydration or alteration up to 300°C. Others, particularly smectites and vermiculites, undergo dehydration below 300°C. Irreversible phase transformations may also occur in these phases at temperatures below 300°C. A commonly cited transformation is the growth of non-swelling, mixed-layer phases from smectite clays. The minimum temperature for incipient mixed-layer growth is arguably as low as 40°-85°C, inferred from diagenetic sequences. The rate of mixed-layer growth is dependent on reaction kinetics, however, which are slow at low temperatures. Therefore, the importance of mixed-layer growth in smectite clay-bearing materials is difficult to assess, although the occurrence of mixed-layer clays may result in decreased swelling ability (and thereby increased permeability of the barrier), decreased sorption, and possibly some embrittlement of the seal or backfill. Some clays may also be

fundamentally unstable at elevated temperatures. For instance, there are indications that kaolinite may break down in open systems at temperatures as low as 60°-70°C. Illites and chlorites display large compositional variation so that their high temperature phase relationships are fairly uncertain at present. Studies of the effects of radiation on clays have shown that morphological changes of clay minerals may occur due to strong irradiation, although the effects of these changes on permeability, sorptivity, or reactivity are not well known.

#### Emplacement Considerations

Emplacement options for clay-bearing materials include in-place compaction, precompaction, and slurries. In-place compaction applies to shafts and tunnels where workers and equipment can apply relatively standard engineering techniques in situ. Control of fabric and maintaining interface integrity, particularly at the ceilings of horizontal penetrations, are major emplacement concerns. Remote in-place compaction methods, for use in sealing boreholes, will require further investigations, particularly with respect to equipment and quality control of the emplaced plug. Precompaction has been considered as a means to emplace bentonite. Manageable size blocks of precompacted bentonite may be emplaced in seal zones, and the swelling of the smectite clays will provide a low permeability fluid flow barrier. Slurries may be applicable in zones where the introduction of water does not jeopardize repository integrity. Pressure grouting of host-rock fractures with bentonite slurries may be one such application.

#### Candidate Seal Materials

Clays, and clay mineral-bearing materials which may be of value as candidate seal or backfill materials because of their occurrences at or near candidate repository sites include:

- Ringold D clay and nontronite at the Hanford site
- Eleana Argillite at the Nevada Test Site

- Illite or smectite-bearing clays at a candidate salt site.

The properties of Oregon (Ca-) or Wyoming (Na-) bentonites make them favorable candidates for specialized seal components, or as additives to the materials listed above. Bentonite appears to offer good control of fluid flow and plastic behavior, and a considerable sorptive capacity. Additives may be used to enhance these properties (e.g., zeolites for sorption) or to alter other properties (e.g., sand or crushed rock to increase thermal conductivity and shear strength, or to reduce swelling or shrinkage). Studies of illite and mixed-layer clays can be useful to understand the changes in seal properties that might arise from the potential phase transformation of smectite to non-swelling phases.

#### Research Requirements

Areas requiring additional evaluation and testing with respect to clay seal properties and performance include:

- Seal-host interface permeability, comparing swelling and non-swelling clays
- Optimization of materials containing swelling clay to achieve low interface permeability without generating excessive swelling pressure
- Fracture-filling capabilities of clays, including controls on fracture filling, fracture width and depth that can be filled, and effects on fracture permeability
- Thermal properties of specific candidate materials under as-placed and water-saturated conditions
- Emplacement techniques and their effectiveness - including such items as emplaced seal quality, reproducibility, and approach to laboratory determined optimum performance
- Sorption of key radionuclides by candidate seal materials in simulated repository conditions

- Solubilities, thermal stabilities, and thermodynamic properties of candidate materials; and the properties of their reaction products
- Radiation effects on clay mineral structure and clay seal properties
- Long-term ground water-seal and host rock-seal interactions in simulated repository conditions
- Long-term interactions between clays and other candidate seal materials

## 1.0 INTRODUCTION

The sealing of penetrations associated with a mined geologic nuclear waste repository is a major consideration in the design, construction, operation, and decommissioning of such a facility. Seals and backfills emplaced in shafts, boreholes, and tunnels at a repository site must be of sufficient quality to limit the release of radionuclides through penetrations to acceptable levels. Depending on site specific conditions, seals will be required to limit ground water inflow. Seals must perform as designed until the disposed waste decays to innocuous levels, and seal designs must address and ensure performance under changing conditions (e.g., variable waste loading, thermal regimes, and geologic and hydrologic conditions). In addition, seals must be designed to perform independently of other barriers to radionuclide migration, such as waste packages or overpacks.

A major consideration in the design of repository seals is the selection of sealing materials (D'Appolonia, 1979; Roy, 1981). Several candidate materials groups have been proposed for use in sealing (D'Appolonia, 1980). Prominent among these groups are earthen materials consisting of relatively pure clay minerals or clay minerals mixed with other materials. Based on extensive data, clays appear to be promising materials for some components in repository seal systems where low permeability is required. Clays are also generally highly sorptive, although there is presently no consensus as to the degree of sorptivity required by seals.

The purpose of this report is to summarize some of the currently available literature regarding clay properties which pertain to repository seal performance. This information will be used to evaluate the potential of clays for sealing repositories and to determine research needs. Emphasis is given to three areas as follows:

- Permeability (Section 2.0)
- Sorptivity (Section 3.0)
- Longevity (Section 4.0)

Depending upon the mineralogy and the manner of emplacement, clays can be expected to either reduce actual fluid flow or adsorb various radionuclides, thereby limiting the release of radionuclides to the biosphere. The effectiveness of each of these sealing functions is dependent upon certain principal characteristics of the clay minerals, and the type of seal required determines what clay minerals are best suited. It is also recognized that these principal properties are dependent upon the chemistry and structural configuration of the clay minerals and any transformations under repository conditions that may affect their behavior as sealants.

The suitability of various clays and clay minerals as physical retardants of fluid flow is evident from the geological and soils engineering literature. The results of numerous mechanical tests under variable boundary conditions can be used to characterize the anticipated behavior in a repository sealing situation. The ability of a clay body to remain an effective fluid flow barrier depends on several of its physical properties and its behavior under a variety of physical conditions. Consideration is given, therefore, to significant properties of clays, including swelling capacity, swelling pressure, compressibility, shrinkage, ductility and deformability, and thermal behavior.

The capacity of clay minerals to adsorb various radionuclides and thereby act as an efficient retardant to ion migration is also documented in the literature. Numerous experiments on the selectivity of certain clay minerals for various ions, both radioactive and stable, and the overall capacity for adsorbing ions on these clays provide some degree of information needed to predict their behavior. There is less complete knowledge of adsorption capabilities at the conditions envisioned in a repository, but probably enough is known about the mechanisms of cation exchange to allow certain extrapolations.

Attention on clays as seal components has shifted from short-term clay function to that of stability and longevity in the repository

environment (D'Appolonia, 1980). While clay minerals may not prove as effective as many concretes for short-term sealing, it is expected that because they are natural materials which will be emplaced in environments relatively close to their conditions of formation, certain clays may persist for very long periods of time, providing the long-term seals required for radioactive waste repositories. One objective of this review is to identify longevity issues related to clays and clay minerals, including the limits of stability fields for various common clay minerals compared with anticipated repository conditions, and the rates at which clay minerals react to more stable phases if subjected to physiochemical conditions outside their stability fields.

Emplacement of clay seals has been described conceptually and demonstrated in a limited number of laboratory tests with attention to equipment needs and the quality of the emplaced seals. Emplacement issues, however, remain a major concern for seal design. It is possible that proper emplacement methods (e.g., a high degree of compaction) may reduce the differences in physical and chemical behavior among clay types, such that with sufficient forethought a satisfactory seal may be produced from virtually any clay or mixture of clays.

It is not intended that this report should include extensive discussions of clay mineralogy or crystal chemistry beyond what is generally necessary to understand the properties of clay minerals relevant to repository sealing. A familiarity with clay mineralogy and nomenclature is assumed, but a brief overview of clay mineralogy is included below. In addition, the following sections include a general summary of the materials of interest to sealing, and a brief discussion of repository seal functions and properties. A further discussion of clay mineral structure is given in Appendix A, and a glossary of specialized terms used herein is given in Appendix B.

## 1.1 CLAY MINERALS AND CLAYS

### 1.1.1 Clay Minerals and Their Crystal Structure

Clay mineralogy is described in detail in several standard texts (e.g., Deer et al, 1966; Mason and Berry, 1968; Grim, 1968). Clay minerals may be classified (Grim, 1968) in several groups:

- Halloysites
- Kandites (kaolinite, dickite, others)
- Smectites (montmorillonite, saponite, others)
- Illites
- Vermiculite
- Chlorites
- Palygorskite group (including attapulgite, sepiolite)

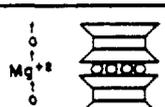
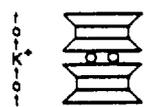
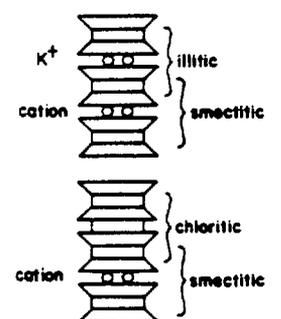
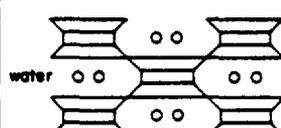
The distinction among these groups is based on crystal structure and chemistry which also account for the variation among the properties characteristic of clay minerals in each group. Clay minerals are fine grained\*, frequently close to the colloidal size range. With the exception of the palygorskite group, the clay groups listed above have a characteristic platy habit, which imparts a very high surface area to mass ratio. The platy habit, combined with high specific surface, are responsible for many of the characteristic engineering properties of clays, such as low permeability and high compressibility. The crystal structure of clay minerals is responsible also for a number of their characteristic chemical properties, including high cation exchange capacity. The palygorskite group of clay minerals has a fibrous habit, including large voids in the crystal structure. The large surface area and open crystal structure impart the distinctive properties of this group, including a high sorption capacity. Table 1-1 depicts the crystal structures and mineral habits of major clay groups.

In light of the numerous clay mineral species and the difficulties inherent in attempting to analyze each type, this section considers only

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\*Alternatively defined as  $<0.004\text{mm}$ , or  $<0.002\text{mm}$ ; clay minerals tend to be concentrated in the  $<0.002\text{mm}$  fraction of clays and soils (Grim, 1968).

Tables 1-1. Generalized Crystal Structure and Crystal Properties of Clay Minerals

CLAY MINERAL GROUP	GENERALIZED CRYSTAL STRUCTURE*	LAYER CHARGE DEFICIENCY	CRYSTAL HABIT	CRYSTAL PROPERTIES
Kaolinite	 dioctahedral	~0.0	often euhedral hexagonal plates; 0.1-4 $\mu\text{m}$ diam., 0.05-2 $\mu\text{m}$ thick	stiff; relatively incompressible; stable edge to face or edge to edge fabric with high porosity; surface area 10-20 $\text{m}^2/\text{g}$
Halloysite	 dioctahedral		tubular, with OD 0.05-0.20 $\mu\text{m}$ and wall thickness 0.02 $\mu\text{m}$	surface area (hydrated) 35-70 $\text{m}^2/\text{g}$
Vermiculite	 trioctahedral	0.6-0.9	small particles usually mixed with other clay minerals	surface area 40-80 $\text{m}^2/\text{g}$ or up to 870 $\text{m}^2/\text{g}$ if interlayer surfaces are included; readily dehydrate with heating
Illite	 dioctahedral	0.6-0.9	irregular, thin flakes, 0.1 $\mu\text{m}$ to several micrometers diam., 30 $\text{\AA}$ or more thick; hexagonal	surface area 65-100 $\text{m}^2/\text{g}$
Smectite	 dioct- or trioctahedral	0.2-0.6	small, filmy sheets, usually <1-2 $\mu\text{m}$ diam., 10 $\text{\AA}$ to $2 \times 10^3$ $\text{\AA}$ thick	compressible, swell with incorporation of adsorbed (or double-layer) water; flexible particles; tend to produce low porosity fabrics with small interconnected volumes; surface area 50-120 $\text{m}^2/\text{g}$ ; 700-840 $\text{m}^2/\text{g}$ if interlayer surfaces included
Chlorite	 dioct- or trioctahedral dioct- or trioctahedral	0.3-1.0	platey; hexagonal when well crystallized	
Mixed-layer				swelling diminished by amount corresponding to non-swelling component
Palygorskite			fibrous with diameters 50-100 $\text{\AA}$ and 4-5 $\mu\text{m}$ length	large void spaces can carry water and large ions

Reference: Grim, 1968; Mitchell, 1976; Brindley, 1981

\*o = octahedral layer  
t = tetrahedral layer

four major clay types: the kandite group (especially kaolinite), smectite group, chlorite group, and illites. (For a brief overview of the major clay groups and illustrations of crystal structures, see Appendix A.) These four clay types are predominant in almost all natural occurrences and represent most of the extremes of properties important for sealing. Kaolinite and smectites are early diagenetic minerals, which are most stable at earth surface conditions, while illites and chlorites are diagnostic of higher temperature, late diagenetic environments. The results of experiments and observations of these widely diverse clay minerals should be applicable to almost all types of clays and their mixtures, in a wide range of environmental conditions.

Virtually all of the various clay minerals are phyllosilicates or layer silicates whose structures are composed of well-defined sheets of linked silica tetrahedra and hydroxide octahedra. It is the combination of these sheets into various types of layers that distinguishes the major clay mineral groups and imparts to them many of their characteristic chemical and physical properties. Tetrahedral sheets consist of linked, oriented silica tetrahedra sharing the three basal oxygens with nearest neighbors, and with the apical oxygens all pointed in the same direction. The linked network of the trigonal basal units of the silica tetrahedra produces a hexagonal framework, the centers of which are positions where hydrated cations are often adsorbed onto the clay mineral surface. Octahedral sheets contain linked octahedral coordination groups in which divalent and trivalent cations are enclosed by an octahedral network of oxygen and hydroxides. A clay mineral unit cell normally includes three octahedra within the sheet. Octahedral sites are filled either by three divalent cations per unit cell, e.g.,  $Mg^{2+}$ ,  $Fe^{2+}$ , creating a trioctahedral sheet, or two trivalent cations, e.g.,  $Al^{3+}$ ,  $Fe^{3+}$ , and leaving one octahedral site unoccupied, forming a dioctahedral sheet. Octahedral and tetrahedral sheets are linked together by the apical tetrahedral oxygen replacing one of the octahedral hydroxides, thereby orienting the basal plane of the tetrahedra toward the outer surfaces of each sheet structure. Various layer configurations

include one octahedral sheet linked with one tetrahedral sheet (1:1), characteristic of the kandite group, and one octahedral sheet intercalated between two tetrahedral sheets (2:1), such that each clay layer is bounded by basal tetrahedral planes joined so as to form a network of hexagonal vacant sites. These 2:1 clays comprise most of the other clay mineral groups. The differences among the various clay groups are attributed to the type and amount of solid solution substitution and to cations bonded between clay sheets or layers.

The octahedral and tetrahedral sheets are seldom isochemical; rather there is a certain amount of substitution by cations of similar charge and size, e.g.,  $\text{Fe}^{2+}$  for  $\text{Mg}^{2+}$ , and cations of similar size and unequal charge, e.g.,  $\text{Al}^{3+}$  for  $\text{Si}^{4+}$ . Both forms of substitution result in structural distortions but the latter substitution also produces a charge imbalance (usually a deficiency of positive charge in the structure). In order to maintain electroneutrality in the mineral structure, cations are adsorbed on the basal surface in the interlayer sites. These interlayer cations perform a significant role in determining some of the properties of clay minerals.

The kandite group, kaolinite, dickite, nacrite, and several hydrous forms, consist of a 1:1 layer dioctahedral structure with minimal substitution within the structure. This lack of substitution means that there is little deviation from the ideal formula,  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ; however, occasionally some  $\text{Fe}^{3+}$  substitutes for  $\text{Al}^{3+}$ . The limited lattice substitution also requires very little cation adsorption in interlayer sites to balance charge deficiencies. The greatest difference among the members of the kandites is the mode of stacking and disorder of the 1:1 layers; one layer per unit cell results in triclinic kaolinite while two stacked layers per unit cell produces the monoclinic structural varieties of dickite and nacrite.

The 2:1 layer silicates are classified according to the type of octahedral sheet, whether dioctahedral or trioctahedral, and the amount of

excess negative charge created by substitution that must be balanced by interlayer cations (Table 1-1; Brindley, 1981).

The smectites are common 2:1 layer silicates with variable composition and several unusual physical properties. The smectite family is distinguished by a limited amount of solid solution substitution such that the excess negative charge is approximately 0.33 equivalents per unit cell [based on  $\text{Si}_4\text{O}_{10}(\text{OH})_2$ ]. In dioctahedral smectites this excess charge is created by substitution in either the octahedral sheet (e.g., montmorillonites  $\text{Mg}^{2+}$  for  $\text{Al}^{3+}$ ), or in the tetrahedral sheet (e.g., beidellites,  $\text{Al}^{3+}$  for  $\text{Si}^{4+}$ ). Trioctahedral smectites are characterized by primarily octahedral sheet substitution, creating such species as hectorite (Li-enriched) and saponite (Fe-enriched).

The relatively low layer charge in smectites permits hydration and solvation of the interlayer cations and a reversible intracrystalline swelling created by the uptake of water. The type of interlayer cation determines the ease and extent of exchange and hydration, e.g., interlayer Na is responsible for the adsorption of numerous water layers while Ca in the interlayers only adsorbs two layers of water molecules.

Illites are often compared with muscovites since they have similar 2:1 layer structures, and roughly 10Å spacing between layers; however, illites have distinctive composition and structural configuration, and are not simply fine-grained micas. True muscovite [ $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$ ] has a layer charge deficiency of 1.0 equivalent per unit cell created by  $\text{Al}^{3+}$  for  $\text{Si}^{4+}$  substitution in the tetrahedral sheet. This excess charge is balanced by one equivalent of potassium, which equals roughly 12% by total oxide weight of the muscovite (Weaver and Pollard, 1973). Illites have a somewhat smaller layer charge deficiency, roughly 0.8 equivalents per unit cell created by less solid solution substitution and requiring less potassium to balance. Most illites contain no more than 7%  $\text{K}_2\text{O}$  which reflects the limited substitution (Weaver and Pollard, 1973).

Chlorites are 2:1 layer silicates with interlayers of octahedral hydroxide sheets with a slightly positive charge to offset the excess negative charge created in the 2:1 lattice. Chlorites are primarily trioctahedral structures;  $Mg^{2+}$  and  $Fe^{2+}$  characteristically occupy octahedral sites, with considerable cation replacement making it difficult to produce a generalized structural formula.

#### 1.1.2 Clays Considered for Repository Sealing

Clay minerals largely control the properties of earthen, granular materials which contain a significant clay mineral component. The clay mineral component required in order to control the material properties is generally only as large as required to fill void spaces among non-clay grains. This frequently requires less than one-third of the total volume to be clay minerals (Mitchell, 1976). For purposes of this report, "clay" will be used to refer to any earthen material containing unfired clay minerals, including shales, argillites and bentonites, regardless of the type or quantity of the other granular materials present so long as the clay mineral component controls the material behavior. One of these clays, bentonite, refers to a natural material, containing a large proportion of smectite clays, derived from the devitrification of volcanic ash.

The clay materials which are of interest for use in repository sealing, and upon which testing with respect to sealing performance assessments has been performed, belong in three broad categories:

- Natural composite materials: pulverized shales, claystones, and bentonite. These are naturally occurring mixtures of clay and non-clay minerals or phases (glass).
- Engineered composite materials: synthetic mixtures of clay minerals, natural composites and non-clay materials. This group includes bentonite-sand, shale-bentonite, and shale-montmorillonite mixtures, among others.

- Relatively pure clays: materials composed almost entirely of one or more clay minerals.

Any one of these groups might be pretreated (e.g., grain size sorted, or conversion of exchange cations) prior to testing or application to sealing.

## 1.2 DEFINITION OF SEAL FUNCTIONS

In order to limit the release of radionuclides to the biosphere through a penetration at or near the site of a mined geologic repository, a repository seal must perform at least one of two primary functions.

- Prevention or retardation of fluid flow
- Limitation of radionuclide mobility (D'Appolonia, 1980)

The first of these functions is required to minimize ground water incursion into a repository or the movement of contaminated fluids out of a repository by way of tunnels, shafts, or boreholes. Seals may be placed also to isolate separate sections of a repository. Limiting fluid movement will also minimize waste dissolution and enhance sorption as steady-state or equilibrium is approached among ground water, rock, waste and seals. A major seal design requirement, therefore, is to achieve and maintain a low permeability seal zone, with consideration given to three components in the seal zone; the seal material itself, the interface, and any "disturbed zone" (resulting from the excavation process) in the adjacent host rocks.

Radionuclide migration may be retarded by chemical processes also, by any reaction which causes radionuclides to be retained in relatively insoluble or immobile forms. For example, adsorption retards radionuclide movement by the retention of dissolved radionuclides on particle surfaces. In a broad sense (see Appendix B), "sorption" refers to any form of reaction capable of the retardation of radionuclide migration.

The functions described above apply to seals placed in all types of penetrations, including shafts, tunnels, and boreholes. The design approach for seals is based on a multiple component concept with a number of separate seal components each designed for a specific function (e.g., low permeability or high sorptive capacity) and for a specific location and environment. Components are repeated in the design in order to provide a degree of redundancy, and to mitigate the effects of the possible failure of any individual component (D'Appolonia, 1980; Kelsall et al, 1982). An important design aspect of the multiple component seal is to assure the physical and chemical compatibility of each seal component with the environment in which it is placed.

Current design concepts for shaft and tunnel seal systems in salt (Kelsall et al, 1982) include concrete bulkheads designed specifically to retard water flow, separated by earthen (clay-bearing) or crushed salt backfills. Earthen backfills are used in the shafts and in tunnels close to the shafts, to function as relatively insoluble and impermeable backups to the bulkheads. Water barriers might also be constructed from blocks of precompacted swelling clay. Another possible use for clays in repository sealing is for grouting and sealing of fractures.

### 1.3 PRELIMINARY EVALUATION OF CLAYS AS SEAL MATERIALS

#### 1.3.1 General Clay Properties

The applicability of clays and clay minerals to sealing requirements is evident from familiar practices, including:

- The use of compacted clays and swelling clays in relatively impermeable structures such as dams, and canal and storage pond linings
- The use of bentonite in drilling and in cutoff slurry trenches to reduce water inflow from permeable materials
- The use of clays as sorbent materials for water, organic compounds, metals and radionuclides

In addition, the widespread occurrence (under many physiochemical conditions) and obvious persistence of clay minerals in geologic time suggest that clay materials may serve the long-term requirements of repository seals.

Basic characteristics and properties of some clay minerals are listed in Table 1-1. Many of these properties can be altered or optimized by physical or chemical pretreatment, such as compaction or conversion of exchange cations.

### 1.3.2 Repository Sealing Considerations

A more specific appraisal of seal materials, including clays, should be based upon the ability of the material to provide seal functions, and its material and functional longevity with respect to seal zone environments. Seal materials in general will be evaluated according to the following characteristics (D'Appolonia, 1980):

- Permeability of the material and its interface with the host rock
- Plasticity (non-brittle response to stress)
- Ability to infill voids or heal fractures by swelling
- Compressibility
- Erodability
- Thermal properties
- Ability to retard radionuclide migration as a result of sorption or reactivity with radionuclides
- Longevity, as measured by chemical and thermodynamic stability, solubility and reactivity
- Freedom from detrimental interactions between adjacent seal materials, and between seals and host materials

- Emplacement feasibility
- Availability and cost

The following paragraphs discuss each of these performance characteristics briefly, and discuss the importance of material properties to seal design and performance. The significance of the characteristics listed above to the use of clay materials for penetration sealing is emphasized.

1. Permeability. The permeability of a seal component designed primarily to reduce fluid flow should approach the undisturbed host rock permeability. For salt and possibly other candidate host media, the bulk seal permeability should be on the order of 1 microdarcy (equivalent to a hydraulic conductivity\* of  $10^{-9}$  cm/sec) or lower. This requirement refers to the permeability of the whole seal zone, including the seal/rock interface and disturbed zone as well as the internal permeability of the seal. It is probably not necessary that all seal components achieve 1 microdarcy permeability. For example, some backfills may be designed to be sorptive or reactive with dissolved radionuclides, in which case a large surface area should be exposed to permeant. Some degree of porous permeability may be desirable in such materials.

The permeability of clay materials is controlled by several parameters, such as water content and composition, mineralogy, and degree of compaction. The parameters which influence clay permeability are reviewed in detail in Section 2.0, from the engineering literature and from testing in support of the NWTs and other radioactive waste storage programs. Section 2.0 also addresses seal material properties, such as swelling, shrinkage and compressibility, which may affect seal-rock interface permeability.

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\*For discussion of terms, see Section 2.1.1.

2. Plasticity. Brittle fracture in response to stresses imposed on a seal is potentially very damaging to seal performance, particularly in regard to fluid flow. Thus, in some seal components, a plastic (or ductile) material which deforms without brittle fracture may be desirable. Clay materials may exhibit varying degrees of plasticity depending on many factors including: clay mineralogy; clay content; exchange cation composition; type, amount and size distribution of non-clay materials; the degree of compaction; water content and composition; temperature; stress state (effective stress); fabric and its orientation with respect to stress direction(s); and strain rate.

3. Fracture Healing and Void Infilling. Some clay materials swell when contacted by water. Swelling may promote fracture healing or infilling, and may be particularly advantageous for forming a tight interface between a seal and the rock. The expansion, or swell capacity of clays, and the minimum fracture size into which clays can extrude, varies according to factors such as clay mineralogy and content, degree of compaction, water content and composition, confining pressures, fabric, and temperature.

4. Compressibility. Some materials used in repository seals may be required to support their own mass as well as compressive stresses resulting from overburden load or from the creep of host rocks such as salt, with a minimum volume change. Other materials may be required to be compressible, in order to accommodate deformation of the penetration.

Clay materials are generally compressible and may be incorporated in repository seals to achieve compressible seal components. The degree of compressibility depends on clay mineralogy and content, the degree to which the material has been compacted, exchange cation composition (if any), and water content and composition. The compressibility of clay materials may alter under cyclic stress regimes or during cyclic swelling and shrinkage.

5. Thermal Properties. The thermal behavior of seal or backfill components may affect seal performance. Although the thermal requirements of seals or backfills have not been fully established and will vary among seal components due to host rock properties and the proximity to heat producing waste, it is probable that seal materials will not be designed as thermal insulators, but will be designed to match or be compatible with the thermal properties of the host rock. Materials matched according to thermal properties will help to assure that high stresses will not be generated in the seal zone in response to differences in thermal expansion of host and seal materials. Among the thermal parameters of importance are heat capacity, thermal conductivity and thermal expansion. The thermal properties of clay materials may depend on the thermal properties of the clay and non-clay phases, and on the proportions of each, and on water content, degree of saturation, degree of compaction, fabric, and temperature.

6. Radionuclide Migration Retardation. The large surface area to mass ratio and large cation exchange potential of clays are the major causative factors in the sorption of ions by clays. Clays may be instrumental in providing radionuclide sorption capacity and migration retardation to repository seals and backfills. Section 3.0 addresses sorption by clays, properties which affect sorption, and the significance of experimentally determined sorption coefficients to the design of repository seals.

7. Seal Longevity. Regulatory guidelines (USNRC, 1982) require that the release of radionuclides from a repository facility to the biosphere be strictly controlled and limited for about 10,000 years after decommissioning of the facility. In addition to assurance that the seal functions are not seriously diminished in time by mechanical or thermal stresses, the physiochemical stability of the material in the host environment is a major consideration. The material stability may be estimated by evaluation of at least the following properties of the material:

- Solubility in ground water
- Reactivity in ground water
- Phase transformations
- Dehydration
- Reactivity with radionuclides, and effects of radiation.

The ability of a clay material to provide long-term performance may depend on factors such as clay and non-clay mineralogy, water content, ground water and pore water composition, temperature, exchange cation (if any) composition, the length of time that given environmental conditions persist, and the rate and frequency of change in environmental conditions. The evaluation of long-term material behavior may require extended periods of testing and/or the examination of the thermodynamics and kinetics of possible reactions. Long-term stability of clay minerals as determined experimentally and from geologic observations is reviewed in Section 4.0.

8. Seal-Host Rock Interactions (Synergistics). Seal systems must be designed so that each component does not interact with adjacent seal components, or with the host rock, in any way that degrades the seal performance. With respect to clay seals, for example, swelling clays could generate significant swelling pressures, the effects of which could be to open or enlarge fractures in seals or in the host rock. Clays which sorb water strongly could also tend to dehydrate hydrous phases in adjacent seal components or in host materials, and alter their properties. Elucidation of these types of synergistic interactions, their likelihood, and the material response(s) with respect to seal integrity, are important to seal design and performance verification.

9. Emplacement Feasibility. Material handling and emplacement will strongly affect important physical properties of emplaced clay seals, such as fabric and density, and will thereby affect seal function and performance. If clays are to be used as seal components, it is essential to find a practical emplacement method such that design requirements are met in situ. Clay materials may be emplaced as repository seals or backfills by several methods, including:

- In-place compaction of clay materials introduced to the seal zone in granular form
- Emplacement of precompacted blocks of clay materials
- Slurried transport of clay materials followed by compaction and/or a period of time to allow the material to set.

In-place compaction may include remote downhole compaction in boreholes (Martin, 1975; McGowan et al, 1976), or direct backfilling in rooms, shafts, and tunnels in which workers and machinery can operate. Precompaction has been proposed for use in the Swedish Karnbranslesakerhet (KBS) repository concept (Pusch, 1978a, b, c; Pusch and Bergstrom, 1980; Pusch et al, 1979). In these studies, highly compacted Wyoming bentonite and bentonite-sand mixtures are proposed as waste package backfill. Precompacted bentonite could be applied equally effectively to backfills and repository seals. Blocks can be uniform or customized for each individual application. Precompacted bentonite can achieve densities far greater than feasible using in-place compaction methods.

Slurries have not been intensely studied for application in repository sealing. Slurry trench and bentonite grouting technologies are useful in gaining insight into the performance of slurries, and estimating their applicability to repository seals. A possible application for bentonite slurries is in pressure grouting of water-bearing zones or zones of disturbed rock adjacent to a penetration.

10. Availability and Cost. Cost is not a primary consideration in material selection but must be taken into account particularly for large-volume seal components such as backfills. Availability of a material at or near a site is also desirable. Ideally, seals will include materials obtained from formations occurring at the site which can be shown to be geochemically compatible with the site ground waters.

### 1.3.3 Data Sources and Scope of Survey

Much information related to clay properties is derived from general engineering, mineralogic and geologic studies. In addition, the NWTS program has actively supported research in support of the use of clay materials in radioactive waste storage. Studies have addressed:

- Clays as a waste form
- Clays as waste package backfill
- Clays as room, tunnel, shaft, and borehole backfills and seals
- Clays and clay-bearing rock as host formations

Several of the NWTS and related studies are summarized in Table 1-2. Many of these studies are cited in this review, being among the primary sources of current data on clay seal performance and stability. In addition, the engineering and soil mechanics literature is a major source of information for clay material physical and hydraulic properties, as is the geochemical literature for clay stability. The scope of the present review is not intended to be exhaustive, but is limited to the major literature in these areas, including familiar review volumes on soil mechanics (Lambe and Whitman, 1969; Mitchell, 1976) and clay mineralogy (Grim, 1968).

### 1.4 ORGANIZATION OF REPORT

In Section 2.0, clay materials are evaluated for their potential use as water flow barriers. This summary focuses on the permeabilities achieved in compacted clay bodies and on the volume stability of clay material. Examples of clay seal performance are presented as determined from experiments on model seals composed of clay minerals and clay-rich mixtures. The experimental results are described according to those properties described in Section 1.3 which may affect seal permeability and fluid flow barrier performance. In Section 3.0, clay materials are evaluated for their potential to retard radionuclide migration. This

Table 1-2. Summary of NWTS and Related Studies on Clays and Clay Minerals

TITLE OF STUDY	CLAY MATERIALS STUDIED	OBJECT OF STUDY	REFERENCE
Geothermal Alteration of Clay Minerals and Shales Diagenesis	Several	The effects on clays and shales of siting a nuclear waste repository in shale strata	Weaver, 1979
Methods for Determining the Thermal History of Shales	Kaolinite, illite Conasauga Shale	Means by which the thermal conditions undergone by clays in shales can be described for purposes of siting a nuclear waste repository	Weaver, 1980
Chemistry/Physics of Nuclear Waste-Rock Interactions	Several shales	Reactivity and phase formations resulting from reactivity between shale (candidate host rock) and waste forms	Pennsylvania State University (ONWI, 1981a)
Hydrothermal Interactions of Clay Minerals and Shales With Cesium	Kaolinite, montmorillonite illite, chlorite, several shales	Determine the effect of interaction between Cs released from waste forms and clay minerals in host rock	Komarneni & Roy, 1980; Komarneni & White, 1981
Waste-Rock Interactions Technology Program (WRIT) Geologic Media-Nuclide Interaction Studies	Eleana Argillite	Sorption (Kd) values and mechanisms, as siting criteria	Pacific Northwest Labs (ONWI, 1981b)
Survey of Argillaceous Rocks	Several	Chemical/physical properties of argillaceous formations for site selection purposes	Oak Ridge National Labs (ONWI, 1979)
Static Distribution Coefficient Determinations Using Basalt and Its Secondary Minerals	Nontronite (vug & vein filling mineral)	Kd determinations, and survey of geochemical parameters which control sorption values	Ames & McGarran, 1980a, b

Table 1-2. Summary of NWTS and Related Studies on Clays and Clay-Bearing Materials

(Cont'd)

TITLE OF STUDY	CLAY MATERIALS STUDIED	OBJECT OF STUDY	REFERENCE
Swedish-American Cooperative Study	Bentonite, bentonite-sand	Physical, thermal, and hydraulic properties of highly compacted bentonite and bentonite sand mixtures for overpack and backfill	Knutsson, 1977; Pusch, 1978a, b, c; Pusch & Bergstrom, 1980; Pusch et al, 1979; Neretnieks, 1979
Backfill Barrier As A Component In A Multiple Barrier System	Bentonite, Dewey Lake Shale, mixes	Sorption (Kd) of candidate backfills and modeling of retardation behavior	Nowak, 1980a, b
Waste Isolation Safety Assessment Program (WISAP) Task 4: Collection and Generation of Transport Data -- Theoretical and Experimental Evaluation of Waste Transport in Selected Rocks	Na-montmorillonite (Belle Fourche clay)	Sorption (Kd) by clays for site selection and assessment purposes, and effects of some geochemical parameters	Silva et al, 1979 b
Laboratory Studies of Radionuclide Transport in Geologic Media	Eleana Argillite	Sorption (Kd) by shale for site evaluation purposes	Erdal et al, 1979
Preliminary Geochemical & Physical Testing of Materials For Plugging of Man-Made Accesses To a Repository in Basalt	Bentonite, Ringold D Clay	Physical, and hydraulic properties of compacted or slurry-emplaced model seals; solubilities at elevated temperatures	Taylor et al, 1980
Interaction of Radionuclides With Geomedia Associated With The Waste Isolation Pilot Plant (WIPP) Site in New Mexico	Clays from halite core (montmorillonite, chlorite, kaolinite, illite, chlorite-montmorillonite mixed layer clay)	Sorption (Kd) values for several radionuclides	Dosch and Lynch, 1978 Serne et al, 1977

Table 1-2. Summary of NWTS and Related Studies on Clays and Clay Minerals  
(Cont'd)

TITLE OF STUDY	CLAY MATERIALS STUDIED	OBJECT OF STUDY	REFERENCE
Determination of Dehydration Temperatures of a Secondary Vug-Filling Mineral (NSTF) Using Differential Thermal Analysis at Various Pressures	Nontronite	Dehydration and phase transformations at elevated temperatures	Koster van Groos, 1981
Feasibility of Sealing Boreholes With Compacted Natural Earthen Material	Minnescah, Dewey Lake and Conasauga Shales, Montmorillonite	Physical and hydraulic properties of model clay seals compacted by various methods	Martin, 1975; Oisen and Martin, 1976, 1980
Getter Backfill Measurement Program	Bentonite, bentonite and non-clay additives	Permeability and heat capacity measurements on backfill materials at in situ stresses and temperatures	ONWI, 1982a, 1982b
Durability of Seal Materials for a Salt Repository	Montmorillonite	Stability in brines at elevated temperatures and pressures	Roy et al, 1982

section focuses first on the cation exchange capacity of clays and second on the ability of clays to "sorb" radionuclides as indicated by experimentally determined Kd values. It includes a discussion of variables affecting sorption and measured Kd's. Discussion of clay-radionuclide reactivity which results in formation of new phases (e.g., pollucite, oligoclase, analcime, etc.) is not included. Temperatures in most seals will not reach the 200°-300°C at which such reactions have been experimentally demonstrated (Komarneni and White, 1981; Sasaki et al, 1982).

The long-term performance of clay materials is addressed in Section 4.0, focusing on clay mineral solubility, phase relationships and transformation rates, but also considering the effects of radiation on clay mineral stability. Section 5.0 assesses various emplacement methods applicable to clay-bearing penetration seals. Section 6.0 is based on the previous sections and summarizes properties of clays as barriers to water flow and radionuclide migration. The data are discussed in the context of applications to repository sealing, and recommendations for future research are made.

## 2.0 CLAY SEALS AS FLUID FLOW BARRIERS

One of the primary functions of a repository seal is to inhibit the flow of water through both engineered pathways (e.g. shaft, tunnel, etc.) and zones of disturbed rock immediately adjacent to such excavations. The success with which this function is performed depends on the internal permeability of the seal material, on the host rock/seal interface permeability, and on the treatment and permeability of any disturbed zone adjacent to the penetration. This section discusses the permeability of clay-bearing materials, and the properties of clay seals which may affect the seal zone permeability.

Clay mineralogy is an important consideration because physiochemical properties vary widely from one clay group to another. Moreover, predictions of long-term clay seal performance may be tied to an understanding of how component clays are likely to behave over time. Naturally occurring clays are discussed most extensively because these materials will be most readily available for large volume seals, and, with the use of clay mineral and non-clay additives, the performance of the clay seal can be altered or enhanced.

The performance of clay seals as fluid flow barriers will be affected by response to stress, temperature and other environmental conditions imposed by the site geology and the nuclear waste repository on the seal zone. For this reason, it is important to examine clay seal properties over a range of conditions. Properties of interest include:

- Permeability
- Response to stress
- Volume stability: shrinkage due to dehydration (dessication); swelling due to water absorption; compressibility; erodability and dispersivity
- Thermal properties

- Geochemical stability (low solubility/reactivity), including freedom from detrimental interactions between adjacent seal materials and between seal materials and the host rock and/or ground water.

A fluid flow barrier may function adequately under changing environmental conditions if materials possess the following properties:

- Low permeability to associated fluids
- High strength, or a high degree of total strain capacity (plasticity) before failure (cracking), including both elastic and inelastic, time-dependent (creep) strain
- No shrinkage or erosion
- Moderate swelling capacity (not so high as to endanger seal integrity)
- Thermal behavior which minimizes temperature elevation or stresses in the seal zone.

Long-term interactions between seals and host, and clay seal dissolution, reactivity and alteration may increase seal zone permeability. The potential for this type of seal degradation is addressed separately in Section 4.0, under material longevity.

## 2.1 ESTABLISHED ENGINEERING PROPERTIES

The physical behavior of clay-bearing materials, particularly soils, but also including fine-grained regolith, sediments, and weathered bedrock, has been most intensely examined in the engineering literature (extensive summaries are Lambe and Whitman, 1969; Mitchell, 1976; Terzaghi and Peck, 1967; Seed et al, 1961). This knowledge can be applied to projecting the general behavior of clay seals in sealing applications.

### 2.1.1 Permeability

The permeability of clay materials is a function of several parameters including:

- Clay mineralogy
- Clay mineral content
- Fabric, or microstructure, of the material
- Degree of compaction
- Molding water content and water composition

Environmental factors which may affect the permeability of a clay seal include permeant composition and temperature, and possibly the hydraulic gradient (especially if high). The permeability of an emplaced seal will also be influenced by the properties (degree of bonding, porosity) of the interface between the seal and the host rock.

Permeability of a geologic medium reflects its ability to transmit a fluid through a given cross-sectional area, across a given distance. Permeability (expressed in units of  $L^2$ ) is an intrinsic property of the geologic medium which is not affected by properties of the permeant. Hydraulic conductivity (expressed in units of  $L/T$ ) takes into account the kinematic viscosity of the fluid (water or brine) along with the intrinsic properties of the medium that define its permeability. In repository sealing applications, water or brine flow is of specific interest. Also, clay-water interactions near the surface of clay minerals resulting in adsorbed water layers, may affect both the intrinsic permeability and the viscosity of the pore fluids. For sealing applications, therefore, hydraulic conductivity is a more useful measurement than intrinsic permeability. In this report, "permeability" is used generally to refer to a property of the clay material; "hydraulic conductivity" is used when water flow is specified. "Permeability coefficient" is used in place of hydraulic conductivity for permeants other than water.

#### Effect of Clay Type and Content

Size, shape, and orientation of the clay particles are the most important factors in determining the size and geometry of pores. One generalization is that smaller clay particles result in smaller pore channels (Diamond, 1970), and numerous observations have indicated that

permeability is roughly proportional to the square of the pore channel diameter (Mesri and Olson, 1971). Hydraulic conductivity values measured on various clay minerals (Figure 2-1) correlate with kaolinite particles being significantly larger than illite particles, which are in turn larger than smectite particles (Grim, 1968; Mesri and Olson, 1971). Smectites have the lowest hydraulic conductivities due to their small size and thick adsorbed water layers. At any given void ratio<sup>1</sup>, illites and kaolinites have larger hydraulic conductivities that are attributed to larger particle sizes and thinner adsorbed water layers.

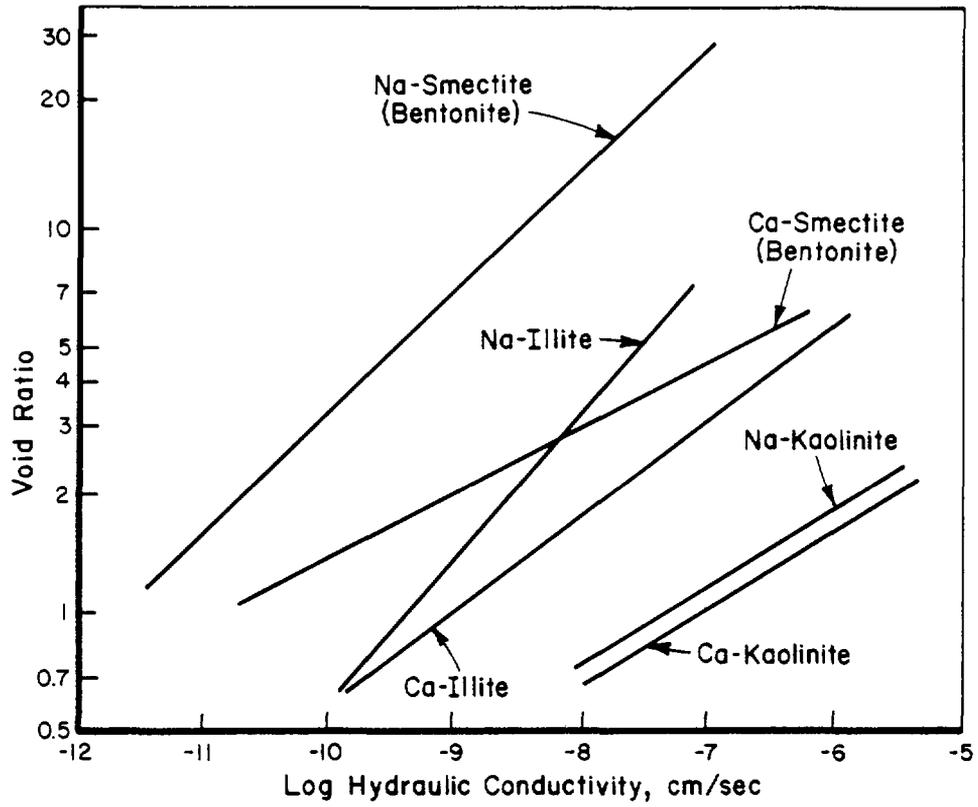
The effect of adding a non-clay material, such as sand or crushed rock, to a clay is to increase the hydraulic conductivity. Figure 2-2 shows the influence on hydraulic conductivity of the proportion of bentonite in highly-compacted sand-bentonite mixtures. This figure illustrates that bentonite contents of greater than 25% to 30% are required to achieve hydraulic conductivities of  $10^{-9}$  cm/sec or lower. Addition of smaller amounts of bentonite to sand can nonetheless effect a major reduction in hydraulic conductivity. Similar relationships between clay content and hydraulic conductivity can be derived for other clay types.

#### Effect of Fabric

The permeability of a clay is controlled to some degree by the number and size of pore spaces, which are, in turn, a function of clay mineralogy. Permeability is also determined by the degree of interconnection of the pores. It is the size and distribution of the connecting channels or pore throats that most directly control the permeability of a geologic medium. Permeability and the degree of communication between pores are primarily dependent upon the material fabric, as determined by the orientation, shape, packing, size distribution, and arrangement of grains. Because of orientation and surface effects, clays typically have relatively large porosities but very small permeabilities.

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<sup>1</sup> Void ratio: ratio of void volume to solid volume



REFERENCE: MESRI AND OLSON, 1971

Figure 2-1. Hydraulic Conductivity as a Function of Void Ratio and Pore Fluid Chemistry for Several Clays

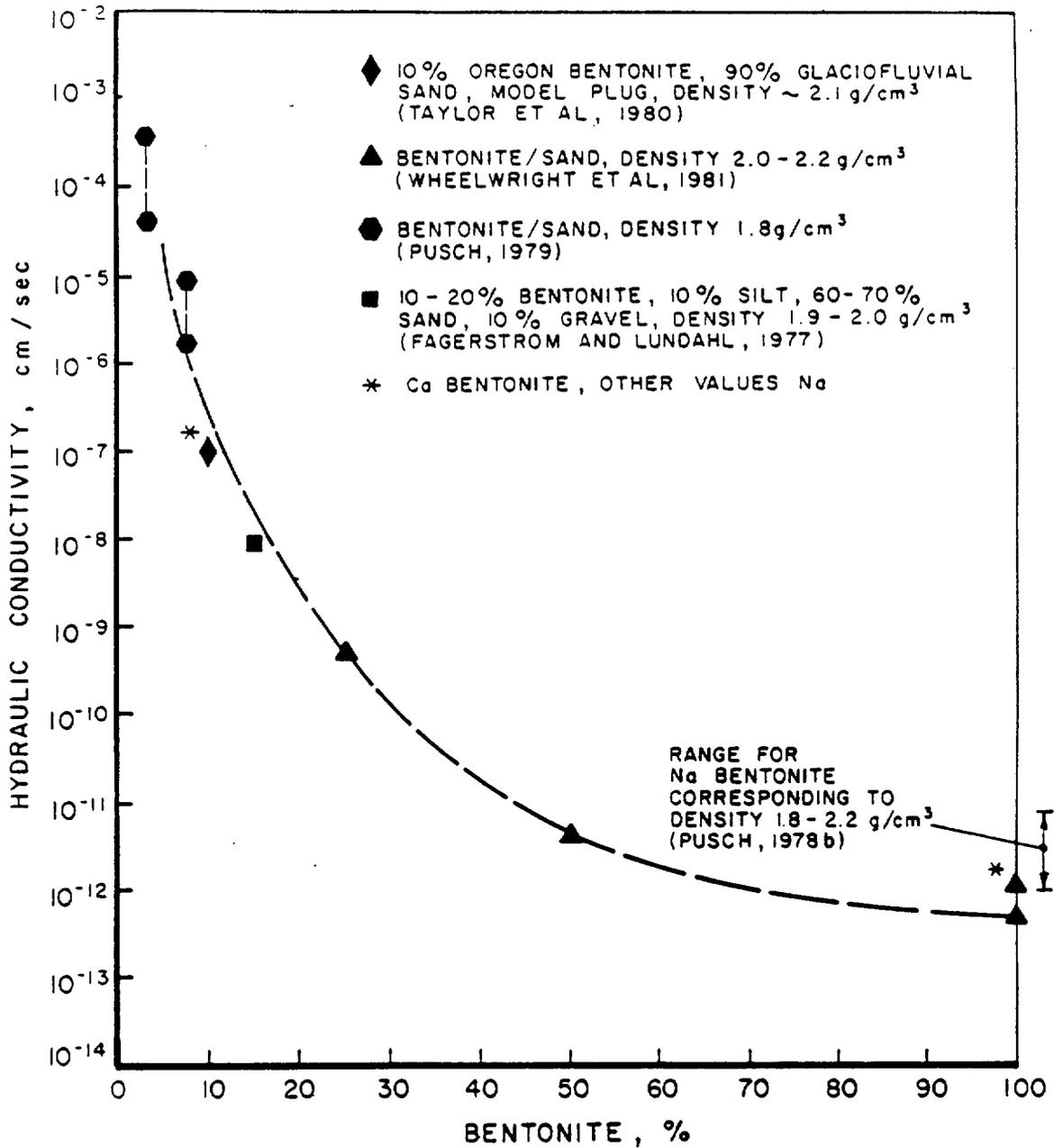


Figure 2-2. Hydraulic Conductivity of Compacted Bentonite/Sand Mixtures as a Function of Bentonite Content

The range in particle size, or sorting, also affects the fabric of the clay, and therefore the permeability. A well-sorted clay composed of particles of the same size has a larger porosity and permeability than a poorly sorted clay. The effect of a wide range of sizes is that smaller grains fall between and lie within the larger particles that constitute the framework (Davis and DeWiest, 1966; Rieke and Chilingarian, 1974).

The orientation of clay minerals also is a major determinant of a clay's fabric. In unconsolidated clays, the orientation is dominated by the electrostatically controlled edge-to-face attractions among clay minerals, producing a "house of cards" or flocculated structure. Under compaction, as water is expelled and electrostatic forces are changed, the flat clay platelets begin to orient themselves in flat aggregates. The principal orientation direction, or direction of elongation, of the clay minerals is normal to the directed stress. Maximum orientation is obtained in clays that are compacted in a dry state or fully drained, compared to clays saturated with water (Mesri and Olson, 1971).

Increased orientation substantially reduces permeability in the direction normal to elongation, but only slightly reduces flow rates parallel to orientation. Permeability measurements in shales indicate that permeability parallel to orientation is an order of magnitude larger than normal to particle orientation (Young et al, 1964). An oriented fabric then has the ability to control effectively the direction of water flow through it.

#### Effect of Compaction

Compaction of clays results in increased orientation and decreased porosity, both of which are responsible for decreased permeabilities. Progressive compaction is measured by either decreased void ratios and porosity or increased bulk density. The amount of stress applied during compaction of a clay is important in how it affects the clay's porosity or bulk density. A series of experiments by Olson and Mesri (1970) on Na- and Ca-saturated clays reveals the magnitude of changes in void ratios when subjected to compaction pressures of 100 to 100,000 psf

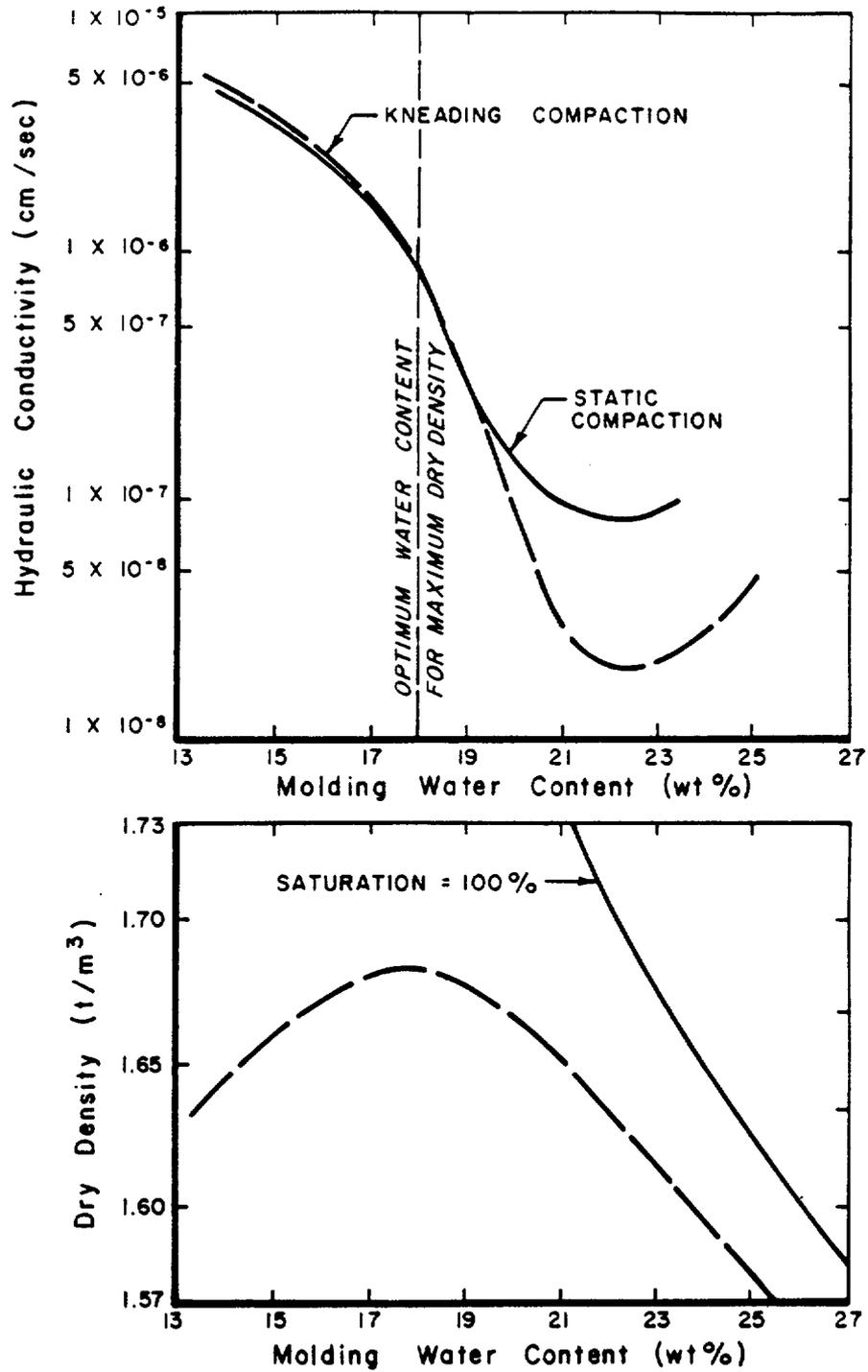
(0.05 to 4.7 MPa). Water-saturated kaolinite has the lowest void ratio of the major clay minerals at atmospheric conditions, 2.5, which decreases to about 1.0 at maximum pressure. In contrast, the smectites have the largest void ratios at 100 psf, 7.0 for Ca-saturated and up to 30.0 for Na-saturated. These values also decrease to about 1.0 at maximum compaction.

#### Effect of Water Content

In a clay the minimum void ratio and hence the minimum permeability are dependent not only on the properties of the granular particles and the compactive stress, but also on the molding water content (i.e., the water content of the clay at the time compaction is started) and the compaction method. For a given clay and a given compaction method, there is an optimum water content corresponding to the maximum degree of compaction (maximum density) that can be achieved with the particular compaction method. Figure 2-3 illustrates the influence of molding water content and the method of compaction on the hydraulic conductivity of silty clay. Figure 2-3 shows that the hydraulic conductivity of the soil reaches a minimum value when the soil is wetter than optimum, which is the point of minimum void ratio and maximum density. Possibly, the pore spaces produced by compaction at molding water contents slightly higher than optimum are smaller than those produced at optimum water content, resulting in lower hydraulic conductivity. This figure also demonstrates the importance of fabric in clay properties. Kneading compaction involves higher shear strains which break down flocculated fabric units and result in smaller individual pores and lower hydraulic conductivity than is achievable with static compaction at the same water content (Mitchell, 1976). In general for cohesive soils, an increase in water content from below to above the optimum water content is likely to cause a large decrease in permeability. This effect is magnified by increasing the clay mineral content of the material (Terzaghi and Peck, 1967).

#### Effect of Pore Fluid Composition

There are several physiochemical variables that also influence hydraulic



REFERENCE: MITCHELL, 1976

Figure 2-3. Effect of Water Content and Compaction Method on the Hydraulic Conductivity of a Clay

conductivity. Most of these factors affect the clays by altering the clay-water relationships, which in turn can disrupt the original fabric. Other factors include some of the chemical properties of the fluid itself.

For a particular compacted clay, permeability coefficients are largest for non-polar fluids. Values of the permeability coefficient decrease across the spectrum of permeants from polar fluids with low dielectric constants to polar fluids with high dielectric constants (Mesri and Olson, 1971). Water, with its highly polar structure and large dielectric constant, generally results in one of the smallest permeability coefficients. This small value results from the adsorption of polar water on the clay surfaces, creating effectively thicker particles which can block pore channels. The behavior of the adsorbed water on clay surfaces is very similar to the behavior anticipated for a more viscous fluid, which has led investigators to consider adsorbed water to be denser, and more viscous than pore water (Grim, 1968; Burst, 1969).

Dissolved cations and those in interlayer exchange sites, which are often very closely linked, also have a significant role in determining a clay's permeability. The size and valence of the adsorbed cations influence the thickness of adsorbed water layers on the clay surface, which in turn affects the fabric. The thickness of these double layers or diffuse layers determines whether attractive forces among individual clay edges and faces is dominant, forming clay aggregates, or whether repulsive forces which result in dispersed, homogeneous mixtures are greater. Clay aggregates form larger pore spaces and therefore are responsible for larger permeability coefficients. A dispersed clay that is homogeneous has a much smaller porosity and lower permeability than a compositionally equivalent aggregated clay.

There is a large amount of literature available on how various cations affect the thickness of the water double layer adsorbed on clay minerals (Grim, 1968; van Olphen, 1977). In general, monovalent cations like  $\text{Na}^+$  tend to form thicker double layers, and adsorb more water in interlayer

sites than polyvalent cations such as  $\text{Ca}^{2+}$ . The thicker double layers effectively reduce fluid flow near the clay particle.  $\text{Ca}^{2+}$  with its limited adsorption of water does not form thick diffuse layers, thereby limiting the retarding effect the water layers have on nearby fluid flow. Figure 2-1 confirms that clays saturated with  $\text{Na}^+$  ions have lower hydraulic conductivities than the equivalent clays saturated with  $\text{Ca}^{2+}$ .

The ionic strength of permeant solutions also is very important in determining the thickness of the diffuse water layers. Low ionic strengths produce thick adsorbed water layers associated with clay minerals, which decrease in thickness as ionic strength increases. This effect of ionic strength is most noticeable in lowering the permeability coefficient for clays with monovalent interlayer cations (Mesri and Olson, 1971). Ionic strength has limited effect in altering the thickness of diffuse double layers on clays with polyvalent cations (Berner, 1971; van Olphen, 1977).

The formation of electric double layers is limited in kaolinite and illite; therefore, the permeability coefficients are primarily affected by mechanical variables. The major exception is the formation of kaolinite floccules with sharp increases in ionic strength (van Olphen, 1977). The floccules form aggregates, with exaggerated porosities and high permeabilities. In this instance, the influence on the permeability coefficient is not dependent upon the restraining effect of thick adsorbed water layers, but upon significant changes in the clay fabric.

#### 2.1.2 Plasticity, Strength and Stress-Strain Behavior

The response of clays to stress may vary widely, depending on:

- Clay mineralogy
- Clay mineral content
- Water content and composition
- Exchange cation composition (if any)
- Degree of compaction
- Degree of cementation
- Fabric or structure

Environmental controls which may also affect the stress-strain behavior of clay include temperature, stress history, strain rate, and confining pressure. Some general patterns of plasticity and strength related to clay mineral type and content are discussed below.

### Plasticity

Water content is one of the most critical controls on the stress-strain behavior of clays. The plastic behavior of soils is conveniently described by index properties known as Atterberg Limits, which are reported in weight percent water. Table 2-1 gives Atterberg Limits for relatively pure clays. The plastic limit is approximately the minimum water content at which the material exhibits plasticity and the liquid limit is approximately the minimum water content at which it behaves as a liquid. Plastic behavior occurs only within a limited range of water contents, defined by the plasticity index ( $PI = \text{liquid limit} - \text{plastic limit}$ ). Atterberg Limits are strongly affected by clay mineral content, clay mineralogy, particle sizes, and the degree of aggregation.

Plasticity of clays involves a combination of attractive forces between particles and the lubricating action of the adsorbed water on these particles. Plastic behavior occurs when sufficient water is adsorbed to overcome these attractive interparticle forces so as to reduce the shear strength of the clay significantly. The variation in values for plastic limits of clay reflects the amount of interlayer water associated with each (Grim, 1962). Clay structure and exchangeable cations are most important in determining plastic limits for smectites, while other clays with few or no exchangeable cations show less variability. Na-smectites have the largest plastic limits and because of the large water content these values are not as well-defined as those for Ca- and Mg- smectites.

Smectites with  $Na^+$  and  $Li^+$  as exchangeable cations are capable of adsorbing the largest amounts of water before losing strength and exhibiting plastic behavior. The high plastic limits associated with smectites are a consequence of their ability to disperse into fine particles

Table 2-1. Plastic (PW) and Liquid (LW) Limits for Common Clay Minerals

Clay	Ca <sup>+2</sup>		Mg <sup>+2</sup>		K <sup>+</sup>		Na <sup>+</sup>	
	PW %	LW %	PW %	LW %	PW %	LW %	PW %	LW %
Smectite (1) (2) (3) (4)	65	166	59	158	57	161	93	344
	65	155	51	199	57	125	89	433
	63	177	53	162	60	297	97	700
	79	123	73	138	76	108	86	280
Illite (5) (6) (7)	40	90	39	83	43	81	34	61
	36	69	35	71	40	72	34	59
	42	100	43	98	41	72	41	75
Kaolinite (8) (9)	36	73	30	60	38	69	26	52
	26	34	28	39	28	35	28	29

- (1) Pontotoc, MS  
(2) Cheto, AZ  
(3) Belle Fourche, SD  
(4) Omsted, IL (25% illite layers)  
(5) Fithian, IL  
(6) Jackson County, OH  
(7) Grundy County, IL (5% smectite layers)  
(8) Anna, IL  
(9) Dry Branch, FA  
(after Grim, 1962)

that maximizes the amount of water that can be adsorbed and oriented. The importance of  $\text{Na}^+$  or  $\text{Li}^+$  exchange cations is in their ability to maximize the dispersion of these particles. Other clay minerals are not as effectively dispersed by the presence of interlayer  $\text{Na}^+$  or  $\text{Li}^+$ , such that these cations have a limited effect in determining plastic limits of illites, for example.

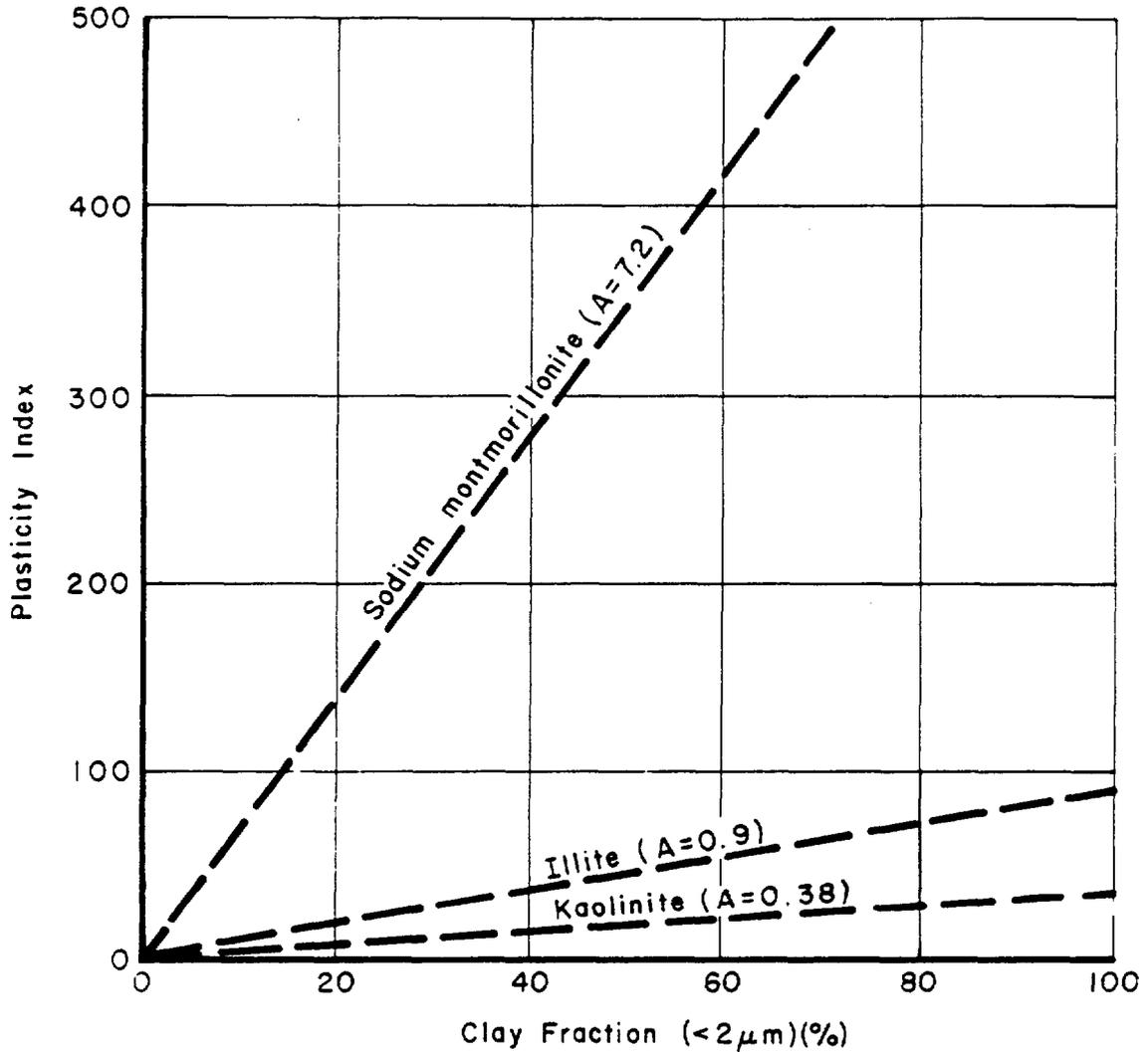
The clay mineral content in a soil or clay also strongly affects its plastic behavior. Figure 2-4 shows the relation between the plasticity index and clay content, for three clay mineral groups. It is apparent that even small amounts of montmorillonite added to a non-clay material such as sand will impart significant plasticity.

### Strength

The strength of a material reflects the stress required to cause failure which is generally manifested by a loss of load-bearing capacity and by cracking. Unconfined compression tests of clays and other materials are very common, but are less relevant with respect to clay behavior in confined conditions in repository seals than are triaxial shear strengths.

Values for shear strengths of clays are dependent upon clay mineral composition, particle size distribution, shape and arrangement of particles, and the composition of the non-clay fraction (Grim, 1962; Grimshaw, 1971). The most important determinant of a clay's strength appears to be its moisture content, and more specifically how the water is oriented on the clay surfaces. The clay mineralogy, the quantity of exchange sites, and the cation(s) located in these sites are the major factors that determine the thickness of adsorbed water layers. Clays such as smectites which have relatively thick adsorbed water layers tend to have lower shear strengths than illites or kaolinite which have thinner water layers.

The influence of clay mineral type and content is best illustrated by observing effects on the residual friction angle, which is a measure of



$$A = \text{activity of clay} = \frac{\text{plasticity index}}{\% \text{ by weight finer than } 2\mu\text{m}}$$

Non-clay fraction composed of quartz sand

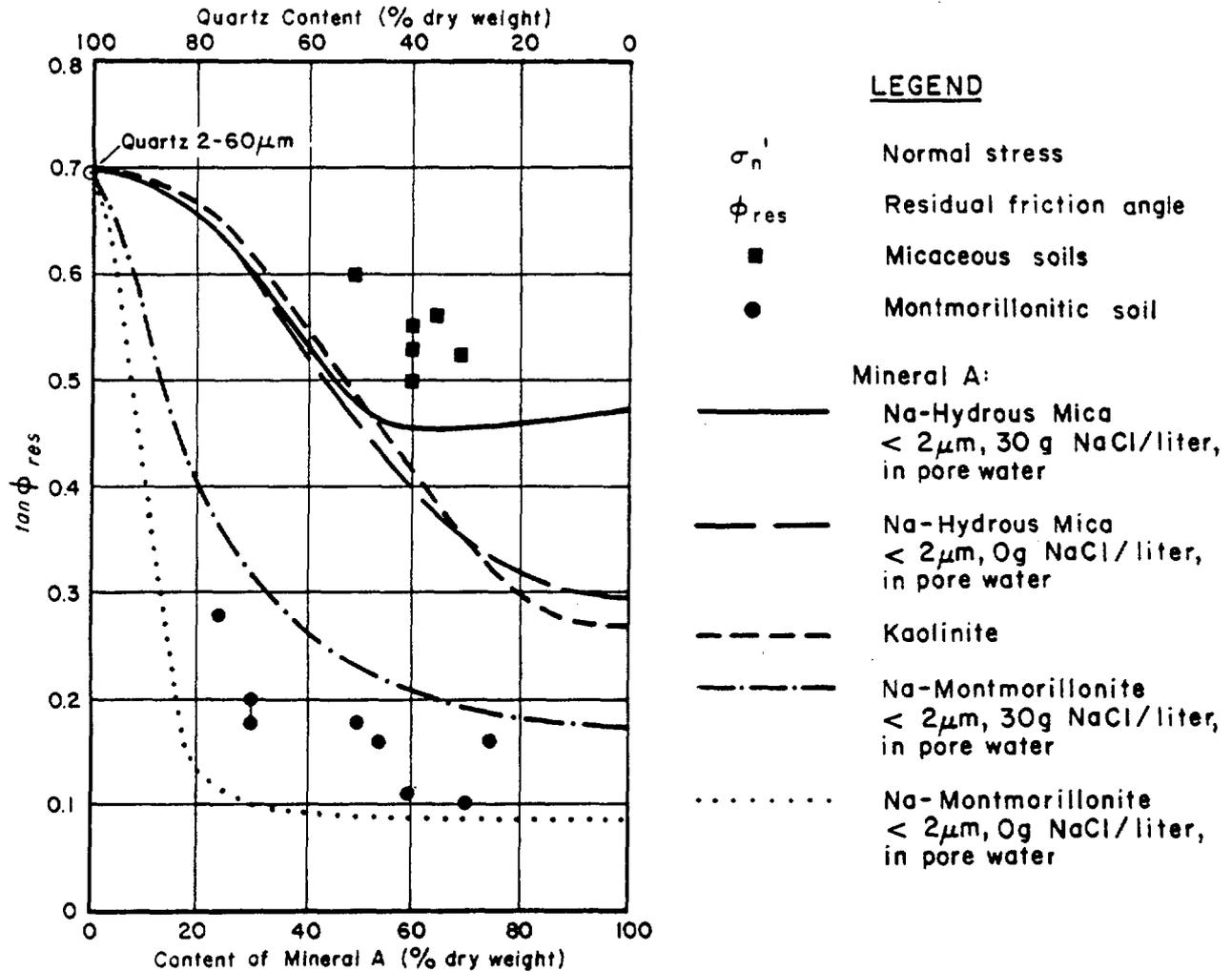
REFERENCE: LAMBE AND WHITMAN, 1969

Figure 2-4. Effect of Clay Content and Clay Mineralogy on the Plastic Behavior of Soils

minimum strength achieved at large shear displacements (Figure 2-5). Smectites have lower shear strengths than kaolinite and illite; also, the clay mineral content required to have a marked influence on shear strength in clays is less for smectite (montmorillonite) than for other varieties. The moisture content of the clay also exerts great influence on the shear strength of a compacted clay. In clays that contain little water, the shear strength is a log function of the moisture content reducing with increasing moisture content (Grim, 1962). This simple exponential behavior does not hold, however, at larger moisture contents because of the increasing importance of adsorbed water layers and a shift from frictional to cohesive forces. Clays used in repository seals may be emplaced at relatively low moisture contents, such that their strength under compressive load will be directly related to water saturation; subsequent to closure, however, clay seals and backfills may reach much higher moisture contents. Clay strength must be known for a range of moisture contents.

As noted previously, the strength of clays is affected by many parameters other than clay mineral type and content, including stress history (e.g., precompaction), fabric (especially as affected by compaction), confining pressure, the rate of loading, the rate of deformation, and temperature. Pre-compacted materials may display greater strength at the same effective normal stress than materials which have not been pre-compacted. Strength frequently increases in a clay with increased loading and deformation rates. Temperature also affects the strength of clays, although the effect is highly variable and depends on both the temperature during consolidation and the temperature during shear. Increased confining pressure also results in increased strength of the material. The reader is referred to standard soil mechanics texts for details of these complex subjects.

Under some conditions, clay materials will undergo plastic deformation, whereas other conditions can promote brittle behavior. Plastic behavior is promoted by isotropic, dispersed clay fabric, freedom from cementation, freedom from leaching and thixotropy, and a high moisture con-



**NOTE**  
 $\sigma_n' = 1.0 \text{ kg/cm}^2$  for all tests.

REFERENCE: AFTER MITCHELL, 1976

Figure 2-5. Effect of Clay Content and Clay Mineralogy, Including Hydrous Micaceous, on the Residual Friction Angle of Soil Under Shear Stress

tent. The environmental conditions present in a seal zone (temperature, and ground water chemistry) will affect the deformation behavior of a clay seal, as will the compaction method and molding water content.

### 2.1.3 Volume Stability

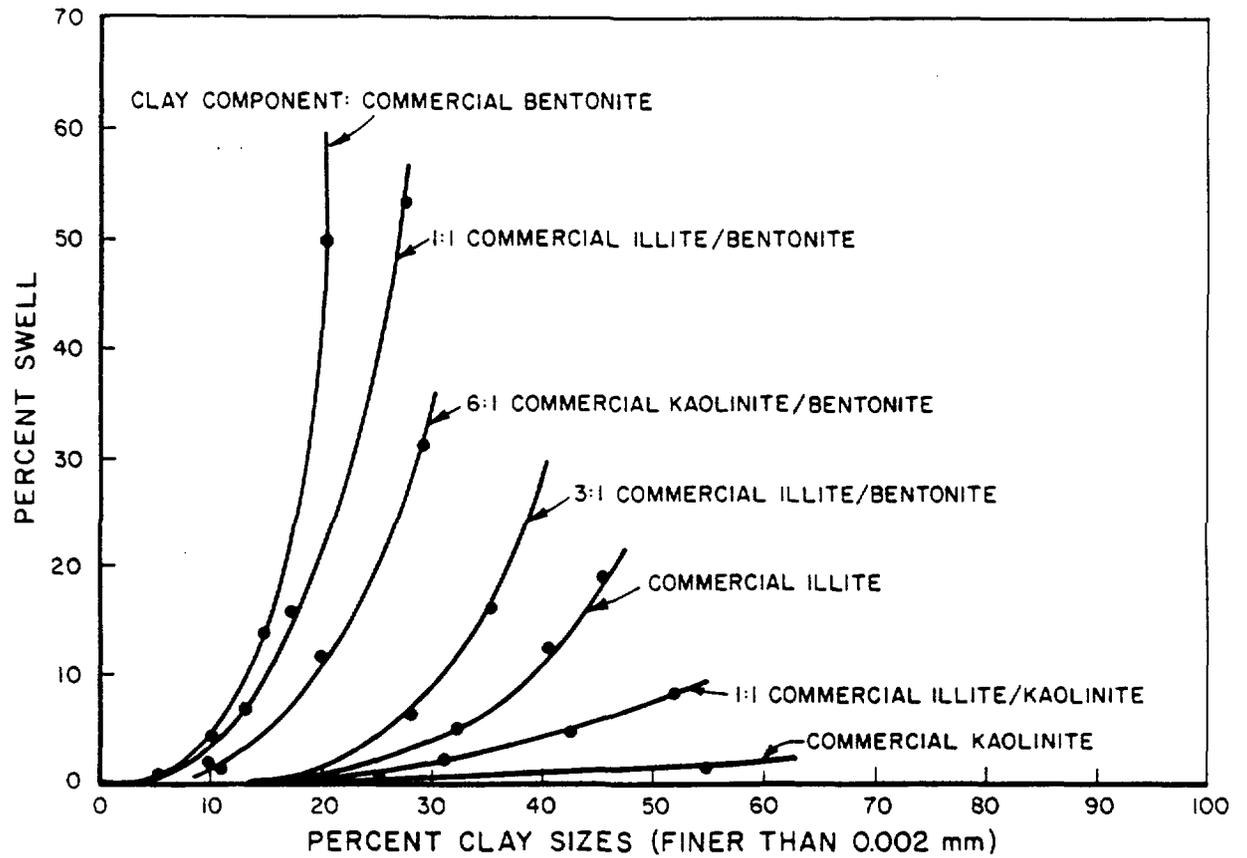
#### 2.1.3.1 Compressibility, Shrinkage, and Swell Pressure

Volume changes in clay seals or backfills may result from compression in response to increased confining stress, shrinkage in response to desiccation, swelling in response to increased water content, erosion, or thermal behavior. Volume stability of a clays will depend upon:

- Clay mineralogy and chemistry
- Clay mineral content
- Precompaction and void ratio
- Stress history
- Fabric anisotropy
- Pore water content and chemistry
- Temperature

Some unsaturated clays swell significantly if water is added. If the clay is confined, this process results in a swelling pressure, the magnitude of which will be affected by the same parameters listed above. In general, the more plastic clays, particularly those containing smectite clays, have the highest swelling capacity if contacted by water, and will exhibit the greatest swelling pressure if confined. These clays also tend to be the most compressible, and they undergo the largest volume shrinkage with drying. Figure 2-6 shows the effect of both clay type and content on swelling capacity for various clays. It can be seen that even a small proportion of smectite (bentonite) imparts a significant swelling capacity. Illite, without added smectite, has a moderate swelling capacity. Among the smectite clays, those with lithium, sodium or potassium in the exchange cation position tend to display greater compressibility, swelling, and shrinkage than other smectites.

Fabric may affect the compressibility and swelling capacity of a clay material. Flocculated structure results in a clay that is generally more expansive than would result from the same material with a dispersed



NOTE: PERCENT SWELL MEASURED UNDER 1 PSI SURCHARGE FOR SAMPLE COMPACTED AT OPTIMUM WATER CONTENT TO MAXIMUM DENSITY IN STANDARD AASHO TEST.

*After Seed, Woodward and Lundgren (1962) and Chen (1975)*

Figure 2-6. Relationship Between Percentage Swell and Percentage of Clay Size Particles for Experimental Soils

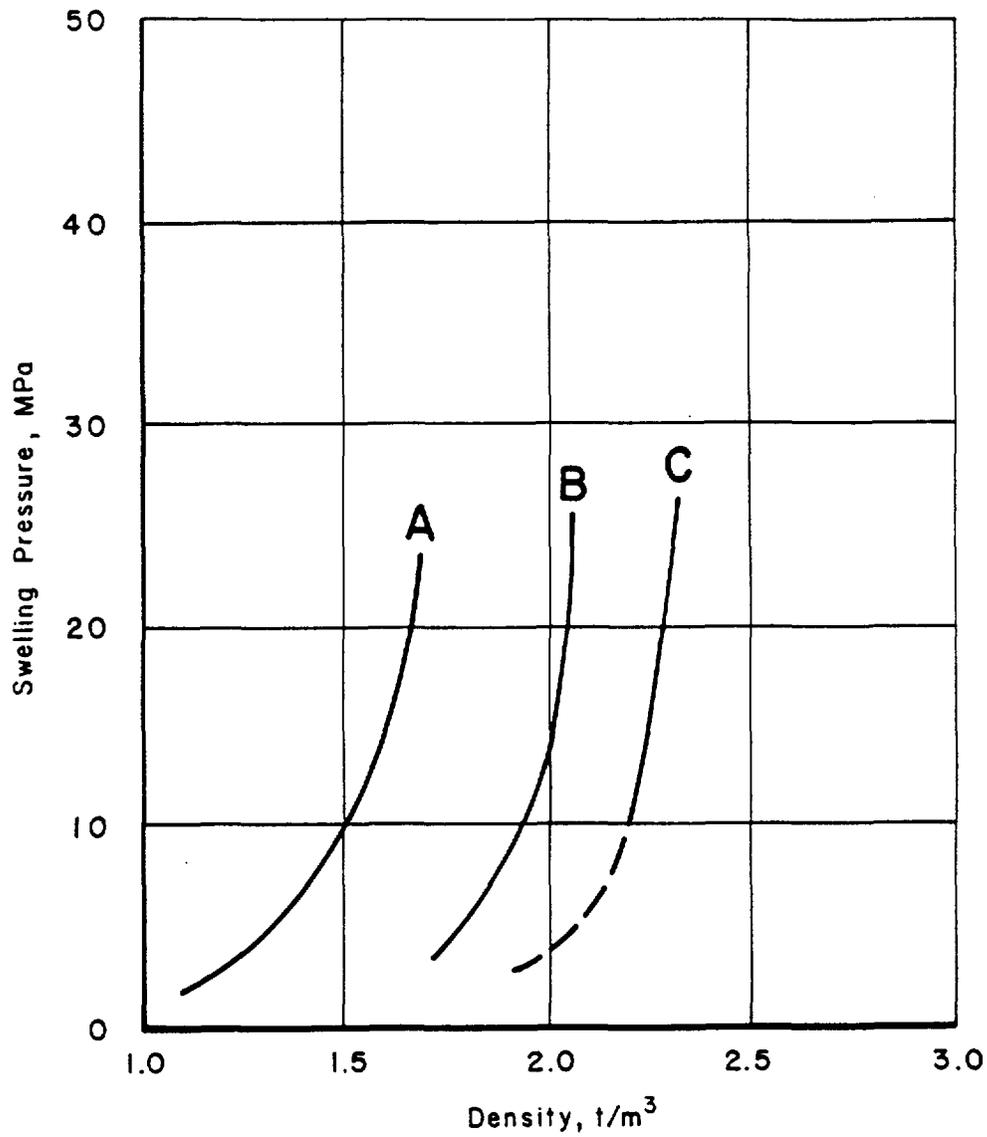
structure. If a clay seal is subjected to compressive stresses lower than its emplacement consolidation pressure, a flocculated structure in the clay may be less compressible than a dispersed structure in the same clay. The effect of structure, however, can be reversed if the compressive stress on the seal surpasses the emplacement consolidation pressure.

Fabric anisotropy may be responsible for differential compressibility and swelling capacity of a material. Because the swelling of individual smectite grains is largely due to water adsorption between silicate layers, alignment of smectite clay platelets might be expected to generate larger volumetric expansion or swell pressure perpendicular to the direction of alignment than parallel to the platelet alignment.

Well compacted clay materials tend to be less compressible and possess a greater capacity for swelling than normally consolidated or unconsolidated materials. As shown in Figure 2-7, the swelling pressure of compacted bentonite increases with increasing density (or lower void ratio). The lower swelling pressures generated by the less dense materials reflect internal expansion into pore spaces. Thus, the compressibility, swelling volume, and shrinkage of a clay seal will all depend on emplaced bulk density or void ratio.

#### 2.1.3.2 Erodability

A clay-bearing seal may not remain relatively impermeable if it erodes by piping or by dispersion in seepage water. Piping of a granular plug or backfill into fractured host rock or adjacent seals may occur when the system is subjected to a hydraulic head. Particle size, fracture width, hydraulic head, and flow velocity are controlling factors in the susceptibility of a granular material to pipe along fractures. Large grain size, small fracture width, and low hydraulic head are factors which tend to allow a granular material to clog fractures, reduce fracture permeability, and prevent further piping. Plastic clays are less susceptible to piping than non-plastic, cohesionless clays or soils.



- A - CALCULATED, BASED ON DRY DENSITY OF COMPACTED BENTONITE  
 B - CALCULATED, BASED ON BULK DENSITY, COMPLETE WATER SATURATION OF COMPACTED BENTONITE  
 C - MEASURED, BENTONITE EXPOSED TO EXTERNAL WATER AT CONSTANT VOLUME

REFERENCE: PUSCH, 1978A

Figure 2-7. Calculated and Measured Effects of Density on the Maximum Swelling Pressure of a Compacted Wyoming (Na-) Bentonite

Dispersion is the deflocculation of a flocculated clay fabric and the removal of the clay material in suspension. Dispersion is potentially a detrimental process because it can result in the displacement of materials from the seal zone, even with little or no velocity of the eroding fluid. Dispersion of Na-bentonite extruded through a fracture was studied by Pusch (1978a).

Dispersion of a clay is dependent on the sodium content of the pore fluid, and on the total dissolved solids (TDS) of the pore fluid. At low TDS, the sodium content of the pore fluid does not affect dispersivity, and few clays tends to be dispersive. As TDS increases in the pore fluid, most soils in which Na in the pore fluid is 60% of the TDS or greater\* are dispersive. The composition of the eroding fluid also affects dispersivity. Fluids which contain the same or greater sodium content as the pore fluid tend to suppress dispersion, whereas fluids with lower sodium contents tend to promote dispersion of a soil (Sherard et al, 1976; Arulanandan et al, 1975).

The dispersivity of a clay-bearing material or soil does not appear to be strongly related to its mineralogy, although clays with a high exchangeable sodium content, such as the Na-smectites found in Wyoming (Na-) bentonite, may be more dispersive than a clay such as kaolinite. Dispersion of sodic clays may be considerable in the relatively fresh ground waters expected in tuff, basalt, granite, or argillaceous formations, whereas saline ground waters might minimize dispersion. Pusch (1978a), however, suggested that Na-bentonite extruded through a fracture will tend not to disperse in granitic ground water to any large extent, because the dissolved ions in granitic ground water will tend to flocculate the very low concentration of bentonite particles at the distal (or leading) edge of a swelling bentonite gel. Thus, Pusch suggests that, in addition to the factors controlling dispersivity

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\* $\frac{(\text{Na}) \times 100}{(\text{Na}+\text{Ca}+\text{Mg})} > 60\%$

mentioned above, the amount or concentration of clay available to the dispersing fluid is a further control on the degree of dispersion a clay material will undergo.

#### 2.1.4 Thermal Properties

Thermal properties of soil vary widely, depending largely on mineralogy (clay and non-clay), density, temperature, and water content (degree of saturation). Fabric will also affect thermal properties, particularly thermal conductivity, and perhaps thermal expansion. Fabric anisotropy will result in thermal behavior anisotropy. Figure 2-8 shows a plot of thermal conductivity of silt and clay soils versus water content, at several compacted densities. Increased density and water content tend to increase thermal conductivity.

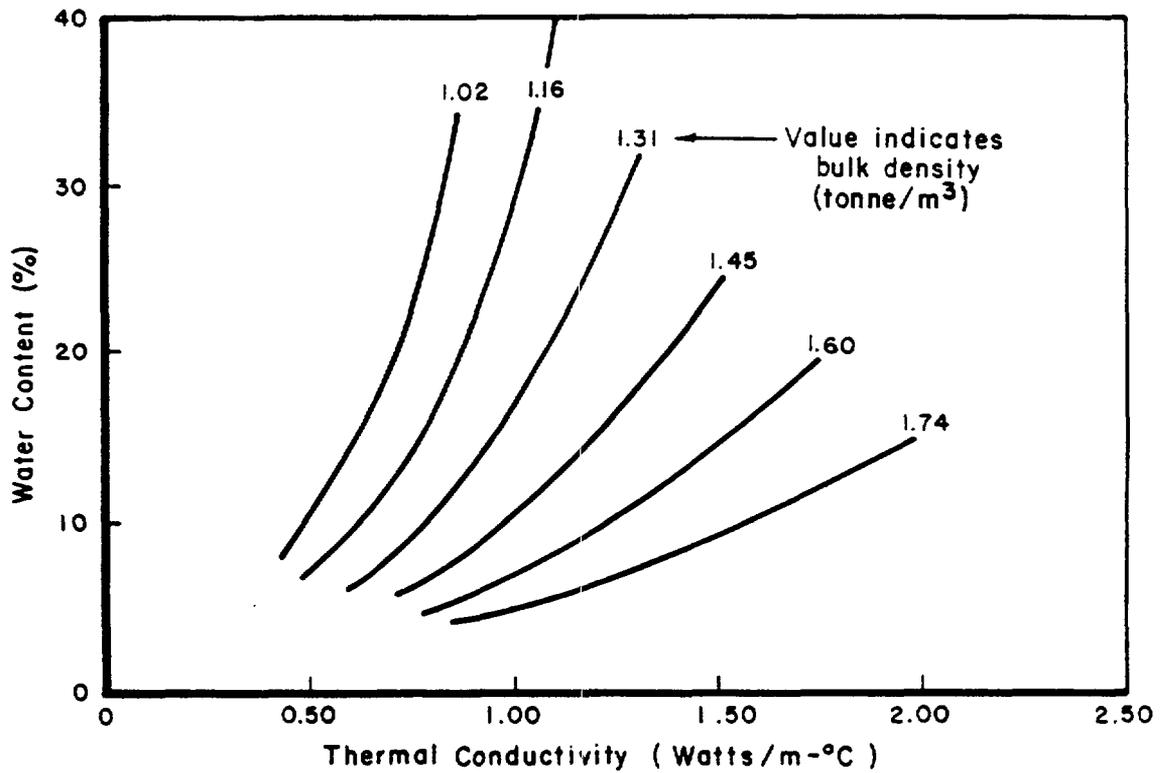
Molecke (ONWI, 1982b) reported thermal conductivities for dry bentonite-sand mixes (100:0, 70:30, 50:50, 30:70, by weight percent bentonite:sand) compacted to 1.98 to 2.12 t/m<sup>3</sup>, in the temperature range 25°-300°C. Lowest values (0.58-0.80 W/m-K) were found in the 100% bentonite samples. Highest values occurred in the 50:50 mix (1.06-1.17 W/m-K). The thermal conductivity of the 70:30 mix is almost equivalent to the 50:50 mix. Molecke (ONWI, 1982a) has also reported thermal conductivity values for 30% bentonite-70% crushed salt mixes under 10MPa axial stress (dry density 1.67-1.71 t/m<sup>3</sup>) between 21°-250°C. Values increased between 21° and 89°C (1.01 to 1.12 W/m-K) falling to 0.99 W/m-K at 250°C.

## 2.2 CLAYS TESTED IN MODEL SEALS

The use of model tests to examine the performance of clay materials specifically for repository sealing and nuclear waste isolation has continued since about 1975 with the initial studies by Martin (1975) and Olsen and Martin (1976). More recently, Taylor et al (1980) reported extensively on model tests of clay-bearing materials for sealing a projected repository in the Hanford, Washington, basalts.

### 2.2.1 Model Test Design

An example of model test design is shown in Figure 2-9. In general,



REFERENCE: MITCHELL, 1976

Figure 2-8. Effect of Water Content and Bulk Density on the Thermal Conductivity of Soil

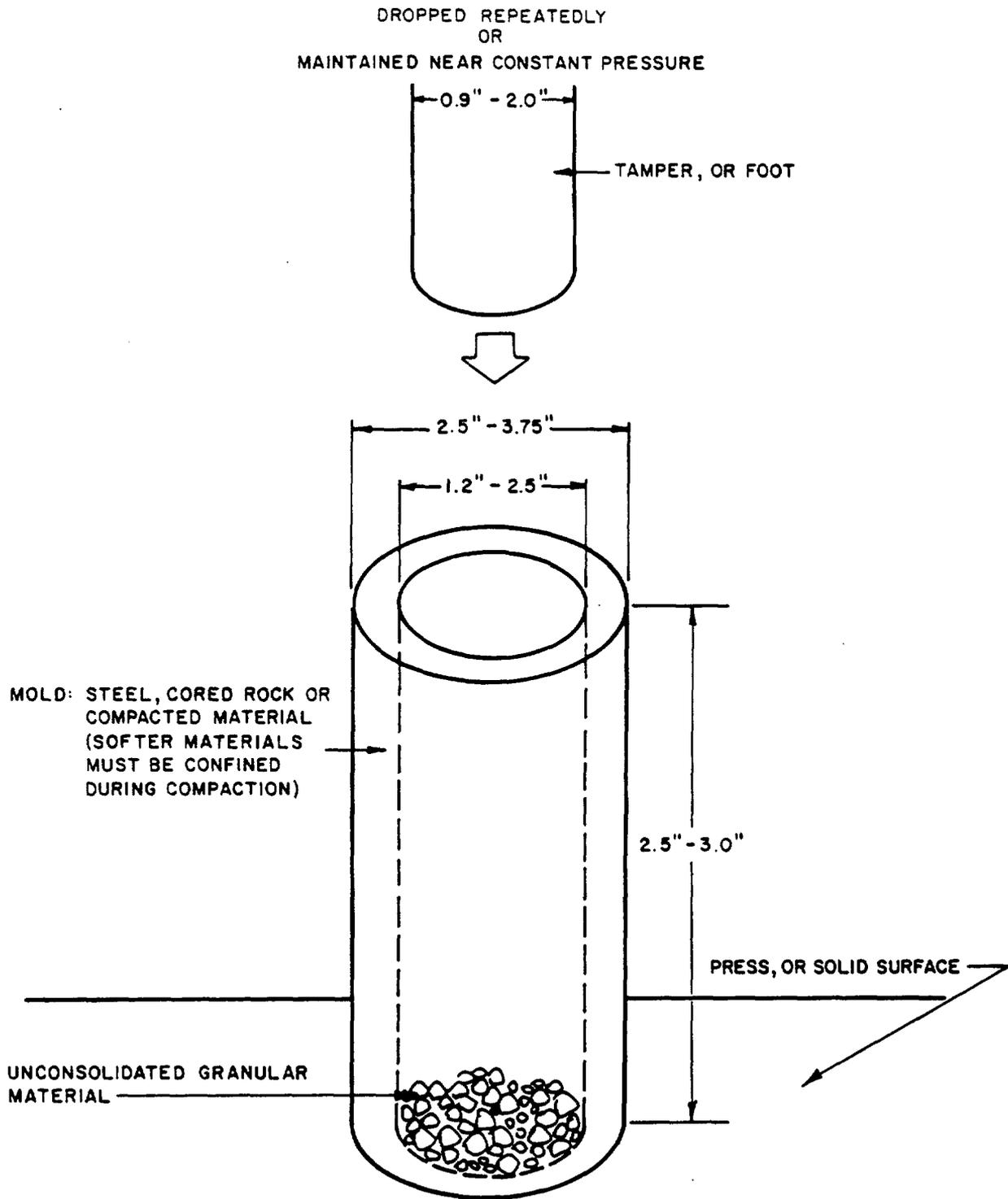


Figure 2-9. Generalized Configuration for the Construction of Model Plugs Composed of Granular Materials, as Described in Martin (1975) and Used in the MIT Model Testing Program

granular materials are placed into a hollow cylinder composed of metal or rock. The inner walls of the cylinder may be pretreated by abrasion, polishing, or by "mudding" the hole, in order to simulate varying bore-hole conditions. The candidate seal materials are compacted in the laboratory, and the consolidation pressures, water contents, and resultant densities are monitored. Compaction methods which are frequently used in model tests are static and impact compaction. In the former method, a constant consolidation pressure is applied for a specified time. In the latter, a mass is repeatedly dropped from some distance, the thickness of individual lifts and the number of impacts per lift can be varied. Alternative compaction methods, such as rollers or kneading compaction have not been studied extensively. Taylor et al (1980) included a limited study of model seals emplaced as aqueous slurries.

In addition to alternative emplacement methods the model test programs have employed a variety of candidate materials. Martin (1975) and Olsen and Martin (1976, 1980) tested three pulverized shales; the Ninnescah Shale (Kansas), Dewey Lake Shale (New Mexico), and Conasauga Shale (Tennessee), plus a montmorillonite (commercial smectite-bearing bentonite) both as a natural composite and as a component in engineered composites. Table 2-2 shows the shale mineralogies. In the tests with the natural shales, both fresh (unweathered) and outcrop materials were used. Taylor et al (1980) employed two bentonites, Oregon (Ca-) bentonite and a Wyoming (Na-) bentonite, and Ringold D Clay (from the Pasco Basin in southeastern Washington) as the major components in their model tests. Additives such as smectite clay, sand, and aggregate have been used in some samples.

### 2.2.2 Model Test Results

The results of model tests (Martin, 1975; Olsen and Martin, 1976, 1980; Taylor et al, 1980) tend to support the conclusions regarding the general behavior of soil and other fine-grained material summarized in Section 2.1. Permeability test results are tabulated in Appendix C, and major model test conclusions are summarized below.

- The permeability of model seals tends to decrease with increased clay content, particularly with

Table 2-2. Mineralogic Composition of Three Natural Shales  
Studied in MIT Model Tests (Weight Fraction)

MINERAL	CONASAUGA SHALE		NINNESCAH SHALE		DEWEY LAKE SHALE	
	CORE	OUTCROP	CORE	OUTCROP	CORE	OUTCROP
Non-clay*	0.52	0.25	0.58	0.38	0.65	0.74
Clay	0.35	0.35	0.27	0.42	0.20	0.10
Total**	0.87	0.60	0.85	0.80	0.85	0.84

---

CLAY MINERALS

Illite	0.5	0.4	0.5
Chlorite	0.05	0.1	0.1
Smectite	0	0.05	0
Vermiculite	0.2	0	0
Mixed-layer	0.15 (illite- vermiculite)	0.5 (chlorite- smectite)	0.4 (chlorite- smectite)
Kaolinite	0.05	0	0

\*Quartz, feldspar, dolomite, calcite, hematite

\*\*Weight fraction data based on x-ray diffraction studies. The 13-40 weight percent unaccounted for may be due to phases amorphous to x-rays or differences between the samples (mineralogic, mass absorption coefficients) and the reference standards used.

Ref: Martin (1975)

increased swelling- and mixed-layer-clay content (Martin, 1975; Olsen and Martin, 1976, 1980). This has been demonstrated for natural clays, as well as for synthetic composites. Smectite clay additive is particularly effective in reducing the permeability of composite material seals. Permeabilities of 1 microdarcy or less were frequently achieved using materials high in smectite clays.

- In tests with compacted shale material, fluid flow was observed to be concentrated at the seal-host interface.
- Smectite clay content of a clay material seal directly controls the swelling capacity and swell pressure of the seal, all other parameters being equal (dry density, water composition and content, temperature, etc.).
- In most cases, for a given compacted clay material, swell pressure is inversely related to water content. Initial dry density shows little relation to swell pressure of compacted shale materials. The addition of non-swelling materials (e.g., sand) markedly decreases the swelling capacity and pressure of materials. Addition of smectite clay enhances the swelling capacity and pressure of materials, particularly when the ratio of swelling clay (smectite or bentonite) to non-swelling component is greater than 1:9.
- Maximum constant volume swell pressure of a given expansive clay-sand mixture is enhanced by increased compaction, which decreases the porosity or void ratio in the plug.
- Volume increase (swelling) causes an abrupt depletion in swelling pressure which can be achieved by a given material. As little as 1% axial strain in compacted pulverized shale model plugs (optimum water content) reduces the swelling pressure by about 50%.
- Shrinkage of clay-bearing materials due to desiccation is least in test samples with lowest molding water contents. In samples with low initial permeabilities (<1 microdarcy), the low permeabilities may be restored after drying and shrinkage under room conditions by reintroduction of water.
- The compressive strengths of composite clay seals compacted to maximum dry density and optimum water

content generally range between 1 to 3 MPa. Samples containing Oregon (Ca-) bentonite developed strengths about 50% greater than samples containing Wyoming (Na-) bentonite, at equivalent sand:bentonite ratios. Maximum compressive strength for sand-bentonite composite materials occurs in 50:50 mixes.

- Young's moduli for sand-clay composite materials, compacted to maximum dry density and optimum water content, were measured as the tangent of stress-strain curves at 1% strain. The highest modulus (80 MPa) occurred in the 50% Oregon bentonite-sand composite. The maximum modulus for Wyoming bentonite-sand composites also occurs in 50:50 mixes.
- Increasing the clay content, particularly the smectite clay content, increases the compressibility of the material. Upon uniaxial unloading (see Figure 2-9 for test configuration), samples with a small (10%) smectite clay component displayed permanent volume reduction. Samples incorporating about 50% smectite clay displayed volume increases upon unloading from consolidation pressures less than 3 MPa, increasing the void ratio of the original material.
- Bonding strength of saturated model seals composed of shale materials compacted into clean or mudded holes was generally greater than 1 MPa, determined by push out tests. Generally, push out strength is greater in clean than in mudded holes. Compacted bentonite or smectite clay seals tend to have much lower push out strengths under the same conditions. Push out tests of sand-bentonite composite materials compacted in clean boreholes in basalt showed maximum values at the highest sand:bentonite ratio tested (90:10), suggesting the importance of the frictional component to the strength of the interface bond. Addition of bentonite to the composite material reduced push out strength markedly. In general, Oregon (Ca-) bentonite produced greater bond strength, at each sand-bentonite ratio, than Wyoming (Na-) bentonite. Bond strength recovered when sand:bentonite ratios were increased above 20%, perhaps due to increase of the cohesive component on the push out strength of the material with the higher clay content.
- Limited tests of slurried clay composite materials showed negligible bond strength, except with bentonite pellets included in the sample. The

lowest hydraulic conductivity measured for slurried materials was  $1.2 \times 10^{-8}$  cm/sec (50% coarse aggregate, 25% crushed zeolite, 19% Ringold D Clay, and 6% Shurgel, a processed bentonite). Under a slight hydraulic pressure (0.025 MPa), piping occurred through a similar seal emplaced as a slurry.

- The consolidation pressure required to achieve a low permeability seal (e.g.,  $<1$  microdarcy) is drastically reduced as the montmorillonite clay component in the material increases.
- Martin's tests also showed that unsaturated compacted montmorillonite model seals may pipe when a high hydraulic pressure (0.6 MPa) is rapidly applied. When permitted to soak up water under a low hydraulic head (0.069 MPa), piping did not occur.

### 2.3 PRECOMPACTED BENTONITE

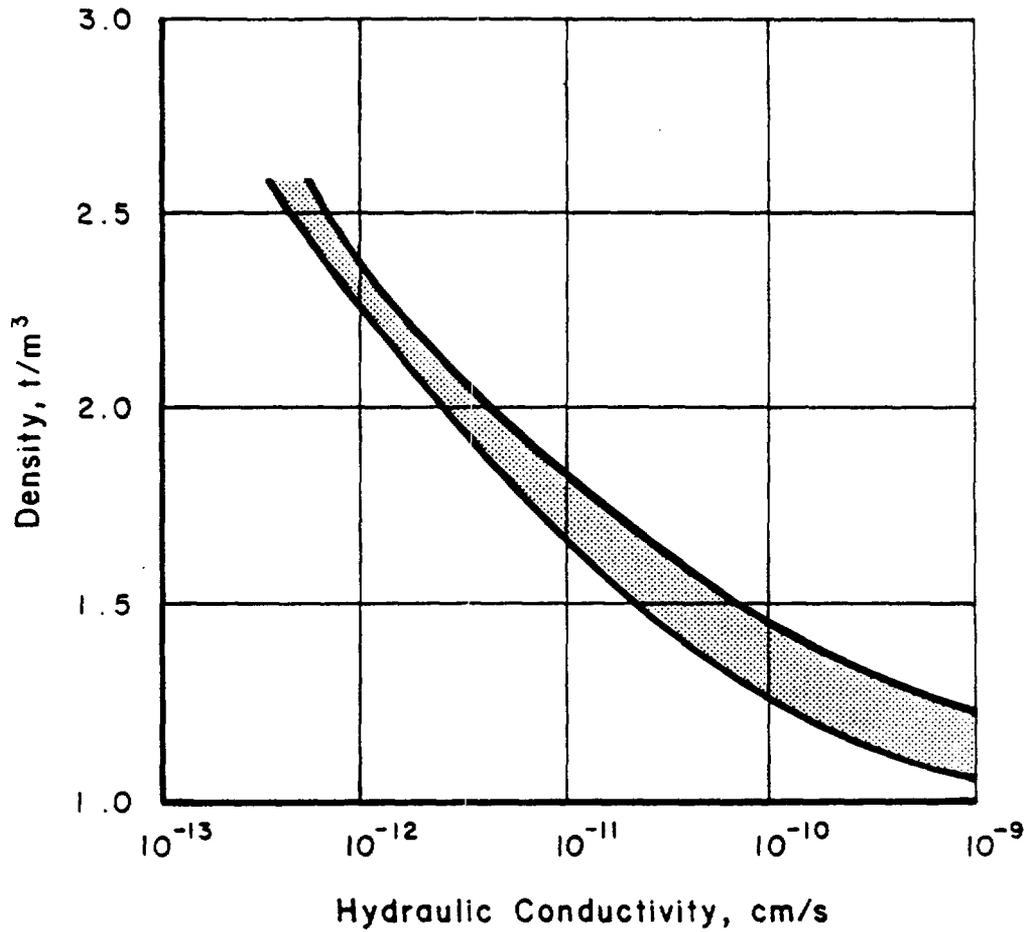
The use of precompact bentonite for nuclear waste isolation has been studied most intensely by the Swedish KBS. Much of the impetus for these studies has been the potential use of bentonite as a waste package backfill and as tunnel backfill (Pusch, 1978a; Pusch et al, 1979; Neretnieks, 1979). Reports have described the use of highly compacted bentonite in borehole sealing (Pusch and Bergstrom, 1980) as well as the application of bentonite for sealing fractures in the host rocks. Bentonite is also being studied within the NWTIS program (e.g., Wheelwright et al, 1981).

The use of precompact bentonite as a sealing material incorporates the following features:

- Pre-emplacment compaction is capable of greater densification than that achievable by in-place compaction.
- The emplacment of seals is by means of pellets or bricks or other manageable units of dry consolidated material.
- The fluid flow in penetrations is decreased by the swelling of the clays, upon contact with water.

Laboratory studies by Pusch (1978a,b) and others (Fagerstrom and Lundahl, 1977; Knutsson, 1977) have examined a Wyoming bentonite, composed principally of Na-montmorillonite, available commercially as Volclay MX-80. Samples are compacted under 50 MPa compression to a bulk density of 2.0-2.3 t/m<sup>3</sup>. The bentonite contains 10% by weight water, which results in a 60% water saturated bentonite mass. Results of these studies include:

- The permeability of precompacted bentonite is inversely related to the bulk density of the material, as shown in Figure 2-10. Hydraulic conductivity is increased by increased temperature and increased concentration of dissolved salts in the permeant. In composite sand-bentonite mixtures, hydraulic conductivity is reduced as the proportion of bentonite is increased (Figure 2-2).
- For Pusch's standard compacted bentonite, the maximum swell pressure achieved was 10 MPa (1450 psi). Figure 2-7 shows the dissipation of maximum swell pressure commensurate with density decrease (volume increase) of the clay body. It is apparent that swell pressure can be tailored by bulk density adjustments or by addition of non-swelling additives.
- Experimental studies have shown the extrusion of compacted bentonite into slots 0.15 mm wide. Extrusion rate is a function of slot (joint) width and the viscosity of the extruding bentonite mass.
- The concentration of dissolved salts in the associated fluid also affects the swelling pressure. Measured swelling pressures were reduced at all water contents when the salt concentration in associated fluids was increased from 10<sup>-4</sup> mole/liter NaCl to 10<sup>-2</sup> mole/liter NaCl (Pusch, 1978a).
- As bentonite swells by the absorption of water, the hydraulic conductivity of the material increases up to a maximum of 10<sup>-9</sup> cm/sec at a bulk density only slightly denser than water itself (density = 1.0 t/m<sup>3</sup>).
- The thermal conductivity of a highly compacted (2.0 t/m<sup>3</sup>) bentonite, at 66% water saturation, was determined to be 0.78 W/m-°C at 73°C. Conductivity increases slightly with temperature. At constant volume the conductivity of a 100% water



REFERENCE : PUSCH, 1978 A

Figure 2-10. Effect of Density on the Hydraulic Conductivity of Compacted Wyoming (Na-) Bentonite

saturated, compacted bentonite increases to 0.9-1.3 W/m-°C (Knutsson, 1977). Roy (ONWI, 1982c) reported thermal conductivities in the range 1 to 3.5 W/m-°C for bentonites compacted to 1.6 to 2.0 t/m<sup>3</sup> with water contents of 5 to 16 percent. For sand-bentonite composite mixtures, with bentonite contents of 10-20%, Fagerstrom and Lundahl (1977) report values ranging from 0.5 to 2.0 W/m-°C for water content ranging from 5-30%.

- Highly compacted bentonite (2 t/m<sup>3</sup>, 10% water content) has a Young's modulus and Poisson's ratio of 300 MPa and 0.15, respectively. Poisson's ratio increases, and Young's modulus and viscosity decrease with the uptake of water

#### 2.4 EVALUATION OF CLAY SEALS AS FLUID FLOW BARRIERS

Clay materials appear highly promising as fluid flow barriers in penetration seal systems. In addition to application as specific fluid flow barriers, clays may be used as a component of backfills (added to rock fill to reduce permeability or increase sorptivity), or as grouts to seal rock fractures. Favorable properties include fine-grain size, low internal permeability, workability and, for some varieties, swelling capacity. Additional study is required, however, in a number of areas.

- Interface Permeability  
Tests are required to compare the performance of seals with swelling and non-swelling clays and to determine optimum clay proportions.
- Volume Stability  
Tests are required to determine the effects of heating (drying) on seal permeability, as well as the reversibility of any changes when water is reapplied. Consideration must be given to the possibility for piping into fractures, or for dispersion in flowing ground water in specific emplacement conditions.
- Swelling Clays  
Tests are required to determine optimum swelling capacity which will minimize interface permeabilities but not produce excessive swelling pressures. Other tests should be performed to evaluate the ability of swelling clays to penetrate and seal rock fractures and to relate clay properties to specific fracture characteristics to

optimize the sealing of fractures. The behavior of bentonites in saline ground water must also be evaluated.

- Synergistics  
Tests are required to determine possible adverse internal interactions between adjacent seal components or between seals and the host rock and the ground water.
- Thermal Properties  
Tests are required to determine thermal properties for candidate clay-bearing materials.
- Emplacement Considerations  
All properties must be considered in terms of possible emplacement techniques. Particular consideration must be given to control of fabric anisotropy, to methods for achieving adequate compaction near to penetration surfaces (especially borehole walls and tunnel ceilings), to the possible effects of compaction methods on the host rock or adjacent components, and to quality control in general.

Further consideration of additional testing for clay materials is given in Section 6.0. Emplacement methods are considered in Section 5.0.

### 3.0 CLAY SEALS AS SORPTIVE MEDIA

The ability of clays and other phyllosilicates to sorb ions from solutions has long been recognized and the mechanisms and controls on the sorptive behavior of clays are moderately well known. In order to minimize the movement of radionuclides from a repository, the use of seals and backfills containing clays as sorbers of radionuclides leached from waste by ground water has often been proposed. Clay sorbent may be used as a waste package backfill, and in room and tunnel backfills in close proximity to the emplaced waste. Sorptive components may be less important in shaft and borehole seal systems in which the primary sealing objective is fluid flow reduction.

The affinity, or sorptivity, of clays and clay minerals for radionuclides dissolved in aqueous solutions has been investigated experimentally using a variety of materials, radionuclides, carrier fluid compositions and physiochemical conditions. The phenomenon of sorption in these investigations is the result of several mechanisms: cation exchange, adsorption, precipitation, chemical reaction, molecular sieving, and probably others. The effects of individual mechanisms on the sorptivity of materials are not investigated in most recent radionuclide sorption studies which account for all sorption mechanisms simultaneously in measurements of the sorption constant or  $K_d$ . The nature and results of these experimental studies on clays and clay minerals are reviewed in Section 3.2.

The geochemical basis of the ability of clay minerals to sorb ions from aqueous solutions has been intensely studied, particularly with respect to the mechanism of cation exchange. Because cation exchange properties in clay minerals are well understood and largely predictable, this property may be used to select candidate clays for use in sorptive seals, to estimate the expected performance of such seal materials, and to select materials for laboratory testing. The following section summarizes the knowledge regarding cation exchange in clay minerals.

### 3.1 CATION EXCHANGE PROPERTIES OF CLAY MINERALS

Cation exchange usually refers to the replacement of one hydrated ion on a negatively charged clay mineral surface for another as a result of changes in the surrounding solution chemistry. As a matter of convention, the creation of negative surface charge required for cation exchange reactions occurs by substitution within the clay mineral lattice of lower valence cations for higher. The cation exchange capacity of a negative double layer is often defined as the excess of counterions (cations on a negative surface) which can be exchanged for other cations (Stumm and Morgan, 1970).

#### 3.1.1 Cation Exchange Capacities of Common Clay Mineral Groups

The various clay mineral groups have a wide range in cation exchange capacities, reflecting their diversity in composition and structure (Table 3.1). The range of values for an individual clay mineral reflects how interlayer cations become increasingly replaceable as clay particle size or crystallinity decreases or the time of treatment increases. As interlayer cations become increasingly replaceable, the cation exchange capacity of that clay also rises.

When comparing exchange capacity results among various studies, it is necessary to recognize that techniques and procedures are as much responsible for the diversity in values as is compositional heterogeneity. Chemical pretreatment exerts considerable influence over cation exchange capacity measurements. A further example of experimental distortion is that at lower pH the additional competition of  $H^+$  for available sites effectively reduces the cation exchange capacity (Grim, 1968). It is only recently that studies have been standardized at pH 7. Cation exchange generally is measured by titration methods or by actual solution analyses, and the results are reported in milliequivalents per 100 grams of sample (meq/100g). The use of equivalents as a concentration unit best reflects the number of available exchange sites on the clay.

Table 3-1. Cation Exchange Capacities of Clay Minerals  
(in milliequivalents per 100 grams of sample)

kaolinite	3-15
smectite	80-150
illite	10-40
vermiculite	100-150
chlorite	10-40

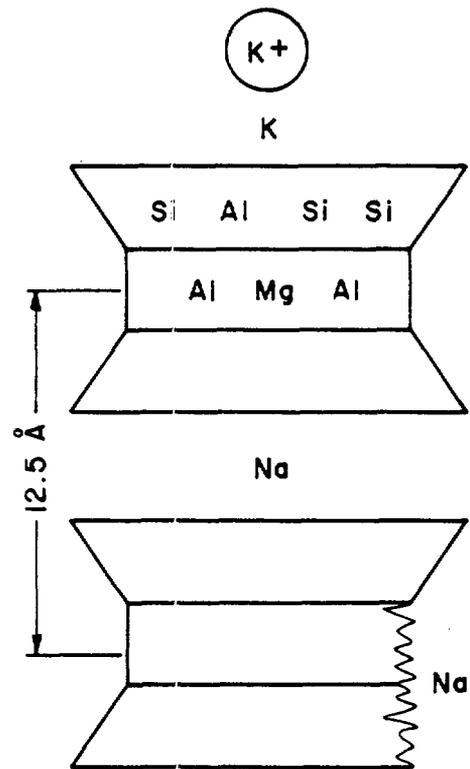
(from Grim, 1968)

Much of the charge imbalance created by broken bonds is focused along noncleavage planes (Figure 3-1). For clay minerals this greater density in unsatisfied charge is parallel to the c-axis. The percentage of broken bonds per unit volume increases with smaller particle size, decreased crystallinity, or an increased structural distortion (Grim, 1968). Exchange sites created by broken bonds comprise most of the kaolin group exchange capacity, but no more than 20% of the capacity exhibited by smectites.

Substitution of lower valence cations for higher within the clay mineral structure creates an excess negative layer charge which is neutralized by the adsorption of cations on the surface. The most common substitutions which occur during progressive diagenesis of smectites are Al for Si in the tetrahedral sheets and Fe or Mg for Al in the octahedral sheets (Hower et al, 1976).

Another means of creating an excess negative charge is by removing hydrogen on exposed hydroxyls. This is a relatively minor cause and is restricted to the kaolin group which has a basal surface defined by the octahedral sheets. Charge deficiencies also are not always balanced by adsorbed cations, but by further solid solution substitution such as filling vacant octahedral sites or  $\text{OH}^-$  groups replacing O.

The low cation exchange capacities of the kaolin group, 3-15 meq/100g sample, indicate that much of the charge imbalance is created by broken bonds around the edges. Despite the isochemical nature of kaolins and



REFERENCE: AFTER MITCHELL, 1976; GRIM, 1968

Figure 3-1. Schematic Figure of Stacked 2:1 Layers Indicating the Two Major Locations of Exchange Sites (Broken Bonds on the Edges of Clay Minerals Provide a Source of Charge Unbalance that is Countered by the Adsorption of Exchange Ions. Substitution Within the Structure Creates Available Sites on the Basal Planes Between Stacked Layers.)

the lack of observed solid solution substitution, it is possible that some of the excess negative charge results from tetrahedral substitution. The replacement of 1 Si atom per 400, which is beyond detection limits for most analytical techniques, can produce an exchange capacity of 2 meq/100g (Grim, 1968). The rate of cation exchange in kaolinites is virtually instantaneous, reflecting the location of the exchange sites along easily accessible particle edges. The increase in broken bonds associated with decreased particle size and crystallinity also serves to enhance the exchange capacity of kaolin minerals.

The chlorite group of clay minerals is also characterized by a moderately low cation exchange capacity, though there is a fairly large range of values between 10 and 40 meq/100g. Despite the large amount of solid solution substitution, especially within the octahedral sheet, the collapsed interlamellar spacings, along with those clogged with hydroxide precipitates which characterize the chlorite structure, effectively reduce the number of available sites. The range of measured capacities reflects the large amount of substitution found in chlorites in addition to the variable degree of isolation of the interlayer basal plane exchange sites.

Illite clay minerals have exchange capacity values very similar to those found in chlorites, 10 to 40 meq/100g. Again, like chlorites, despite the large amount of solid solution substitution the inaccessibility of basal plane exchange sites limits the exchange capacities of illites. Exchange capacities for illites increase with decreased particle size or crystallinity as the number of broken bonds is increased. Rates of exchange for illites are very slow, at times requiring days to affect a complete exchange in laboratory experiments. Since most of the lattice substitution in illites is located in the tetrahedral sheet, the attractive forces between the clay structure and an adsorbed cation are often great enough to dehydrate the cation, collapse the interlayer by expelling that water, and thereby fix the cation within the illite.

The smectite family of clay minerals has the largest cation exchange capacities, 80 to 150 meq/100g, rivaled only by the similar-structured vermiculites. Most of the exchange sites in smectites are associated with lattice substitution, though as many as 20% may be attributed to broken bonds around the edges. Despite less solid solution substitution and a smaller excess negative body charge than found in illites and chlorites, the smectites have a much greater exchange capacity due to the expansion of all the interlayers. This swelling of the interlayers with two or more layers of water molecules allows access to the exchange sites on the basal surfaces. The limited charge within the structure, usually localized in the octahedral sheet, is insufficient to attract the exchange cations close to the basal surface and effectively fix them to the structure as in the illites. Inasmuch as cation exchange is often considered as a diffusional process, the open channelways through the expanded interlayer spaces only enhance the total exchange capacity.

The rate of cation exchange in smectites is slow, with laboratory rates measured in minutes and hours. Parabolic rate laws are often directly applicable to exchange rates. Often when exchange is accompanied by swelling, as occurs with different sized cations that have different sized hydration spheres, a hysteresis effect is observed in the exchange rates (Grim, 1968).

Unlike the illites and kaolins, the smectites experience no increased exchange capacity in the smaller particle size fractions. This phenomenon occurs despite the increased access to the basal plane and, at this time, has not been fully explained. Smectites are also very susceptible to clogging of the interlayer exchange sites by the formation of Al-hydroxide precipitates, or various organic and sulfur compounds. These actions all have the effect of reducing the exchange capacity of the smectite clay minerals.

### 3.1.2 Adsorption

The terms adsorption and cation exchange are often used interchangeably in discussions of clay mineral surface reactions, yet each refers to a

distinctly different process. Adsorption is the general term that refers to the attraction of ions to a charged surface, while cation exchange is restricted to the stoichiometric exchange of cations located on or in the mineral structure.

Adsorption is a process in which ionic species are attracted to a surface and held to that surface by weak electrostatic or chemical bonds. In aqueous solutions, the mechanism by which the process occurs probably requires a decrease in the high surface tension that commonly exists between fine-grained particulates and the water that surrounds them. As part of the mechanism, dissolved materials (e.g., hydrated cations, organic molecules) compete with water to satisfy the surface energy of the solid. In instances where the water-solid surface tension is reduced sufficiently, water may be replaced by dissolved materials which are then held (or adsorbed) onto the surface. The binding force which holds the dissolved material is very weak and in many cases approaches that of a van der Waals bond. In these cases, adsorption is perfectly reversible, i.e., material is attracted and/or removed from the surface with equal ease. In other cases (chemisorption), the bond is somewhat stronger, which leads to less reversible behavior. In either case, however, the adsorption phenomenon is surface related and involves satisfying a surface energy that may be equated with a surface charge. Processes and circumstances which commonly lead to surface charge development include: 1) chemical reactions which ionize functional groups in the structure, a common phenomenon in oxide and hydroxide minerals; 2) structural imperfections and substitutions; 3) ion adsorption by either van der Waals forces or hydrogen bonding.

Adsorption reactions are most dependent upon the first alternative whereas cation exchange reactions are usually associated with the second alternative of isomorphic substitution within the structure. The importance of this mechanism is that adsorption must be related to the nature of the solution. For example, most oxides and hydroxides are amphoteric, that is the surface charge which is created by the ionization of functional groups is highly pH dependent. At normal

ground water pH, most oxide and silicate surfaces are negative and have a preferential attraction to positively charged ions. That the zero point of charge (ZPC, pH where surface charge=0) is not at pH 7 for all materials reflects the preferential ionization of the major functional groups and the adsorption by the most prevalent potential determining ions,  $H^+$  and  $OH^-$ .

### 3.2 EXPERIMENTAL STUDIES OF CLAY SORPTION

Adsorption, as noted above, applies strictly to surface-related phenomena. Under some circumstances, processes such as diffusion extend the effects beyond the surface layer. When this occurs, elements of adsorption and cation exchange may be present, and the combination (or possible combination) is referred to simply as "sorption." Because sorption is the more conveniently measured parameter, empirical tests are referred to as sorption experiments, and results are expressed through sorption coefficients,  $K_d$ 's. This practice is done because the surface energy of a particle commonly receives contributions from all three of the processes which cause surface charge (Section 3.1.2), which are difficult to distinguish in practical terms (Grim, 1968).

Experimental studies are an alternative means to estimate the radionuclide migration retarding capacity of a clay seal as backfill, by examining the sorptivity of seal materials with respect to radionuclides under a range of physiochemical conditions. In these studies, sorptivity is generally expressed in terms of a sorption coefficient ( $K_d$ ) as defined as:

$$K_d = \frac{\frac{\text{g radionuclide on sorbent}}{\text{g sorbent}}}{\frac{\text{g radionuclide in fluid}}{\text{ml fluid}}}, \text{ in ml/g}$$

$K_d$ 's measured for several clays and clay bearing materials with respect to various radionuclides are shown in Table 3-2. The table includes a range of available measured results for each radionuclide-sorbent combination. In many cases, there is a wide range in values corresponding to variations in experimental conditions. The table is presented for

Table 3-2. Reported Sorption Coefficients for Clays and Clay Minerals

ELEMENT SORBENT	ELEMENT																SOURCES OF VARIABILITY	REFERENCE							
	Am	Be	Ce	Cf	Cm	Cs	Es	Eu	Gd	I	La	Np	Pm	Pu	Ra	Rb			Se	Sm	Sr	Tc	U	Yb	
Na-MT.	2.2-33.9	0.4-600		16-43.5	2.4-3.7	4-70	3.1-54.0	20-100,000			1.7-38.5							1.5-48.7	0.2-500			1.7-59.2	Na CONC., pH? Na CONC., R-N CONCENTRATION pH, TEMPERATURE, FLUID COMP.	BEALL ET AL, 1979 SHIAO ET AL, 1979 NOWAK, 1980 a, b	
Ca-MT.		3-100					200-11,000												0.4-50				R-N CONCENTRATION, Ca CONC.	SHIAO ET AL, 1979	
HECTORITE						0.4-3.4		370-7200												0-1	1		FLUID COMP., pH, TEMPERATURE	NOWAK, 1980a, b	
VERMICULITE		450					1500									120	47							KOMARNENI & R. ROY, 1980 BIRD & LOPATA, 1980	
KAOLINITE	0.2-4.3			0.2-5.2	0.3-3.2		0.5-4.9	60-1600			0.2-3.0							0.2-4.0		3-500		0.1-1.8	pH, FLUID COMP. Na CONC., pH? INITIAL R-N CONC.	NOWAK, 1980a BEALL ET AL, 1979 BIRD & LOPATA, 1980	
ATTAPULGITE	168-20,000				100-1000					0.01-0.1						10-30					8		Na CONC., TIME pH, FLUID COMP.	BEALL ET AL, 1979	
MONTRONITE, BASALT FRACTURE/YUG MINERALIZATION	3200-47,200					80-225,000				0-11.8	9-76		415-25,000	9-553		0-14.1			4-225,000	0	12-3034		pH, R-N CONC., Eh, TEMP., SOLUTION:SORBENT RATIO	AMES & MCGARRAH, 1980a, 1980b; SALTER ET AL, 1981	
BELLE FOURCH CLAY (Na FORM)						5.6-9700																	pH, FLUID COMP.	SILVA ET AL, 1979b	
MT. ARIZONA						750										300					260			KOMARNENI & R. ROY, 1980	
Na-BENTONITE	4100-14,000					3.0-4.9		350-5200							2300-40,000					0-1	0		pH, TEMPERATURE, FLUID COMP.	NOWAK, 1980a, b	
ELEANA ARGILL.	77-75,000	3900-31,000	26-42,000		44-48,000	300-5100		18-100,000					1.5-48.7		145-33,000				0-2100	3-6500	0.7-39		MEASUREMENT METHOD SORBENT SOURCE, FLUID COMP., R-N CONC. TEMPERATURE, DESORPTION	SILVA ET AL, 1979a LYNCH & DOSCH, 1980 ERDAL ET AL, 1979	
CONASAUGA SHALE						100										82					57			KOMARNENI & R. ROY, 1980	
DEVEY LAKE REEBEDS (SHALE)							200-14,000																pH, TEMPERATURE, FLUID COMP.	NOWAK, 1980a	
SEA FLOOR SEDIMENT	20-40,000	4-32,000	3-1300		40-20,000	100-10,000		10-320,000	6-300				10,000-40,000		100-1600						100	0	160-100,000	R-N CONCENTRATION, pH, PRE-TREATMENT OF SORBENT, TEMPERATURE pH, FLUID COMP., SOLUTION: SORBENT RATIO, R-N CONC. (SOME TESTS REMOVED METAL HYDROUS OXIDES)	ERICKSON, 1979 ERICKSON, 1980
VERMICULITE + CONASAUGA SHALE (1:1)		370			1340											120					41			KOMARNENI & R. ROY, 1980	
VERMICULITE + MT. (1:1)		490			1109											192					3800			KOMARNENI & R. ROY, 1980	
VERMICULITE + GIBBSITE (1:1)		530			1520											77					260			KOMARNENI & R. ROY, 1980	
VERMICULITE + ZEOLITE (VARIOUS) 1:1		2300-992,000			1300-3750										130-3215						300-44,500			ZEOLITE SPECIES	KOMARNENI & R. ROY, 1980
BENTONITE + SAND (1:9)	9400-9900														490-3800									FLUID COMP., pH	NOWAK, 1980a
BENTONITE + QUARTZ (1:9)	20-7980		79-6300		6-32		200-10,000		<1		10-20		63-158	40-251							32-63	<1	2.5-20	FLUID COMP., TEMPERATURE, R-N CONC.	ALLARD ET AL, 1979
HECTORITE + SAND (1:9)	16,000													400-1300										FLUID COMP., pH	NOWAK, 1980a

MT. = MONTMORILLONITE

general comparisons and to highlight the range in  $K_d$  values that may occur due to changes in experimental (or repository environment) conditions. Narrow ranges of values usually indicate a lack of data or replicate experiments, rather than an actual insensitivity of the  $K_d$  to environmental conditions.

Although a large body of experimental knowledge of radionuclide sorption by clays, shale, and clay-bearing composite mixes exists and steadily grows larger, the interpretation and comparison of these data and their application to actual repository conditions and seal design requires caution. This caution must be exercised because measured sorption by a material is dependent on experimental conditions (pH, Eh, T), as well as on fluid compositions and radionuclide concentrations. Furthermore, the measured sorption coefficient ( $K_d$ ) is also dependent on analytical measuring methods (Moody, 1982). The result is that the relationship between individual sorption measurements and actual system performance is usually obscure.

One of the most systematic sorption studies conducted to date is a program described in Ames and McGarrah (1979, 1980a,b), and Salter et al (1981a). This continuing study has been designed to investigate effects of individual experimental parameters on one group of materials and ground waters from a potential repository site, the Hanford basalts. Although much of this study is devoted to sorption of radionuclides by basalt, fracture mineralization is also being considered. Since this mineralization is dominated by the smectite clay nontronite, many of the results of this investigation are relevant to the evaluation of clays as sorptive media.

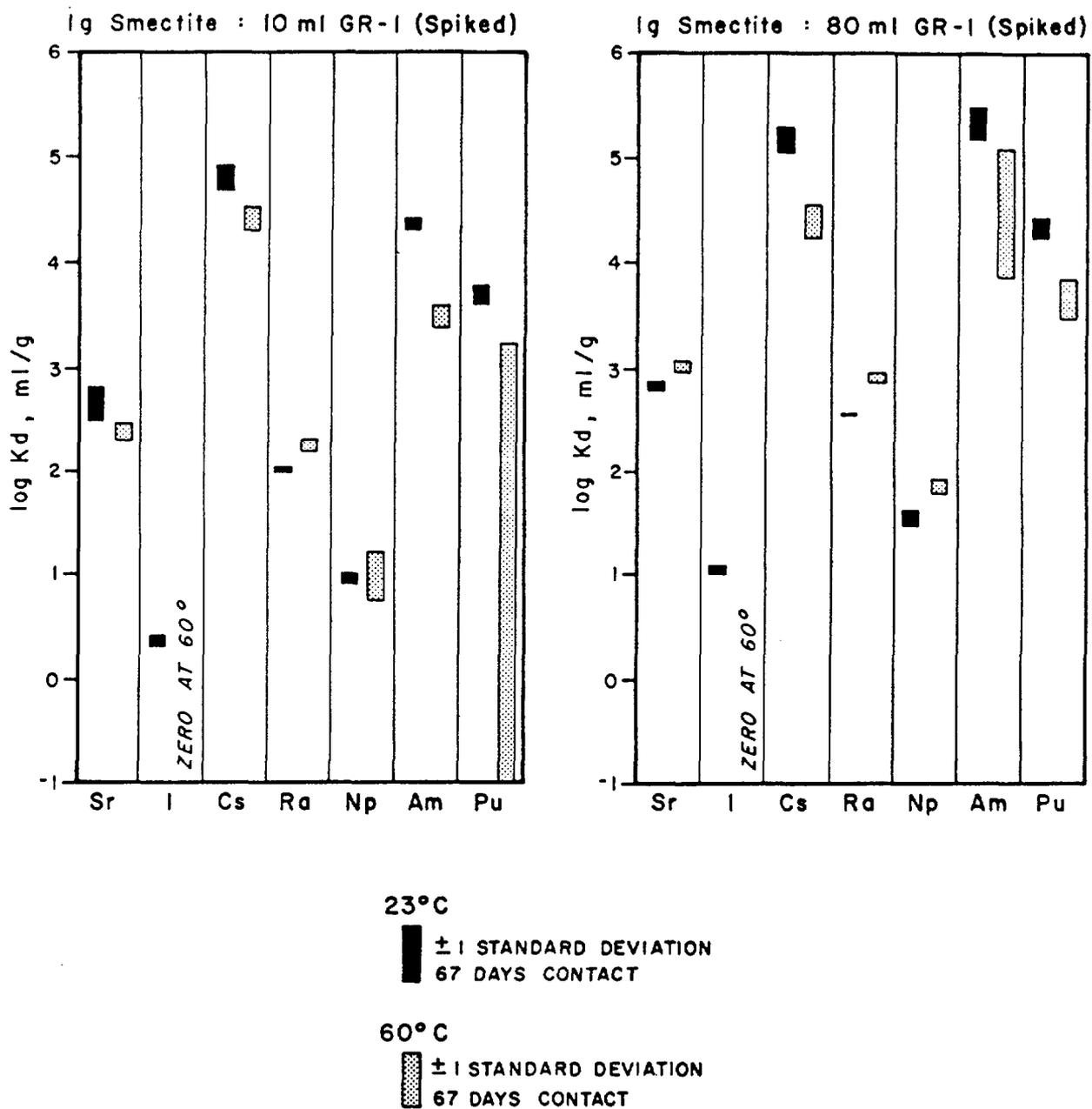
Several other studies of radionuclide sorption by clays have investigated the effects on measured sorption coefficients by various physiochemical parameters using several clay minerals and clay-bearing materials. Nowak (1980a, b) examined the sorptivity of smectite clay, as well as kaolinite and Dewey Lake Shale, with varying fluid compositions, pH and temperature. Erickson (1979, 1980) investigated the sorptivity of sea floor sediments (smectite with hydrous metal oxides) at varied pH, radionuclide concentrations, fluid compositions, temperatures, and

solution-sorbent ratios. Pretreatment to remove the hydrous metal oxides was investigated to determine the individual effects of the clays and the oxides on radionuclide sorption. These and other studies are summarized in the following sections with respect to the effects of experimental conditions on sorption.

### 3.2.1 Effects of Temperature

One of the controls on clay sorptivity is temperature. Using smectite fracture filling from Hanford basalt, Ames and McGarrah (1980a, 1980b) and Salter et al (1981a) tested the temperature effects on sorption at 23°, 60°, 150°, and 300°C for 7 radionuclides. Data for 23° and 60°C are given in Figure 3-2. Two solid:ground water ratios (1g:10 ml and 1g:80 ml) were used. Synthetic ground water, GR-1, was used in all tests. This solution closely resembles analyzed ground water from the Grande Ronde Formation basalts ( $\text{Na}^+ = 30.7 \text{ mg/l}$ ,  $\text{HCO}_3^- = 63.0 \text{ mg/l}$ ,  $\text{SO}_4^{2-} = 3.0 \text{ mg/l}$ ) (Ames and McGarrah, 1979). The pH and Eh were not buffered in these runs, although pH was monitored and the fluids were maintained in atmospheric equilibrium in all runs. Three replicate data sets were obtained for all conditions. Samples were measured at 37 and 67 days. The highest of the three mean Kd values obtained is shown in Figure 3-2.

In general, the temperature effects between 23° and 60°C are not great, and are not consistent. Iodine, americium, and plutonium sorption decreased by an order of magnitude or more, as did cesium with 80 ml of GR-1 to 1 g smectite. The sorption of other elements decreased or increased between 23° and 60°C by lesser amounts. Therefore, a measured Kd may increase or decrease, depending on the radionuclide. Increases or decreases in Kd may depend more upon the changing nature of the solution with temperature than upon a direct influence of temperature on the sorption of ions by the solids. For example, the changes in sorption of some nuclides, particularly the actinides, with changing temperature may be the result of complexes whose stabilities are temperature sensitive.



REFERENCE : AMES AND Mc GARRAH, 1980a

Figure 3-2. Effect of Temperature and Solid:Fluid Ratio on the Sorption of Seven Radionuclides by Clay Fracture Filling from Hanford Basalts

Other tests of thermal effects on radionuclide sorption by clay materials are included in studies by Erdal et al (1979), Nowak (1980a, b), Allard et al (1979) and Komarneni and D. Roy (1978, 1979, 1980). The fluid used by Erdal et al was a simulated ground water typical of water-bearing limestone overlying the Eleana Argillite at the Nevada Test Site. The sorbent used was the Eleana Argillite, containing the active phases montmorillonite and kaolinite. Sorption at 22° and 70°C was examined. Although the results are not conclusive, increased temperature decreased the Kd of lanthanides and actinides (Ce, Eu, U, Pu, Am) and increased the sorption of alkalis and alkaline earths (Sr, Cs, Ba). Nowak studied sorption by commercial bentonite and hectorite at 23° and 70°C in WIPP Brine B spiked with Eu-152. For both sorbents, Eu sorption increased at 70°C in Brine B, by approximately 300%. Allard et al (1979) noted a small increase in the Kd's of several nuclides with increased temperature for bentonite+quartz sorbent (to 65°C). Only Cs regularly displayed the opposite effect. Two fluid compositions were used, one representing "average" granitic terrain ground water, and another several times more concentrated in major ions.

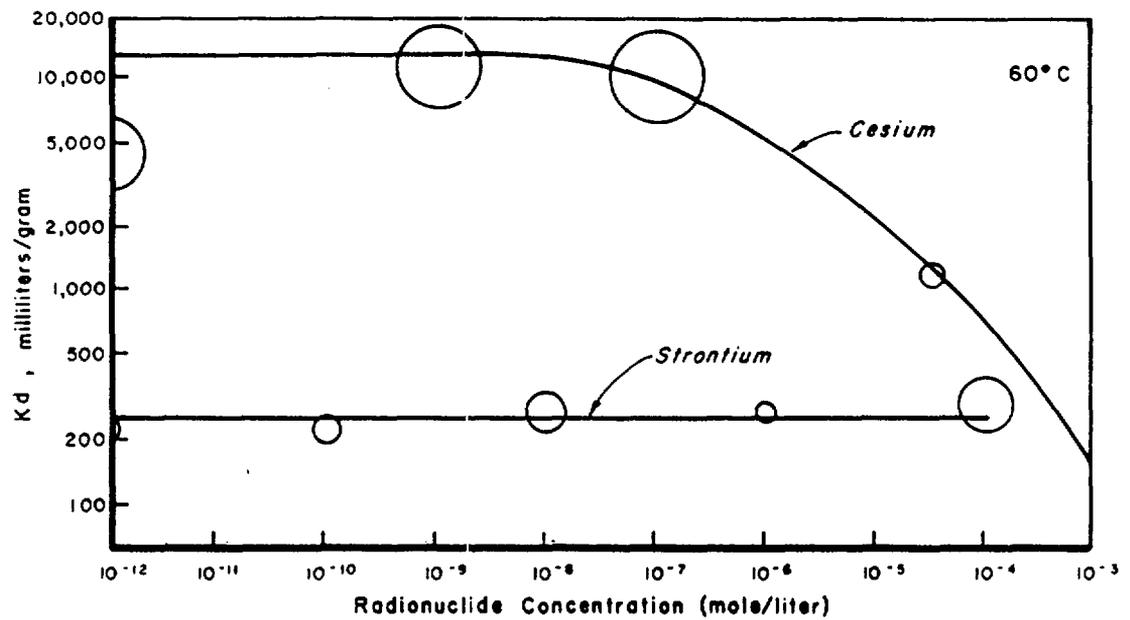
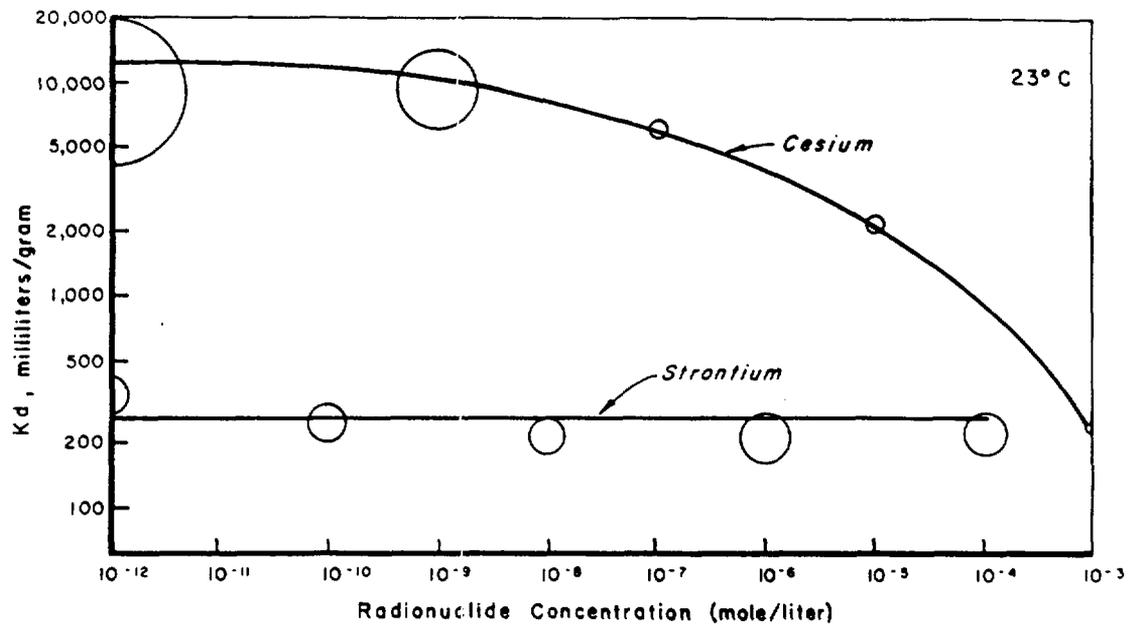
An overall pattern of temperature effects on clay sorption does not emerge from this comparison of experimental results, even though smectite clay is the major sorbent in all cases, temperature ranges are comparable, and some of the same dissolved elements are used in the experiments. One obvious difference among experiments, and a probable cause for variation, is the fluid composition used in the studies. Fluid composition is important because it strongly affects the degree of competition for exchange sites on clay minerals and determines whether radionuclides will form complexes. These directly affect sorptivity and solubility of radionuclides. It is apparent, therefore, that sorption of individual elements must be tested with respect to either fluid compositions occurring at a specific repository site, or fluid compositions which may result from waste-rock-water interactions at elevated temperatures. Although fluid composition probably has a major effect on sorption and measured Kd's, the nature of the sorbent may also affect the results; for example, flocculation of colloids, or mineralization at higher temperatures may extract nuclides from

solutions. Therefore, in spite of measurable temperature effects on sorption by clays and Kd values, the trends of these effects, and the underlying mechanisms are specific to the system under study.

### 3.2.2 Radionuclide Concentrations Effects

Ames and McGarrah (1980a, 1980b), and Salter et al (1981a) investigated the effects of radionuclide concentration in the starting fluid on Cs-137 and Sr-85 sorption by a smectite (Figure 3-3). At trace radionuclide concentrations (i.e., less than  $10^{-8}$  -  $10^{-9}$  mole/liter) in synthetic ground water, the Kd of Cs is unaffected by the Cs concentration. At higher concentrations, the Kd of Cs shows a gradual decline from >10,000 ml/g to 200-300 ml/g (at  $10^{-3}$  mole/liter), depending on temperature. The concentration at which the Kd begins to be affected by loading appears to be a function of the sorbed element, as shown by the strontium Kd curve which displays no marked variation over the concentration range tested. Tests reported by Smith et al (1980) show that the concentration of Cs resulting from the leaching of spent fuel and reprocessing waste forms in distilled water are in the range ( $10^{-3}$  -  $10^{-5}$  mole/liter) in which sorption by the fracture filling is decreased by the loading effect. Increased temperature (60°C) causes only a slight change in the loading effect for Cs or Sr. The gradual decrease in Kd with increased concentration of radionuclide is probably due to saturation of sites on the surface of the sorbent to which the ions become attached.

Lynch and Dosch (1980) produced data which generally follow the same trends as Ames et al's experiments. Using Eleana argillite (the clay fraction is identified as illite, with minor chlorite and other minerals), 1 gm solid: 50 ml synthetic ground water, and radionuclide concentrations less than  $10^{-7}$  mole/liter, the measured sorption coefficients for Cs and Sr remained fairly constant with respect to radionuclide loading. Increasing the radionuclide concentrations, however, reduced Kd values for Cs and Sr. In addition to Cs and Sr, Eu, Ce, Pu, Am, Cm, and Tc were sorbed on Eleana argillite from progressively more concentrated solutions. Excluding spurious data identified by Lynch and



REFERENCE: AMES AND Mc GARRAH, 1980a

Figure 3-3. Effect of Concentration of Cesium and Strontium on Their Sorption by Vug Filling Material Composed Chiefly of Nontronite, at 23°C and 60°C

Dosch as caused by loss of activity in control solutions, most of these elements displayed relatively constant  $K_d$ 's in the concentration ranges studied (well within trace concentrations), or slightly decreased sorption with increased loading of radionuclides. Plutonium, the single exception, is increasingly sorbed from progressively more concentrated solutions, although a maximum  $K_d$  as a function of loading was not determined. It should be noted that Pu readily sorbs on many surfaces; therefore, a constant  $K_d$  value may indicate that a large surface area (i.e., the container) is controlling the result.

Erickson (1979, 1980) investigated the sorption of individual nuclides in a 0.68 mole/liter NaCl brine by abyssal red clay composed largely of iron-rich smectite clays with phillipsite and Fe-Mn hydrous oxides. Temperatures were 4-11°C to duplicate sea bed conditions and the pH was buffered. Erickson's data show a decrease in the  $K_d$  of Cs from >10,000 ml/g to 100 ml/g as the loading of Cs increases from  $10^{-8}$  to  $10^{-3}$  mole/liter. This result is in complete accordance with Ames and McGarrah (1980a). Strontium sorption coefficients were measured only at  $10^{-4}$  mole/liter Sr loading, yielding values comparable to those of Ames and McGarrah.

Concentration effects on the sorption of lanthanides, Ce, Pm, Eu, and Gd were also examined by Erickson. The trend of decreasing sorption coefficients with increased loading is apparent in Erickson's data, although constant  $K_d$  values for these elements are not readily apparent even at very low nuclide concentrations. It should be noted, however, that the sorptive behavior of the abyssal clay is due, at least in part, to the other phases in the sorbent, especially the hydrous oxides.

Another study of radionuclide concentration on the potential for nuclide retention by smectite clays was conducted by Shiao et al (1979). The sorbents in this study were relatively pure Na- and Ca- montmorillonites. The fluids were sodium chloride and calcium chloride solutions at several concentrations, both with and without acetate pH buffers. Nuclides of Cs, Sr, and Eu, alkali and alkaline earth elements were

studied. Shiao's data for Na-montmorillonite show a steady, but slight decrease in the measured Cs sorption coefficients (from 70 ml/g to 50 ml/g) with increasing Cs concentration up to 0.1 mole/liter Cs solutions. Above 0.1 mole/liter Cs, the decline in Kd is more pronounced. Increased Sr concentration up to 0.1 mole/liter Sr solutions displays little variation in measured Kd values. Only at Sr concentrations greater than 0.1 mole/liter Sr does the Kd gently fall off. In 0.6 mole/liter Na solutions (similar to Erickson's 0.68 mole/liter NaCl solutions used in his experiments), the maximum Sr Kd measured by Shiao et al is 5 ml/g. Ca-montmorillonite and Na-montmorillonite behaved similarly with respect to Cs and Sr concentrations, except that a much lower Cs concentration was required to cause a rapid decline in the Cs Kd values using the Ca-montmorillonite sorbent.

Progressively greater concentrations of Eu in pH buffered (pH=5) and unbuffered solutions resulted in trends in Kd values like those for Sr sorption. The maximum measured Eu Kd was 2000 ml/g in trace concentrations of Eu. The Eu Kd decreased rapidly with radionuclide concentrations greater than  $10^{-2}$  mole/liter Eu.

The results of these studies show that concentration can affect the sorption coefficient of a clay-bearing material perhaps by several orders of magnitude. As the available exchange and other sorption sites on the clays are filled by the ions dissolved in associated fluids, the activity of sorbed ions on the clays decreases relative to the activity remaining in solution. Therefore, with increased concentration above certain values which depend on the radionuclide, water composition and sorbent, clays can be expected to become less efficient as sorbers of radionuclides.

### 3.2.3 Fluid Composition--Competing Ion Effect

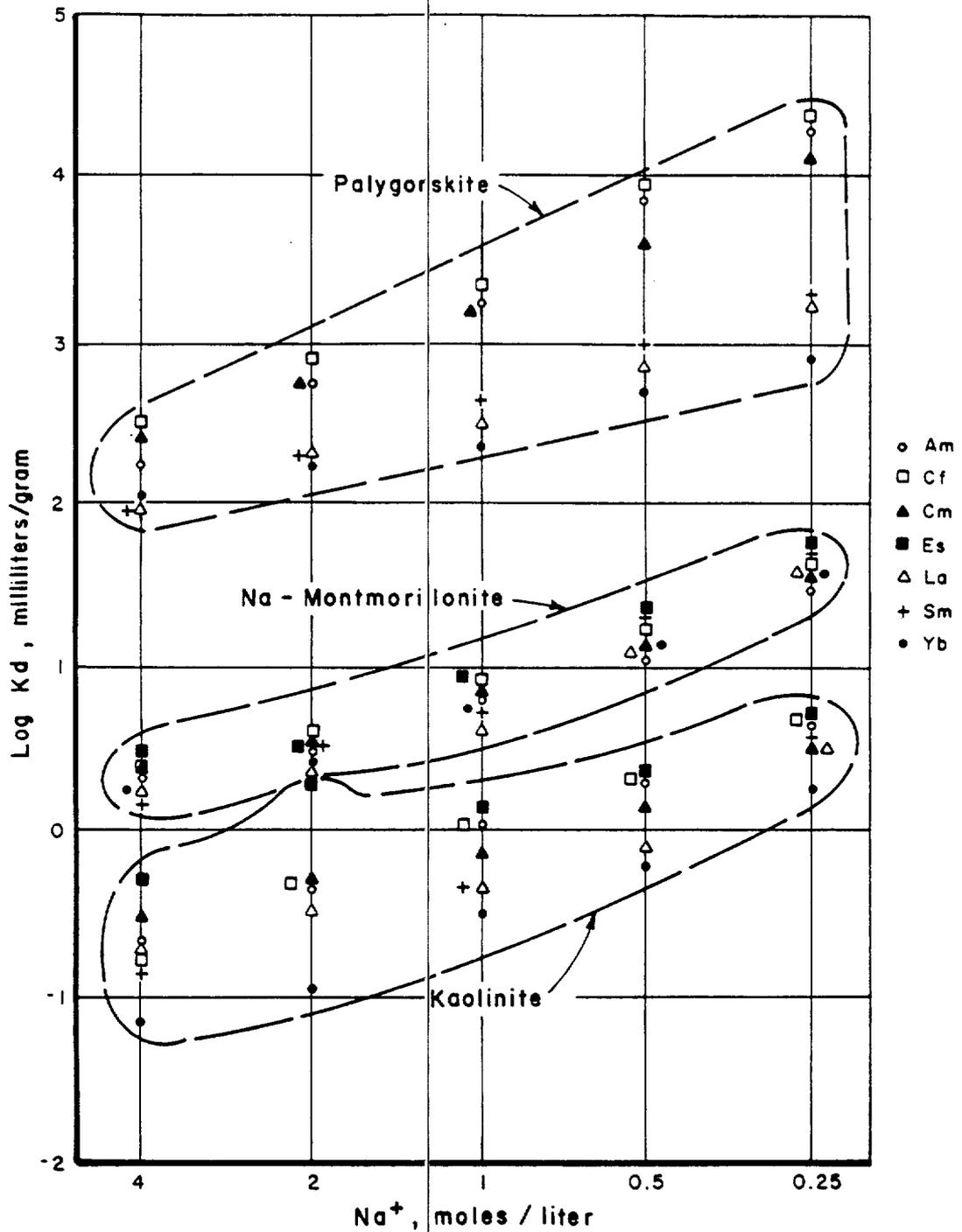
As stated earlier, the composition of the carrier fluid can affect the sorption of radionuclides by a clay material. Two phenomena may be important, complexing of radionuclides and the competing ion effect. In general, the presence of non-radioactive ions capable of taking up ion

exchange sites in clays prevents radionuclides from filling those sites. Thus the measured  $K_d$ 's of radionuclides dissolved in high ionic strength solutions are frequently lower than those measured in comparable systems using distilled water. Several studies have documented this effect with respect to clays or clay material sorbents (Beall et al, 1979; Shiao et al, 1979; Ames and McGarrah, 1980a; Salter et al, 1981a).

Beall et al studied sorption of several nuclides on relatively pure kaolinite, Na-montmorillonite, and palygorskite as a function of Na concentrations in the fluid, varying from 0.25 to 4 mole Na per liter. The results, shown in Figure 3-4, show a consistent decrease in the sorption of nuclides as the sodium concentration increases for all three clays studied. For example, the measured  $K_d$ 's using Na-montmorillonite are about one order of magnitude lower in the most concentrated Na solutions than in the least concentrated.

Similar behavior was described by Shiao et al (1979) for Cs and Sr sorption by Na-montmorillonite with NaCl solutions. The radionuclide loading was maintained within the range in which radionuclide loading effects on sorption are negligible with increasing NaCl concentration. A similar effect was also noted for Eu (III).

The efficiency of clays as sorptive media may thus be affected markedly by the ionic strength of the carrier solution. The experimental work on simple NaCl solutions and clays has shown that the sorption coefficient for a given radionuclide will probably be lower in concentrated brine carrier fluids relative to dilute carrier fluids. The above results clearly indicate that the use of distilled water as an experimental material may overestimate the efficiency with which radionuclides can be retarded by a sorptive backfill. Accordingly, such tests are insufficient for estimating the amounts of sorbent likely to be required for repository sealing. The need for site specific data relevant to actual repository conditions is clearly indicated.



REFERENCE: BEALL ET AL, 1979

Figure 3-4. Competing Ion Effect: Effect of Sodium Concentration in the Carrier Solution on the Sorption of Several Radio-nuclides by Three Clays: Palygorskite, Na-Montmorillonite and Kaolinite

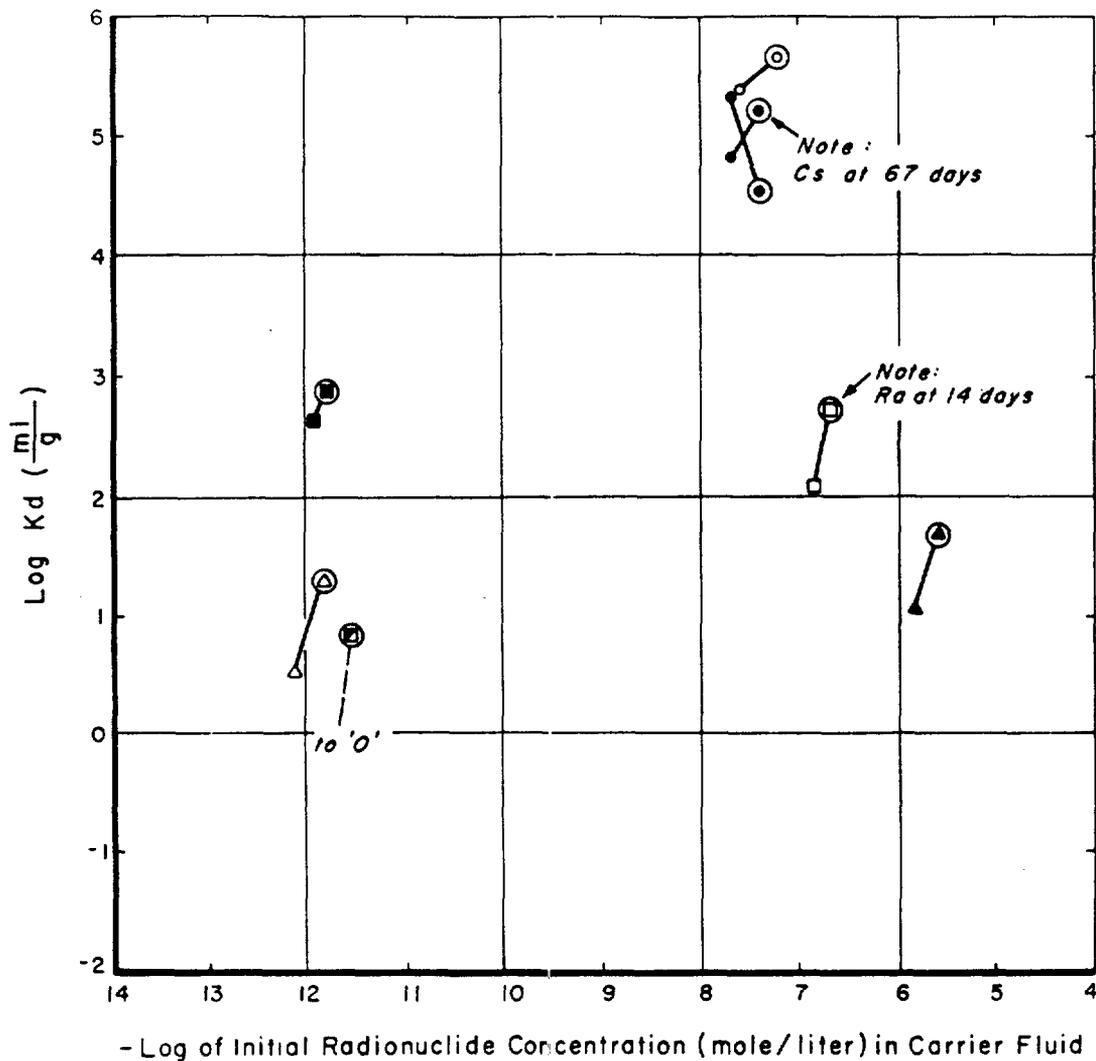
#### 3.2.4 Effects of Solid:Fluid Ratio

The effect of the relative quantities of clay material and carrier fluid on radionuclide sorption has been studied by several researchers. Ames and McGarrah (1980a) studied the sorption of radionuclides at two solid:fluid ratios (1 g smectite fracture filling:10 ml GR-1 synthetic ground water, and 1 g smectite:80 ml GR-1). Data from Ames and McGarrah are plotted on Figure 3-5, showing experimental Kd's at 23°C, and 37 days contact time, for both ratios. Except for Cs-137, the Kd is greater in the 1:80 runs. At 37 days, the Cs Kd showed large variations among duplicated experiments. At 67 days the variation in the Cs data was reduced (as indicated by the standard deviation of the data tabulated by Ames and McGarrah) and Cs shows the same pattern with respect to solid:fluid ratio as the other nuclides. At 60°C, the same trend in measured Kd's emerges, including the Cs behavior at 37 and 67 days contact time.

The sorption coefficient should not be affected by the solid:fluid ratio if sorption is an equilibrium process, presuming the activities of all dissolved constituents in the fluid remain constant. The small increase apparent in the measured Kd values, and the implication of somewhat improved sorption efficiency at low solid:fluid ratios may be the effect of 1) experimental procedures, or 2) some phenomenon coincident with the greater quantity (not concentration) of nuclides with the increased volume of solution. Ames and McGarrah (1980a) showed that the first effect could occur, but controlled experimental procedures to minimize it. The second mechanism may be operable, suggesting sorption and Kd are not entirely describable in terms of conventional thermodynamic equilibrium.

#### 3.2.5 Effects of pH.

Nowak (1980a, b) studied the pH effect on sorption by relatively pure clay minerals, as well as Dewey Lake Redbeds (shale) from southeast New Mexico. The effect of the pH of the carrier fluid on the sorptivity of clay materials has been studied systematically by Erickson (1979, 1980) with abyssal red clays.



○ 1 gram Solid : 80 milliliters Fluid

● 1 gram Solid : 10 milliliters Fluid

REFERENCE : AMES AND Mc GARRAH, 1980a

#### Radionuclides

- Am - 241
- Cs - 137
- △ I - 125
- ▲ Np - 237
- Ra - 226
- ▣ Se - 75
- Sr - 85

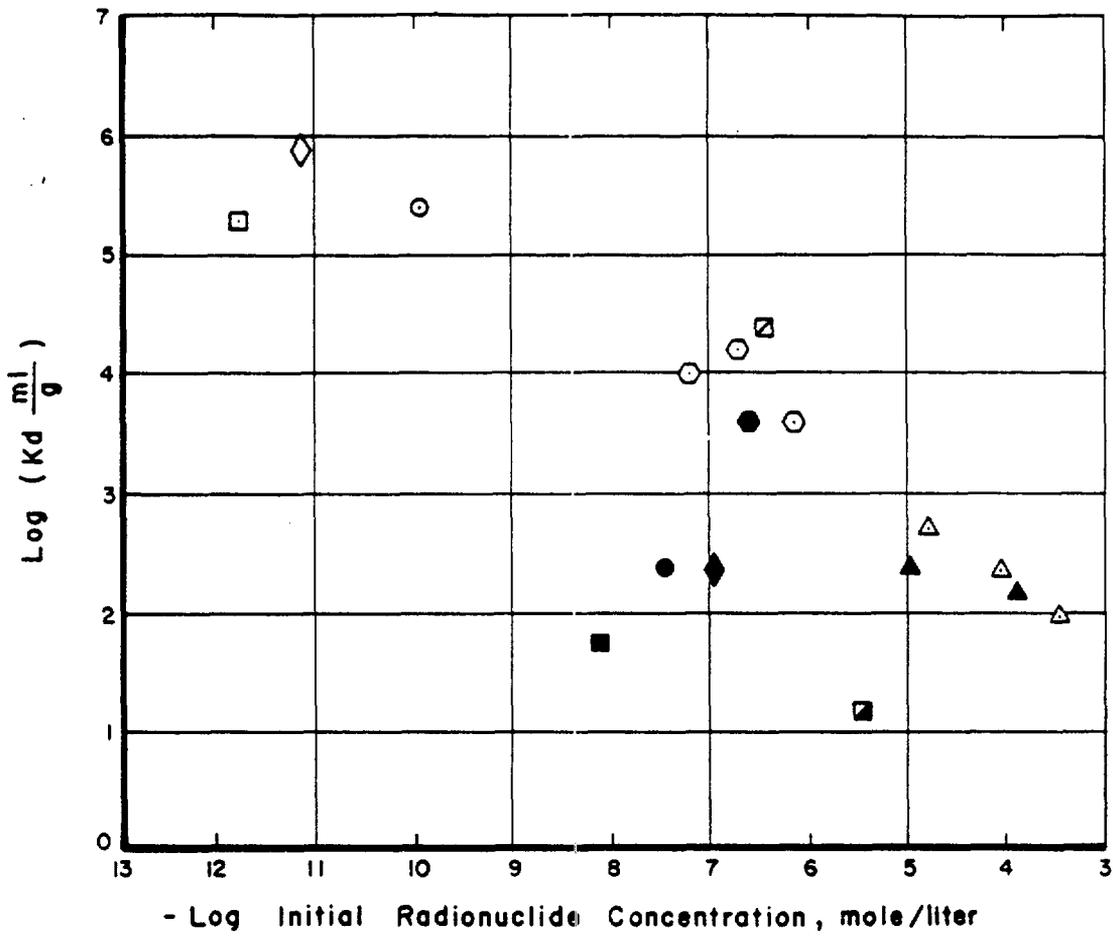
Figure 3-5. Effect of Solid:Fluid Ratio on the Sorption of Radionuclides by Clay Fracture Filling from Hanford Basalts at 23°C and 37 Days Contact Time

Nowak's screening tests, using Eu-152 as the radioactive tracer (initial concentration =  $2 \times 10^{-7}$  mole/liter) in WIPP brines A and B, and Na-montmorillonite, kaolinite, and Dewey Lake Redbed material as sorbents, showed a marked increase in  $K_d$  with pH increase from 5.5 to 6.5, at 23°C. Part of the change is due to decreased solubility of Eu-bearing solids at higher pH. The pH effect may be similar for Am and Pu.

Erickson's studies were conducted using neutral and acidified (pH buffered) 0.68 M NaCl solutions, several nuclides, and abyssal red clay sorbent. These clays include smectites and hydrous metal oxides. In general, the  $K_d$  at pH 2.7 is sharply lower than at neutral to alkaline pH, with the exception of Cs and Ba (Figure 3-6). At low initial Ba concentrations, the lower pH causes only a relatively small reduction in  $K_d$ , and at higher Ba concentrations, the pH effect is not clear. The overall result may be attributed to a loss of hydrous metal oxide cation exchange capacity, which appears to contribute to the clay sorption significantly at lower initial radionuclide concentrations. Erickson's data for Eu are in agreement with Nowak's screening tests on Eu. The results are probably due to the solubility of europium-bearing solids ( $\text{EuCl}_3$  or  $\text{Eu}(\text{OH})_3$ ) or the relative stability of ionic complexes at high and low pH. A similar phenomenon may account for some of the pH effects on Cm, Am, and Pu sorption.

Silva et al (1979a) examined the pH and fluid composition effects on Cs sorption on size sorted and purified montmorillonite from the Belle Fourche Clay, which was fully converted to the sodium form. The pH effect was slight. Cesium was sorbed slightly more effectively at high pH in dilute (0.002 mole/liter) NaCl solutions, but in more concentrated (0.1 mole/liter NaCl) solutions, the pH effect was negligible.

Studies such as these suggest that pH affects fluid phase chemistry, which in turn controls the sorption of radionuclides by the clays. The solubility of radionuclide-bearing phases and the stability of radionuclide complexes, which control the measured  $K_d$ 's for Eu, for example, may vary with changing pH. Low pH may possibly affect clay sorption by



pH of Solution	
Am	○ 6.9      ● 2.7
Ba	△ 7.0 - 8.1      ▲ 2.6
Cm	□ 6.9      ■ 2.7
Cs	⊙ 6.3 - 8.0      ● 2.7
Eu	⊠ 5.9 - 8.2      ⊠ 2.7
U	◇ 7.1      ◆ 2.8

REFERENCE: ERICKSON, 1980

Figure 3-6. Effect of pH on the Sorption of Several Radionuclides by Abyssal Red Clay

permitting  $H^+$  to take up ion exchange sites in clays, thereby reducing the availability of such sites for radionuclides, or by increasing clay solubility. In addition, non-clay phases which may occur in composite clay materials (such as the hydrous metal oxides in abyssal clays) may be affected by pH change, so that their ability to sorb radionuclides may be altered, either by limiting their exchange or adsorption capability, or by dissolution of these phases.

### 3.2.6 Effects of Eh (Redox Conditions)

Oxygen fugacity (redox potential or Eh) will affect measured Kd's, particularly the solubility of multivalent ions or complexes in the carrier solution. The importance of Eh as a control on radionuclide migration, however, may be expected to vary from candidate repository site to site, depending on the natural controls on Eh provided by the site geology, and the length of time after repository closure that the natural system will require to re-establish its control on Eh.

Ames and McGarrah (1980a) reported Kd values determined on basalt fracture mineralization (nontronite) and several radionuclides (Se-75, Sr-85, Tc-99, Np-237 and Pu-241) at equilibrium with the atmosphere (approximately  $2.8-3.7 \times 10^{-2}$  atm  $O_2$ ), and at a lower oxygen fugacity, but still oxidizing condition ( $7.9 \times 10^{-7}$  atm  $O_2$ ). Strontium sorption was unaffected by the changing oxygen fugacity because it is not multivalent nor does it form complexes. Se and Pu sorption was depressed by the lower oxygen fugacity, and Np sorption was enhanced. Except for Pu, all changes in measured Kd's were less than an order of magnitude.

These data may not pertain to the sorptivity of smectite fracture mineralization at very reduced conditions expected at the Hanford basalt site, upon re-equilibration between host rock and ground water. Nonetheless, Salter et al (1981b), in a study of basalt sorptivity, found that low oxygen fugacity (low Eh) controls the solubility of U, Pu, Np, and Tc and, therefore, the migration of radionuclides of these elements in solution from a reducing environment. Presumably, the

sorption of several radionuclides in a clay-ground water system under very reducing conditions would be largely controlled by radionuclide solubility.

### 3.2.7 Sorption of Anionic Species

The sorption of radionuclides which are expected to occur in aqueous fluids in anionic forms is of particular interest in designing repository backfills. These species, including  $\text{SeO}_4^{2-}$ ,  $\text{TcO}_4^-$ , and most importantly  $\text{I}^-$ , are not readily sorbed by most materials. Anionic exchange is expected to be the major mechanism of anion sorption associated with clays, because of the availability of exchangeable  $\text{OH}^-$  groups in the clay crystal structure. According to Grim (1968), smectites and kaolinite have the largest anion exchange capacities (20-31 meq/100g). The availability of  $\text{OH}^-$  groups for exchange appears to be increased by grinding. The size and shape of exchange anions and exchange sites are major factors in the exchange capacity of a given clay for respective anions.

Experimental results for the sorption of anionic radionuclide forms by clays are not extensive. Bird and Lopata (1980) tested sorption of Se, Tc and I by kaolinite and vermiculite, in distilled water at room temperature. Measured  $K_d$  values are shown in Table 3-3.

The sorption of anionic species appears to be controlled strongly by the initial anion concentration, and is much more efficient at very low concentrations. Bird and Lopata did not identify the mechanisms for sorption, but suggested that  $\text{SeO}_4^{2-}$  sorption may be due to iron hydroxide formation and co-precipitation of Se on the iron-bearing clay surfaces. No mechanism for  $\text{TcO}_4^-$  sorption was proposed, and  $\text{I}^-$  showed little affinity for either clay. Because these values were determined in distilled water, the sorption may be greater than in natural ground water.

Allard et al (1980) studied iodine ( $\text{I}^-$ , only) sorption by several media including palygorskite (attapulgite), halloysite and montmorillonite, in

Table 3-3. Sorption Coefficients for Anionic Species  
 ( $\text{SeO}_4^{2-}$  and  $\text{TcO}_4^-$ ) by Vermiculite and Kaolinite

Clay Mineral	Anion	Steady State pH	Initial Concentration (mole anion/kg clay)	Kd (ml/g)
Vermiculite	$\text{SeO}_4^{2-}$	6.8	0.1	47
Kaolinite	$\text{TcO}_4^-$	6.8	0.01	3
	$\text{TcO}_4^-$	6.8	$1 \times 10^{-5}$	500

(recalculated from Bird and Lopata, 1980).

a 4M NaCl solution and a synthetic ground water similar to that from granitic terrains. Sorption coefficients for clays ranged between 1-100 ml/g, and were increased at higher pH, possibly because of mineral dissolution and co-precipitation of the iodide and species released from the clay. Sorption coefficients were generally lower in the salt solution, except when montmorillonite was the sorbent. The authors suggest that  $\text{I}^-$  sorption efficiency in clay materials would be improved with the addition or availability in a sorbent backfill of metals such as mercury, copper, lead, or silver. These materials provide a retardation mechanism similar to that described above for selenium on iron hydroxide.

### 3.3 REPOSITORY SEALING CONSIDERATIONS

#### 3.3.1 Material Selection

Material selection for sorptive media should, in theory, be a relatively straightforward task. High sorption values indicate efficient sorption of radionuclides. For example, the cation exchange capacity of smectites (e.g., montmorillonite, beidellite, and hectorite) is greater than other clay groups, with the possible exception of vermiculite [smectite = 80-150 meq/100g; vermiculite = 100-150 meq/100g (Grim, 1968)]. Palygorskite group clays have significant sorption capacity for cations, probably due to the large surface area afforded by the fibrous mineral habit (Barrer, 1978). The smectite, vermiculite and palygorskite clay minerals and materials containing them in significant quantities, appear to be effective candidate sorbents.

Nevertheless, the task of identifying appropriate or efficient sorbents remains non-trivial. The foregoing sections suggest that theoretical and experimental sorption data must be judiciously applied as a means to assess material performance in seal zones. Principles to be applied in selecting sorptive materials include:

- Selection of materials for specific repository sites and specific emplacements where specific fluids and environmental conditions are known
- Selection of materials with significant sorption of critical radionuclides. For example, critical radionuclides have been identified by Barney and Wood (1980), and Moody (1982).
- Selection of materials whose sorptive behavior is least affected by changes in environmental conditions. Temperature, fluid composition, and the concentration of dissolved radionuclides may be the most significant of these.
- Selection of materials which do not impair the function of other seal components or damage the host rock.

The same materials may not serve each of the above criteria for all radionuclides in all seal emplacement environments. Moreover, two other separate problems arise in the selection of sorptive sealing materials:

- Sorptivity does not imply radionuclide fixation in the clay mineral structure. Both radionuclides and ions dissolved in ground water will compete for exchange sites on clays, and will displace ions not strongly fixed by the clay minerals.
- The physical properties of clays are frequently altered by new exchange species in the interlayer sites in clay minerals.

Numerous studies purpose to show the high selectivity of various clays, mostly smectites, for aqueous radionuclides (e.g., Nowak, 1980b; Tamura, 1972). However, the chemistry of fission products and transuranic species varies drastically such that no one clay would adsorb all the available cations. Smectites are generally praised for their high selectivity of transuranics, but there is no evidence that these species

would be fixed within the clay structure (Tamura, 1972). Smectites also selectively adsorb various fission products, e.g.,  $\text{Cs}^+$ ,  $\text{Sr}^{2+}$ , but their retention of these species is also limited (Komarneni and R. Roy, 1980), while vermiculites and illites retain much larger proportions of the adsorbed  $\text{Cs}^+$  (Komarneni and D. Roy, 1978, 1979, 1980).

Fixation of exchange cations requires large attractive forces between the mineral structure and the cation. This fixation is accomplished by the creation of a suitably large excess negative charge on the lattice,  $\pm 0.67$  equiv/unit cell, located primarily in the tetrahedral sheet and the presence of cations with relatively small hydration energies. Only illites or vermiculites provide a suitable clay substrate for cation fixation. Of all the hydrated cations, only the relatively large alkalis,  $\text{K}^+$ ,  $\text{Cs}^+$ ,  $\text{Rb}^+$ , have sufficiently small dehydration energies such that the attractive forces between structure and cation can drive off the water, affect a collapse, and fix the cation. The fission product Sr-90, like other alkaline earths, has too large a hydration energy to be fixed in the interlayer space of common 2:1 layer clays. It should be noted that there may be major differences in the sorptivity and fixation of  $\text{Cs}^+$  of different illites and vermiculites; however, fixation for these clay minerals is invariably higher than in montmorillonite, at  $\text{Cs}^+$  concentrations of  $1 \times 10^{-3}$  to  $2 \times 10^{-4}$  M (Komarneni and D. Roy, 1978).

The transuranics may be selectively adsorbed by smectites or other solid solution substitution dominated clays on the basis of high valences and large atomic numbers. Their fixation within the clay structure, however, is limited by the energy required to dehydrate adsorbed water (Roy, 1981).

The hydrolysis of hydrated lanthanides is proposed as the likely mechanism for ion adsorption on smectites, with most of the adsorption location in the interlayer basal oxygen surfaces (Miller et al, 1982). With increased temperature more water is driven off, and the cations are irreversibly fixed into hexagonal holes in the basal surface.

The second problem associated with cation exchange of clay minerals in the repository seal design is the change in physical properties of the clay and clay minerals as the dominant exchange cation is replaced. Smectites are expected to play a major role in borehole plug and backfill designs because of their swelling characteristics and low permeability. Optimal swelling behavior and other properties conducive to the formation of impermeable barriers are obtained when  $\text{Na}^+$  is the dominant exchange cation. The ease with which  $\text{Na}^+$  can be exchanged from the smectite sites, however, suggests that if the ground water in the repository is not predominately  $\text{Na}^+$ -enriched, the clay will behave less than optimally.

### 3.3.2 Radionuclide Migration

The use of sorption data to assess radionuclide transport and the effects of sorptive clay material backfill on radionuclide migration were examined by Neretnieks (1979). An analytic model was used to evaluate the migration of radionuclides leached from spent fuel enclosed in a backfill of dense, compacted bentonite. The hydraulic conductivity of the compacted bentonite was assumed to be very low ( $1 \times 10^{-10}$  cm/sec), so that diffusion was the controlling transport mechanism ( $2.0 \times 10^{-7}$  cm<sup>2</sup>/sec for cations, equal to about 1/100 the diffusion rate in water). Radionuclide retention times were calculated for a waste package backfill 0.4 m thick, using sorption coefficients for bentonite measured specifically for the KBS program in Sweden. The model showed that three relatively short-lived radionuclides (Sr-90, Cs-137, and Am-241) were retained within the backfill for 30 or more half lives, resulting in innocuous releases of these species. The migration of other radionuclides (Tc-99, I-129, Ra-226, Th-229, Np-237, Pu-239, Pu-240, and Am-243) was not retarded by the backfill sufficiently to result in innocuous release levels. Nonetheless, with the exception of I and Tc, the radionuclide retention times for each radionuclide modeled was greater than 1,000 years. I and Tc were poorly sorbed under the oxidizing conditions assumed for the model.

This study is an example of performance assessment of sorbent materials used for radioactive waste isolation. A similar approach could be used

to design the thickness of sorbent material needed to retain radionuclides for longer periods of time, given radionuclide inventories, flow rates of permeant fluids (or the mass transfer rate), radionuclide concentrations, and accurate sorption coefficients for radionuclides and backfill materials of interest.

### 3.3.3 Additional Design Considerations for Sorptive Media

Restricting fluid flow through a sorptive medium is an important seal design consideration. When fluid flow is low, a static steady state between dissolved radionuclides and the sorptive medium should be approached. Experimental studies show that the greatest radionuclide concentration on the sorbent occurs under these conditions. Low flow rates prevent the sorptive medium from reaching sorptive capacity rapidly, at which point its sorptive efficiency would become negligible. In addition, rapid flow through sorptive media could cause the rapid desorption of radionuclides if some change in the chemistry of the associated fluid occurs (e.g., the incursion of brine into a system containing relatively fresh water). The means to maintain low fluid flow through sorptive media may be to use a low-permeability sorptive material, or to intersperse low-permeability and sorptive seal components. Whichever method is used, care must be exercised to prevent fracture formation and fracture flow in the sorptive medium. Sorption is surface area controlled and is most effective in porous media when large areas of sorbent are exposed to contaminated fluids. Clays, such as bentonite, may be ideally suited for this seal function because of their ability to resist fracturing and to heal internal fractures upon contact with aqueous fluids, and because of their low permeability combined with high surface area and sorptivity.

It must be noted that sorption by seal systems cannot be depended upon to retain dissolved, mobile waste indefinitely. It is likely, however, that the introduction of selected radionuclides into the biosphere can be significantly delayed by the incorporation of well-chosen backfill materials in repository seal designs.

Research recommendations for clays and clay-bearing materials with respect to their sorptive behavior are given in Section 6.0. These recommendations are based on the established behavior of clays with respect to radionuclide sorption, and on the known environmental controls on measured sorption coefficients.

#### 4.0 LONGEVITY OF CLAY SEALS

A major aspect of the design of repository seals is to assure that the seal function will persist for an extended period of time (10,000 years) under a range of environmental conditions. Because human experience with material stability does not extend much beyond a few thousand years, and because repository conditions will be unlike those experienced in ordinary circumstances, material longevity must be inferred from natural analogs and experimental studies. The apparent longevity of clays under some geologic conditions has contributed to the appeal of using clays in repository seals.

The environmental conditions in which a seal material must remain stable will vary from site to site, and within an individual site depending on the proximity of heat producing waste, the amount and composition of associated fluid, pressures, time after waste emplacement, and abutting seals and host rocks.

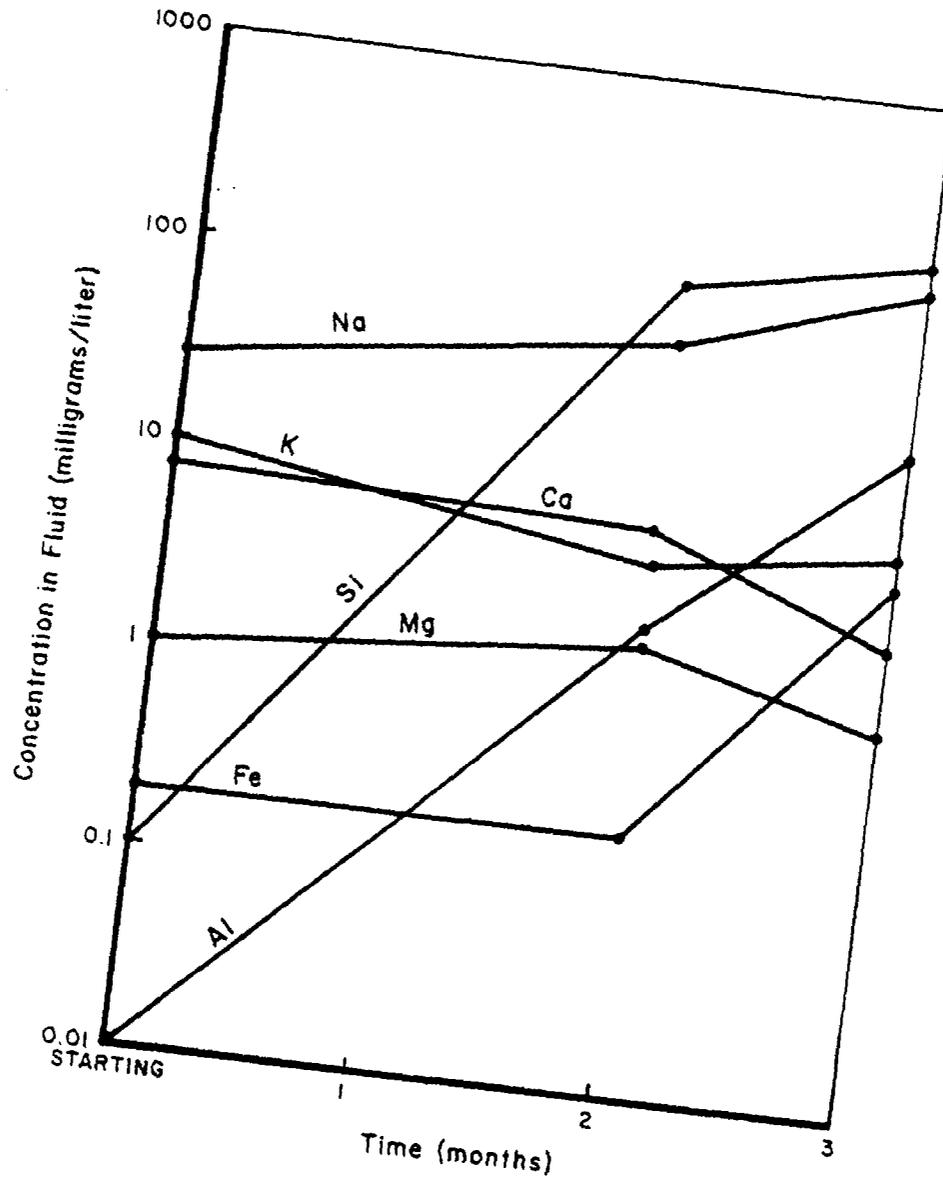
This section will review current knowledge of the solubility of clays, the stability of clays inferred from sedimentary/diagenetic sequences and experimental studies, and the effect of ionizing radiation on clays, as these relate to seal longevity considerations.

##### 4.1 SOLUBILITY OF CLAYS

Solution of clay seals could result in mass and volume loss, as well as substantially altered physical properties of the seal. For sealing purposes, the solubility or degree of dissolution of clays in ground water(s) occurring at a candidate site, under the range of temperature, pressure, and pH conditions likely to prevail at a site, in a period of about 10,000 years, should be determined. An actual repository would be an open system, where mass (and energy) is not conserved. Localized systems, however, may behave as closed systems.

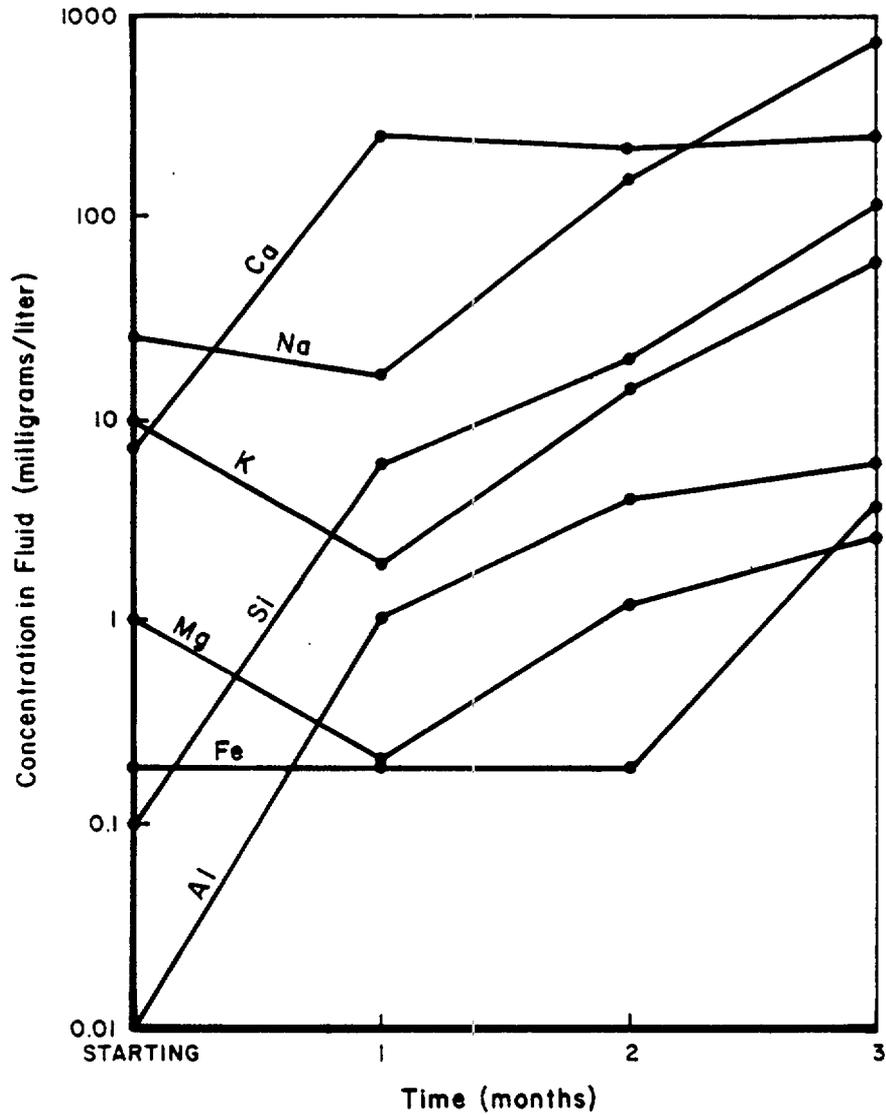
Depending on ground water movement rates through clay seals, equilibrium or steady-state conditions between the clays and the fluid may or may not be approached. Therefore, both closed and open systems may be valuable models for actual repository conditions and behavior. The solubility of clay minerals has been studied under various physiochemical conditions (for example, Grim, 1968; Kittrick, 1966, 1971a,b) in closed systems. These studies suggest that at temperatures expected in a repository seal or backfill (100°C or less) (Kelsall et al, 1982) with fluids near neutral pH, clay minerals are essentially insoluble. Current seal designs, however, call for composite clay seals, containing both clay and non-clay minerals. In addition, studies of clay (and clay mineral) solubility in ground waters at candidate sites are somewhat limited in number. In one such study, Claasen and White (1978) showed the rapid supersaturation of ground water with respect to montmorillonite when in contact with vitric tuff from southern Nevada. This would suggest that dissolution of a montmorillonite-bearing seal material is minimal if the ground water remains in equilibrium with vitric tuff host rock. The pH of the ground water affects the rate at which montmorillonite saturation is reached, and increased temperature may further affect montmorillonite stability.

Taylor et al (1980) investigated the solubilities of several natural materials including Hanford clays, Oregon and Wyoming bentonite, and mixtures of these materials in Hanford ground water at 250°C in static tests. Results of experiments using Wyoming (Na-) and Oregon (Ca-) bentonites, without admixtures, are shown in Figures 4-1 and 4-2 respectively. The bentonite contained about 25% quartz, so that the large increases in dissolved Si cannot be entirely attributed to clay dissolution. Exchangeable cations in the fluids (Na, Ca, K, and Mg) are also unreliable as indicators of dissolution of the smectite clay. Aluminum may be used to estimate the mass of clay dissolved; however, the dissolution of montmorillonite is incongruent, and the activity of dissolved ions may be controlled by an intermediate phase, which is silica-rich and aluminum-poor relative to the montmorillonite (Churchman and



REFERENCE: TAYLOR, ET AL, 1980

Figure 4-1. Concentration of Seven Major Ions in Synthetic Hanford Groundwater in Association with Wyoming (Na-) Bentonite, at 250°C in Static Tests, at Two and Three Months



REFERENCE: TAYLOR, ET AL, 1980

Figure 4-2. Concentration of Seven Major Ions in Synthetic Hanford Groundwater in Association with Oregon (Ca-) Bentonite, at 250°C in Static Tests, at One, Two, and Three Months

Jackson, 1976). Thus, use of Al as an indicator of montmorillonite dissolution is only approximate and leads to minimum values for the mass of clay actually dissolved or altered.

In the three-month run, using Na-bentonite (Figure 4-1), the dissolved Al increased almost 18 mg/liter. Assuming an ideal formula for montmorillonite,  $(\text{Na}_{0.66} \text{Al}_{3.34} \text{Mg}_{0.66} \text{Si}_8 \text{O}_{20} \text{OH}_4)$  (Grim, 1968), at least  $3 \times 10^{-6}$  moles ( $2.2 \times 10^{-3}$  g) montmorillonite or 0.2% of the original Na-montmorillonite was dissolved. The conclusion reached by Taylor et al, that the clay is relatively inert, at elevated temperatures, may not be well supported by these results, since the short-term experiments show no evidence of reaching steady state. In larger fluid volumes, the dissolution of the clay phases (as well as coexisting phases) in the bentonite may become significant.

The work of Dayal (1977) and others quoted in his work, has shown that clay dissolution is incongruent, and silica is preferentially dissolved from the clay. Silica dissolution rates are diffusion controlled, but are more rapid in kaolinite and illite than other crystalline aluminosilicates (e.g., feldspars). Montmorillonite showed no release of silica in Dayal's short term (two weeks) experiments (sea water, 22°C, 1 and 640 atmospheres) and in fact, silica was apparently sorbed at the higher pressure. Possibly, any released silica combines and precipitates with sea water constituents. The insolubility of montmorillonite cannot be inferred from Dayal's work. The study by Churchman and Jackson (1976) concluded that montmorillonite dissolved incongruently in acidic (pH 1.5-4.2) aqueous solutions. The activities of dissolved constituents were controlled not by the montmorillonite but by a secondary, silica-rich phase which occurs due to the dissolution process. The occurrence of this silica-rich phase is an important consideration in the derivation of thermodynamic properties for montmorillonite from solubility data.

From the limited information available, it is apparent that the insolubility of the clay in the long term remains to be demonstrated, for a range of geochemical conditions appropriate to candidate repository sites and repository designs, including fluid composition. The consequences to seal functions of silica dissolution from bentonite and the removal of exchange cations from clays have to be determined.

#### 4.2 STABILITY OF CLAYS

Temperature is expected to be a major factor in the stability of sealing materials and consequent seal integrity. Temperatures which are relevant to shaft and tunnel seals might range from 30° to 100°C with temperatures lower in the shafts than in the tunnels closer to the waste. Temperatures may be even higher in the disposal rooms and may reach 200° to 300°C at the surface of the waste package. To assess the application of clays in all components of repository seals, as well as waste emplacement hole backfill, will require knowledge of their behavior and stability under a wide temperature range of at least 50°-300°C.

##### 4.2.1 Dehydration

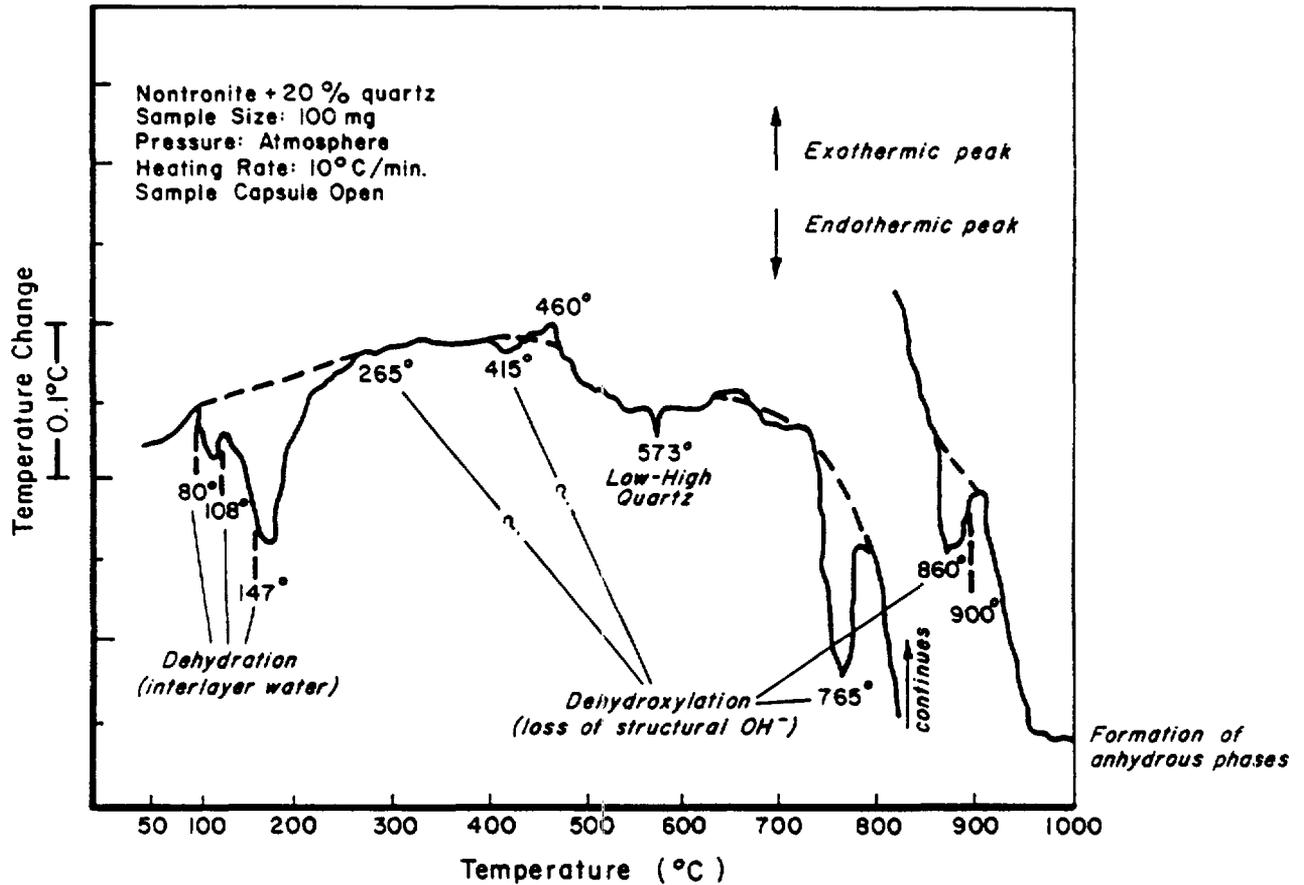
Grim (1968) cites several studies in which individual clay minerals were heated and the effects determined. A general conclusion from Grim's summary is that many clay minerals undergo some degree of dehydration of interlayer water at temperatures up to 300°C. The amount and rate of water loss vary among clay minerals and are dependent upon the environment in which the clays are heated. Under hydrothermal conditions, in which the partial pressure of water is significant, dehydration of clays occurs at higher temperatures than under dry conditions. The difference between the dehydration temperature under dry and hydrothermal conditions depends on the clay mineral.

Under dry temperature conditions, the water loss in most clays due to heating up to 300°C is generally interlayer (or absorbed) water only, and is not due to dehydroxylation (removal of OH<sup>-</sup>) from the crystal

structure. As such, the dehydration occurring with heating up to 300°C does not disrupt the clay structure, although shrinkage along the c-axis may be evident. Except for Li-montmorillonite, which will permanently dehydrate at 105°-120°C, hydrated halloysite which will not rehydrate lost interlayer water, and kaolinite and chlorite which display little or no dehydration up to 400-500°C, clays will rehydrate rapidly upon cooling from 300°C, particularly if interlayer water is not completely removed in the heating cycle. In general, dehydroxylation will occur at a lower temperature when the clay minerals are treated hydrothermally than when heated dry because of reaction kinetics.

Differential thermal analysis (DTA) curves under dry conditions (Figure 4-3) show that smectites tend to lose considerable interlayer water at 200°C or lower, and some expulsion of structural hydroxyl ions ( $\text{OH}^-$ ) may occur as low as 300°C. The rate and amount of loss of both interlayer and structural water depends on the interlayer cation to some extent, as does the ability of the clay to rehydrate (Eberl, 1978; Eberl et al, 1978). Nonetheless, the structure of the silicate framework, and the rehydration ability of most smectites (Li and possibly  $\text{NH}_4^+$  smectites, excepted) are largely unaffected at temperatures up to 300°C.

Illite and vermiculite may lose interlayer water at or below 100°C. The interlayer cation can affect the amount of interlayer water present in vermiculite, as well as the amount of water and the rate at which it is released by heating. Structural water is largely retained in vermiculite up to 500°C when heat is applied slowly (abrupt heating to at least 300°C causes the exfoliation which distinguishes vermiculite). Although the vermiculite structure shrinks due to loss of water accompanying gradual heating to 100°-300°C, vermiculite will rehydrate and expand readily upon temperature reduction and the reapplication of water. Illite retains structural water to at least 300°C, only losing its small amounts of inter-layer water at lower temperatures. It undergoes little volume change up to 200°C and should retain its ability to rehydrate if exposed to no greater than 300°C (Grim, 1968).



REFERENCE: AFTER KOSTER VAN GROOS, 1981

Figure 4-3. Differential Thermal Analysis (DTA) Curve for a Smectite (Nontronite) with Quartz Added as an Internal Standard. The Magnitude and Locations of Peaks are Characteristics of Exothermic or Endothermic Reactions Occurring at Elevated Temperatures

Clays in the palygorskite group dehydrate rapidly at or below 100°C, largely due to the loss of adsorbed water in the open channels in the silicate structure. Bound water will not be driven off until at least 275°C, and no structural disruption occurs at 300°C. Kaolinite and chlorite generally display little dehydration, dimensional changes, or structural disruption up to 400°-500°C. The behavior of kaolinite, however, is partly grain size controlled, and the composition of the brucite and mica layers in chlorite may affect the degree of dehydration evident at lower temperatures (Grim, 1968).

Dehydration does not, in itself, carry an especially serious consequence for the application of clays to sealing. Most seals, particularly in shafts and tunnels will not be subjected to temperatures significantly higher than ambient (Kelsall et al, 1982). Should volume reduction and cracking occur, with a concomitant increase in the permeability of the seal, aqueous fluids in contact with most dehydrated clays would rehydrate and heal the clay seal to some degree. The low permeability of the seal or backfill may be largely restored, assuming temperatures did not exceed the restorative ability of the clay. Other consequences may be worthy of some consideration. A dehydrated clay mass will not respond to mechanical stresses as do the clays examined in past research, which are frequently at or near saturation. Similarly, the thermal properties of clays may be substantially changed by dehydration. The use of admixtures such as quartz sand, which remain relatively unaffected up to 300°C, may be required to minimize these effects of dehydration.

#### 4.2.2 Phase Transformations and Reaction Rates

Although Grim's (1968) summary shows that heating of pure clay phases to 300°C during DTA causes no phase transformations and little or no breakdown of the crystal structure of clays, evidence exists that equilibrium phase transformations in clays may occur at temperatures well below 300°C when time and reactive fluids are available to overcome sluggish reaction kinetics (Weaver, 1976, 1979).

The longevity of an engineered clay barrier is dependent not only on its physical properties but also on the stability relationships among clay minerals in a repository environment. Many clay minerals which are formed by various processes near or at the earth's surface might be expected to alter when emplaced at depths in a repository. Most previous work on clay mineral stability relationships has focused on the energetics involved in the development and maintenance of stable equilibrium mineral assemblages. With the results from equilibrium-based experiments and thermodynamic calculations it is possible to define the limits of a mineral's stability. Longevity of a clay mineral assemblage at equilibrium with existent conditions is assured as long as conditions do not change. It can be expected that certain factors will change with time in and near a nuclear waste repository sited in geologic media; therefore, the rates at which a stable clay mineral assemblage may alter are a prime determinant of longevity.

The literature on clay mineral stability is divided between laboratory synthesis experiments, where particular phases are created and destroyed under varying run conditions, and observations of natural clays undergoing diagenetic and low-grade metamorphic alteration. Hydrothermal experiments emphasize the definition of boundary conditions under which each clay mineral species is presumably most stable. The rate at which many of these reactions proceed and the mechanisms involved have received little attention, until recently.

The fact that many clay minerals undergoing diagenetic alteration do not attain an equilibrium state is apparent in many observations of metamorphosed clays. The persistence of metastable species under anticipated repository conditions requires an understanding of the kinetics of these various transformations along with simple thermodynamic, equilibrium state calculations.

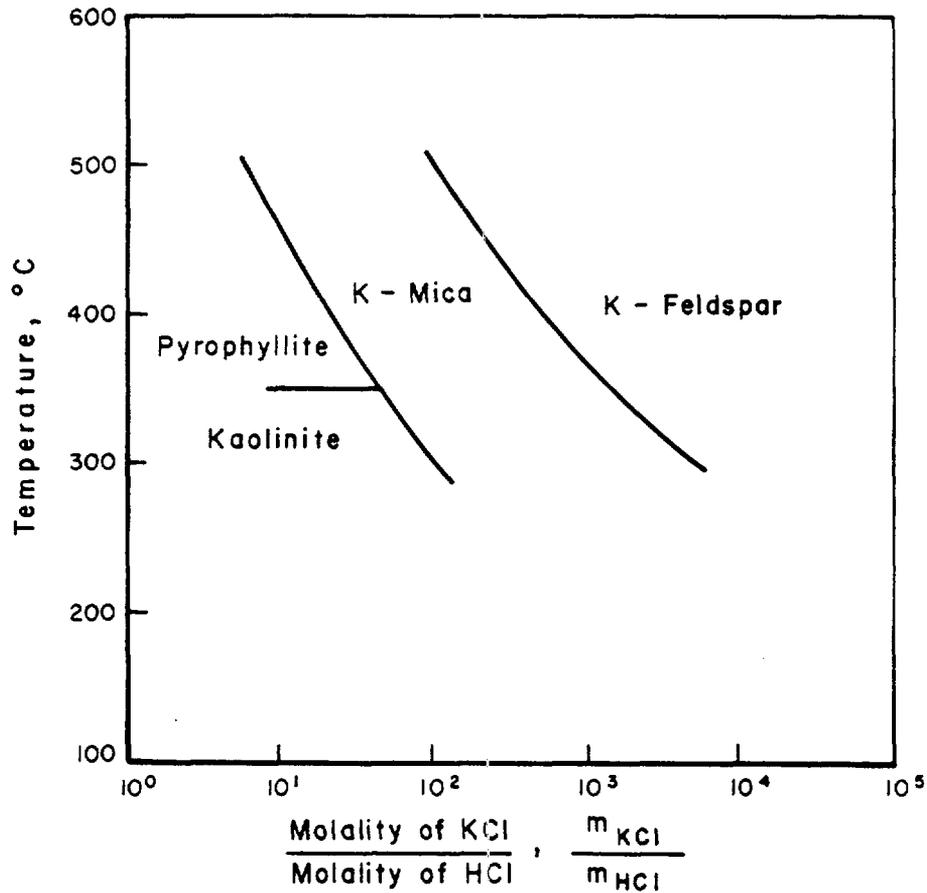
#### 4.2.2.1 Kaolinities

The genesis of the kaolinite group of clay minerals is usually related to intensively weathered soil profiles in subtropical to sub-humid

climates. Laboratory experiments of granite weathering indicate that kaolinite is the stable "pure" aluminosilicate, in terms of there being negligible solid solution substitution at 25°C and 1 atmosphere (Hemley, 1959). Kaolinite is also found at the other end of the temperature spectrum, precipitating in low-grade metamorphic and hydrothermal milieux at depths of up to several kilometers.

Since kaolinite is primarily a sedimentary mineral often incorporated in the sediment at the time of deposition, most studies have focused on the upper limits of its stability in metamorphic terrains. To best illustrate these limits, stability fields for kaolinite, pyrophyllite, mica, and K-feldspar are established in terms of temperature and  $[K^+]/[H^+]$  (Figure 4-4; Hemley et al, 1961). At a sufficiently high  $K^+$  content, mica and K-feldspar could possibly form from kaolinite, but this reaction is seldom observed in natural assemblages. At 350°C kaolinite is decomposed to form a 2:1 layer silica-enriched phyllosilicate, pyrophyllite (Hemley et al, 1961). Other workers put the transition temperature at 300°C. In clay seams associated with coal beds, pyrophyllite is found to have formed at temperatures around 200°C (Kisch, 1974). There has also been limited experimental work on the transition of kaolinite to dickite, a high temperature polymorph of greater crystallinity, from which it appears that dickite is favored at temperatures exceeding 200°C with large amounts of low pH water circulating through the system (Weaver, 1979). There are several descriptions of kaolinite that is altered to illite (Millot, 1970) which is similar to K-mica with less solid solution substitution and interlayer potassium.

While experimental studies on the synthesis of kaolin minerals are rather sparse, stability relationships at surface conditions among kaolinite, aluminum hydroxides, and other aluminosilicates have been extensively evaluated with thermodynamic data. The most common graphical representation of these relationships is the activity-activity diagram where the log of dissolved silica activity is plotted against the log of the ratio of the alkali activity divided by the hydrogen



REFERENCE: HEMLEY ET AL, 1961

Figure 4-4. Stability Relationships Among Kaolinite, Pyrophyllite, Mica, and Feldspar at Elevated Temperatures, 103 MPa (15000 psi) in KCl-HCl Solutions, Quartz in Excess.

activity (Figure 4-5). The extent of the kaolinite stability field varies with the alkali being considered; nevertheless, several generalizations concerning kaolinite stability can be made. Kaolinite is favored over gibbsite, an aluminum hydroxide, by the presence of very small amounts of dissolved silica (<1 ppm). Kaolinite is also favored over illites, montmorillonite, and feldspar phases by low alkali<sup>+</sup> /H<sup>+</sup> ratios. This ratio is usually manifested in the sedimentary environments by low pH, as acid is often generated by decomposed organic material or hydrolysis reactions.

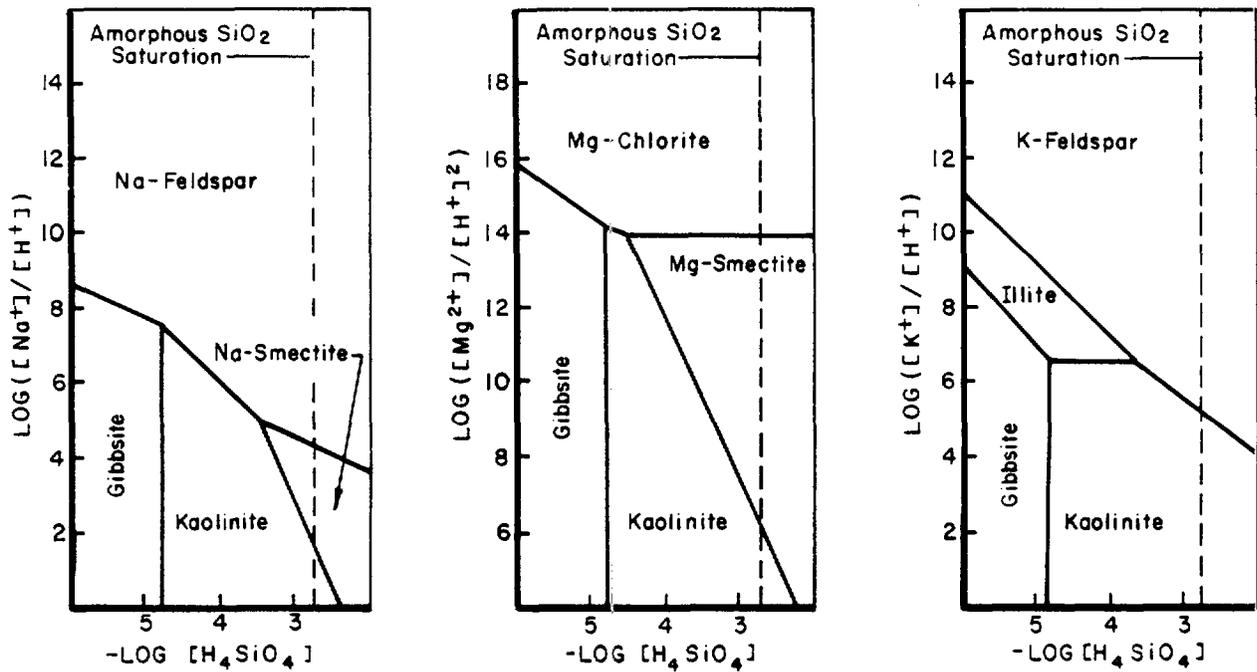
In most predominantly shale sequences undergoing diagenesis, kaolinite seldom appears above temperatures of 100°C. Its disappearance is often countered by the appearance of chlorite (Hower et al, 1976), though no actual reaction between these two phases has yet been observed.

Abundant authigenic kaolinite is found in many sandstones and siltstones undergoing burial metamorphism. These large, vermicular "books" of kaolinite are favored by the acidic conditions and the relatively fast interstitial fluid flow associated with the more porous rocks. This authigenic kaolinite is very effective in reducing the permeability of water-bearing sands as earliest growth occurs in narrow pore throats.

In summary, kaolinite appears to be most stable at temperatures well below 200°C, at low pH, with moderate silica activities and low alkali activity. These conditions are relatively simple to determine for a potential repository seal environment, and should be weighed in assessing the value of kaolinites for a particular sealing application.

#### 4.2.2.2 Illites

Illites are the most common clay minerals found in sedimentary rocks and those undergoing low-grade metamorphism. Along with variations in chemical composition, there are several variations in structural type, which correspond to the mode of origin of illites. The manner of stacking of the 2:1 layer results in either 1 Md type illite which is



REFERENCE GARRELS AND CHRIST, 1965

Figure 4-5. Stability Relationship Diagrams for Several Common Low-Temperature Clay Minerals Calculated for the Activity of Several Cations ( $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{H}^+$ ) Against Silica Activity, at  $25^\circ\text{C}$ , 1 atmosphere

associated with low temperature forms or a 2 M variety which is formed only at elevated temperature (Velde, 1977).

The experimental work on illite stability has several different aspects: attempts to synthesize a 1 Md polytype at surface conditions, the formation of 1 Md illites by transforming smectites, temperatures for the 1 Md to 2 M transition; and factors that promote increased crystallinity with advanced metamorphic grade. The transformation of a smectite mineral to a 1 Md illite is the most common means of forming illite, and the experiments detailing this reaction are discussed below in the smectite section. Illite is recognized as a potential weathering product of K-feldspar, but there have been no detailed laboratory studies. Attempts to synthesize illite from gels at 25°C have met with limited success. A product with an approximate composition is formed, but the long-range order required for phyllosilicate structures is not observed (Harder, 1974).

Limited experimental information is available on the temperatures required for the transition from 1 Md to 2 M polytypes. Most estimates come from observations of metamorphosed sediments, often where the shallow buried illites are 1 Md varieties and those more deeply buried are 2 M. Most sedimentary sequences undergoing burial metamorphism appear to retain a 1 Md variety at temperatures below 200°C, while any 2 M variety at these depths is generally attributed to a detrital origin (Dunoyer, 1970; Hower et al, 1976).

Thermodynamic calculations of illite stability relationships are severely hindered by the large variations in composition, making both experimental determinations of thermochemical values and calculation algorithms very difficult (Helgeson et al, 1978). Gibbs free energies of formation for illite that are evaluated by various sums of oxides techniques have more negative values than those for equivalent amounts of smectite, suggesting that at a temperature of at least 25°C illite would be more stable (Tardy and Garrels, 1974; Niiagu, 1975). At elevated temperatures the difference between illite and smectite is

exaggerated, suggesting an increase in the likelihood of illite stability. For strict comparisons, however, similar compositions must be considered for the illite and smectite.

Because of the compositional uncertainty of illites, their position on an activity-activity diagram with log silica activity and log of activity of  $K^+/H^+$  ratio as axes is somewhat uncertain. As a first approximation, though, illite is generally assigned a field that includes and often overlaps the one for K-feldspar (Figure 4-5).

Most of the generalizations that deal with illite stability relationships come from observations of natural mineral assemblages. Most of these assemblages occur in sedimentary rocks, some of which have undergone low-grade metamorphic reactions, or contain some hydrothermally altered zones. Illite is commonly associated with chlorite, biotite, and quartz rocks that have not exceeded 200°C (Velde, 1977). Illites also dominate the argillic zone of hydrothermal alteration, generally very close to the heat source. Farther away are found kaolinite and expandable clay minerals, such as smectites, as lower-temperature alteration products. Authigenic illite is also found in deep sea sediments and in sandstones that have not experienced high temperatures (Güven et al, 1980). Since illite minerals appear to be found over a wide range of environments, care should be taken to identify them by composition and structure type.

Illite stability appears to be only moderately known, with some compositions displaying a degree of stability over a wide temperature range. Illite must be carefully characterized before its long term performance in a repository seal can be thoroughly assessed. When  $Mg^{2+}$  is abundant, chlorites compete for the position of importance of illites.

#### 4.2.2.3 Chlorites

Chlorites are recognized in a wide range of shales but a complete understanding of their genesis is hampered by their relatively small

abundances, fine-grained nature, and large variations in composition and structural type. Much more information is available for the large, spectacular chlorites that often possess unusual compositions and that are associated with sandstones, carbonates, or evaporites. The task here is to determine some of the more important generalizations concerning chlorite stability relationships in the unusual rock types and to apply that information to expected repository conditions.

There are six observed chlorite polytypes, or ways in which the 2:1 layers are stacked with respect to each other (Hayes, 1970). The two most common forms are the Ib and IIb polytypes. The IIb form which includes roughly 80% of all chlorites is associated with high-grade metamorphic rocks and is found in high temperature environments in addition to its occurrence as detritus in soils. The Ib form is associated with low-temperature environments and is most commonly identified as a diagenetic cement in shallow-buried sandstones. As with the illite polytype sequence, the transition from Ib forms to IIb forms is observed with increasing depth in many thick, continuous sedimentary sequences (Hayes, 1970; Weaver, 1979).

In short-term hydrothermal experiments chlorite is formed from illite and mixed-layer clays at temperatures nearing 300-400°C at 2 kbar pressure (Velde, 1977). Other experiments on illite/smectite diagenesis produce minor amounts of chlorite at lower temperatures and longer run durations (Eberl, 1978). Taking into account kinetic factors these results tend to reinforce observations made in many sedimentary rocks that indicate that chlorite can be an early diagenetic product. Experiments and observations of phase relationships among chlorites and other silicate minerals reveal a propensity for illite-chlorite stable assemblages at the expense of smectites (Velde, 1977).

Thermodynamic calculations that may be applied to chlorite stability relationships suffer problems similar to those associated with other clay minerals, namely the large variation in composition and structural

types. Chlorite, however, has such a wide range of compositions and is found under an equally wide range of environments, from hydrothermal alteration zones to evaporites, that they are not easily placed on an activity-activity diagram. Sedimentary chlorites are found in primarily alkaline waters, hence high cation/ $H^+$  ratios, and are usually not associated with free silica (Velde, 1977). Chlorite would be placed very near or in the kaolinite and feldspar fields so exact positions have not been determined (Figure 4-5).

On a preliminary level of observation, chlorites seem to occupy the complete range of sedimentary-diagenetic-metamorphic environments in virtually all types of host rocks. More careful determination of structural polytypes and compositions results in a more discernible pattern of chlorite distribution and in turn enhances the likelihood of determining the mechanisms and reactions involved in chlorite paragenesis and alteration. With increasing grade there are discernible patterns in dominant structural polytypes, but chlorite composition appears to be dependent upon host rock and interstitial water chemistry, and temperature.

In many sandstones at shallow burial depths, Ib chlorite is present as an authigenic cement coating quartz grains (Wilson and Pittman, 1977). The occurrence of authigenic chlorite cement is often associated with the disappearance of various unstable components in the sandstone: rock fragments, plagioclase feldspar, and mafic heavy minerals. Chlorite is also observed replacing feldspars and rock fragments in some sandstones. With increasing diagenetic grade the Ib authigenic cements are replaced by the IIb polytype that is often a major component of graywacke matrix.

In sandstones the composition of the interstitial waters along with temperature determines whether chlorite is potentially stable. The high Mg/Ca ratio in the interstitial fluids of upper Cretaceous deltaic sandstones produce corrensite as an authigenic pore-filling cement. This regularly interstratified chlorite/trioctahedral smectite is

contrasted by pure authigenic montmorillonite produced by normal Mg/Ca ratio seawater fluids associated with proximal marine sandstones (Almon et al, 1976). This relationship follows from simple activity-activity diagrams and suggests that chlorites would replace smectites as the stable phase in the Mg-rich brines found in many evaporites. Chlorites and mixed layer species with chlorite are indeed common in different strata in the evaporites of southeastern New Mexico (Powers et al, 1978).

In shales the most common observation is the appearance of non-detrital chlorite at temperatures around 75°C along with the concomitant loss of kaolinite and the progressive illitization of smectite. The association of chlorite appearance with illitization is evident in Tertiary sediments of the Gulf Coast where, at 70°C in some Oligocene shales and at 80°C in Miocene shales, authigenic chlorite is observed (Weaver and Beck, 1971; Hower et al, 1976). The chlorites and smectites in these shales have different Fe/Mg ratios, indicating that chloritization is a solution-reprecipitation reaction and that Mg and Fe release rates from dissolving smectite are unequal (Weaver, 1979).

The appearance of chlorite in many shales has also been correlated with the diminished presence of kaolinite over a fairly wide range of temperatures. The kaolinite to chlorite reaction, though never actually observed to be a simple one-step process, begins at temperatures as low as 100°C (Dunoyer, 1970; Fuchtbauer, 1974). The high end of the temperature range for the kaolinite-chlorite reaction is around 150°-200°C (Boles and Franks, 1979).

Chlorite found in the kaolinite-rich tonsteins of Australia is associated with temperatures as high as 200°-250°C as determined by coal rank (Kisch, 1966). The formation of corrensite from smectite is believed to have occurred around 170°-220°C, with the temperatures being estimated by illite/smectite expandability (Suchecky et al, 1977). In this case, the high temperature stability for the corrensite is explained by the

trioctahedral nature of both the smectite and chlorite. Both cases illustrate the difficulty in assessing paleotemperatures of clay mineral reactions which are often controlled by kinetic aspects.

Chlorites are also recognized in hydrothermal environments. In Salton Sea sediments a Mg-rich chlorite is first observed at temperatures of 130°-165°C (Muffler and White, 1969). At Wairakei, New Zealand, an Fe-rich chlorite that has a smectite precursor is found at temperatures of 100°C (Steiner, 1968). Chlorite and mixed-layer corrensite are common alteration products in contact metamorphic zones in pelitic rocks. Usually, chlorite is formed in cooler parts of the argillic zone than illite, another common hydrothermal alteration product (Blatter et al, 1973; Rose and Burt, 1979).

The chlorite group of clay minerals is associated with a wide range of depositional environments and diagenetic grades. The stability of chlorites appears to be relatively insensitive to low temperature, diagenetic regimes. In shales, their appearance as authigenic minerals is first noted around 75°C and they persist beyond 350°C. As more work is done on polytypes and their identification becomes a standard procedure for all shale studies, it may become possible to create a more sensitive diagenetic scale. The only generalizations about chlorite composition and their relative stabilities that can be made are that Fe-rich and aluminum dioctahedral chlorites are more stable at low temperatures, while Mg-rich trioctahedral chlorites tend to be more stable at higher temperatures (Moody et al, 1983). Chlorite composition otherwise appears to be more dependent upon host rock and interstitial fluid chemistry than the low temperatures found during diagenesis.

Perhaps as more and better analyses of chlorites become available it will become possible to relate diagenetic history with composition and thereby, to estimate the expected longevity of chlorite containing repository seals, or to tailor chlorite bearing clays to meet seal environment compatibility requirements.

#### 4.2.2.4 Smectites

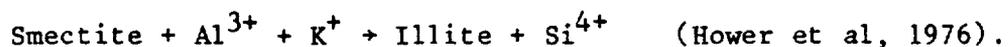
Stability relationships for smectites in anticipated repository environments are viewed to be more important than those for other clay minerals because of the proposed usage of large amounts of this highly sorptive and relatively low permeability clay mineral in backfills and seals. Increasingly, attention is being given to the stability of smectite, and the retention of its favorable properties at elevated temperatures. At the heart of the matter is the possible transformation of smectite to a non-expandable illite at temperatures proposed in many repository designs. The solution of this problem lies in the ability to determine the rate of this diagenetic transformation accurately and to identify those factors that can retard the reaction rate.

Smectites are stable and pervasive phases at the earth's surface and at slightly elevated temperatures. Smectites have also been formed experimentally at higher temperatures, though equilibrium states in most cases have not been established; i.e., reaction reversibility is not documented. In these very short duration hydrothermal experiments (runs usually are less than 14 days), smectites are identified as remaining present at temperatures of 300°-400°C (Velde, 1977). With longer duration experiments, the maximum temperatures at which smectites are still stable decrease significantly (Eberl and Hower, 1976). This result agrees with observations made in many low-grade diagenetic sequences that smectites which may be millions of years old begin to disappear at temperatures below 100°C.

Several generalizations concerning smectite stability can be deduced from the high temperature laboratory work. Trioctahedral smectites tend to persist longer at high temperatures than their dioctahedral equivalents (Velde, 1977). Within the dioctahedral series the dehydration of the interlayer cation also influences thermal stability; a Na-smectite is stable at higher temperatures than an equivalent K-smectite (Eberl, 1978).

The most frequently observed alteration of smectite clays is the incorporation of illite layers as the smectite is progressively transformed to illite through a series of intermediate steps represented by a mixed-layer illite/smectite (I/S) clay. The progressive increase of non-expandable illite layers in the I/S clays with increased burial depth and temperature is observed in sedimentary basins of all ages throughout the world (Perry and Hower, 1970; Weaver and Beck, 1971; van Moort, 1971; Heling, 1974; Hower et al, 1976; Srodon, 1979; Boles and Franks, 1979; Weaver, 1979). Therefore, it is of prime importance to identify the causes of the transformation of smectite to illite and to determine whether the illitization reaction is controlled by equilibrium or kinetic considerations.

The transformation of a smectite layer to an illite layer requires an increase in the negative charge in the structure and the incorporation of potassium in the interlayer which collapses to a 10Å spacing and irreversibly expels interlayer water. The increased negative charge is usually created by Al<sup>3+</sup> for Si<sup>4+</sup> substitution in the smectite tetrahedral sheet, though substitution within the octahedral sheet of Mg<sup>2+</sup> for Al<sup>3+</sup> or the reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup> can also enlarge the structure's positive charge deficiency. A generalized equation for the illitization of smectite is:



The actual reaction is not as simple as this, for water is also released (Burst, 1969; Perry and Hower, 1970). Magnesium released to solution is also a common byproduct associated with illitization and is often correlated with the appearance at depths of authigenic chlorite (Weaver and Beck, 1971; Hower et al, 1976; Boles and Franks, 1979). The dissolution of K-feldspar and discrete illite or mica flakes which is also observed with increasing burial depths is the most probable source of the Al<sup>3+</sup> and K<sup>+</sup> required for illitization (Hower et al, 1976).

The observation that the percentage of illite layers in the mixed-layer I/S clay increases at greater burial depths led early investigators to consider that temperature is the primary driving force behind the illitization process (Burst, 1969; Perry and Hower, 1970; Weaver and Beck, 1971). Contrary to early work by some Europeans, the illitization mechanism is not significantly affected by increases in pressure (Dunoyer, 1970). Pressure plays a minimal role because illitization is not simply a dehydration reaction, but rather one that includes major chemical changes in the clay structure.

A major uncertainty concerning the observed illitization of smectite is whether the reaction is controlled by equilibrium or by reaction kinetics. If the illitization reaction is controlled by equilibrium considerations, then the percentage of illite layers in the I/S mixed-layer clay is determined by prevailing temperature, pressure, and chemical conditions. The attraction of the equilibrium model is its potential for using I/S clays as a geothermometer in thermally altered shales. The kinetic argument implies that illite is an inevitable reaction product of smectite subjected to increased temperatures, and that the rate at which the end product is achieved is dependent upon those factors which affect the rate constants. These rate determining factors include temperature, thermal history of the sediment, and the presence of inhibiting ions in the interstitial fluid.

The resolution of this controversy is not readily apparent from observations of I/S clays in natural diagenetic sequences. A plot of I/S expandability against temperature reveals that from basin to basin, and sometimes within the same basin, there is a wide range in I/S clay mineral expandabilities at any temperature (Figure 4-6). The first occurrence of illite layers in the smectite clays occurs around 50°-80°C, while expandable layers seem to persist at temperatures as high as 250°C (Weaver, 1979). The major change in I/S expandability between 90% to 20% expandable layers occurs over a fairly short temperature range, the magnitude of which is dependent upon geothermal gradient (Weaver, 1979). At a low geothermal gradient this change in I/S expandability

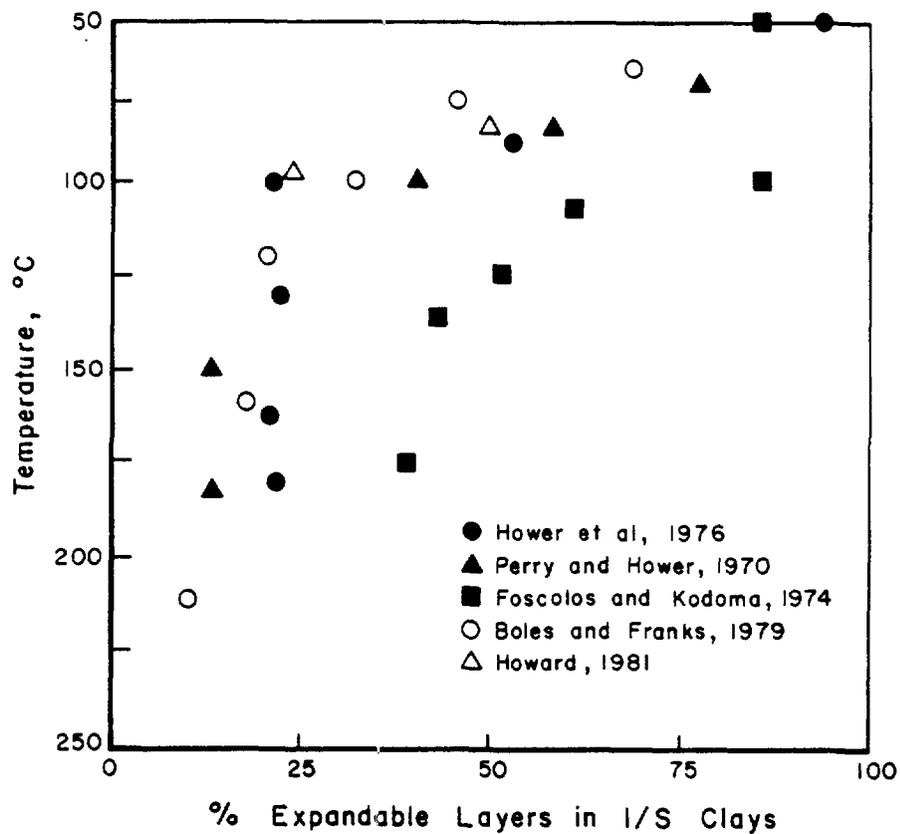
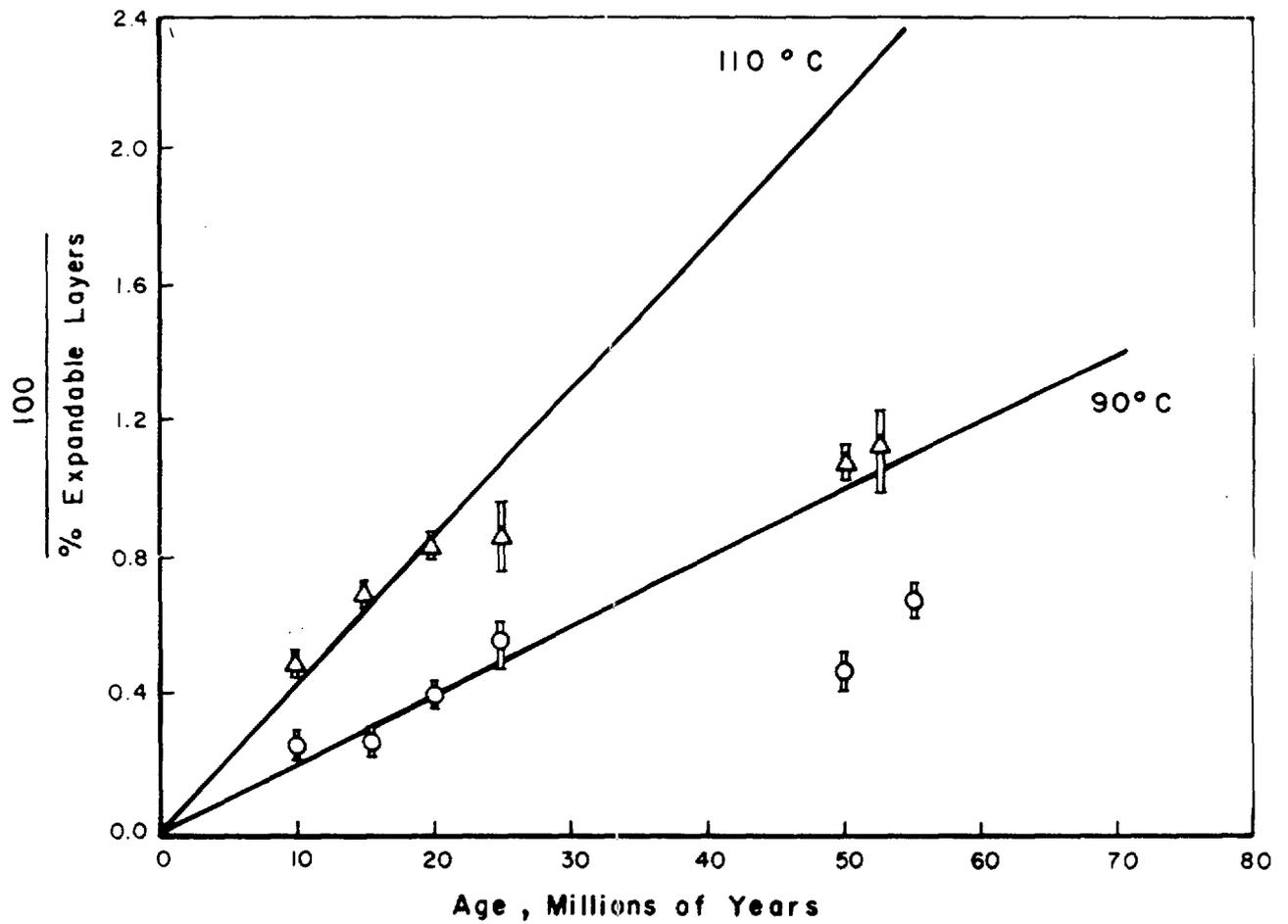


Figure 4-6. Illite/Smectite Expandabilities in Natural Mix-layer Clays vs. the Temperature of the Formation in Which They Occur

occurs over a 70°C temperature range, while the same change in I/S clays found in high geothermal gradient areas occurs within a 40°C range. Eberl and Hower (1976) also found that the rate at which a minimum reaction temperature is attained influences illitization rates. This minimum reaction temperature is associated with the activation energy required to break bonds in the lattice, the first step in the creation of excess layer charge and subsequent collapse of the expandable layer.

The kinetic interpretation of the illitization reaction is hampered by the lack of simple, observable time dependency on I/S expandability. A plot of I/S expandabilities versus age of sediments, shows that a first-order kinetic model does not fit and that the illitization process may be more than temperature dependent (Figure 4-7). Figure 4-7 does show, however, that within the time frame of interest to repository sealing i.e., far less than 20 million years, the first-order kinetic model fits the data reasonably well. This evidence, therefore suggests slight collapse of smectite clay layers (10 percent collapsed) would occur at the end of  $10^6$  years at 110°C. This interpretation, however, must be tempered by the fact that reaction rates are controlled by possibly several physio-chemical factors, which are largely unknown, and which may not pertain to seal environments in repository sites.

The chemistry of the interstitial fluids also plays a significant role in the rates of illitization. Within intercalated sandstones and shales buried at the same depth, with equal present-day temperatures and equal thermal history inferred from sedimentation rates, the I/S clays found in sandstone laminae are more expandable than those found in adjacent shale laminae (Howard, 1981). The only difference between the two environments is the greater salinity in the sand pore waters. The presence of abundant  $\text{Na}^+$  and  $\text{Ca}^{2+}$  in the interlayer spaces effectively competes with  $\text{K}^+$  and retards the illitization reaction.

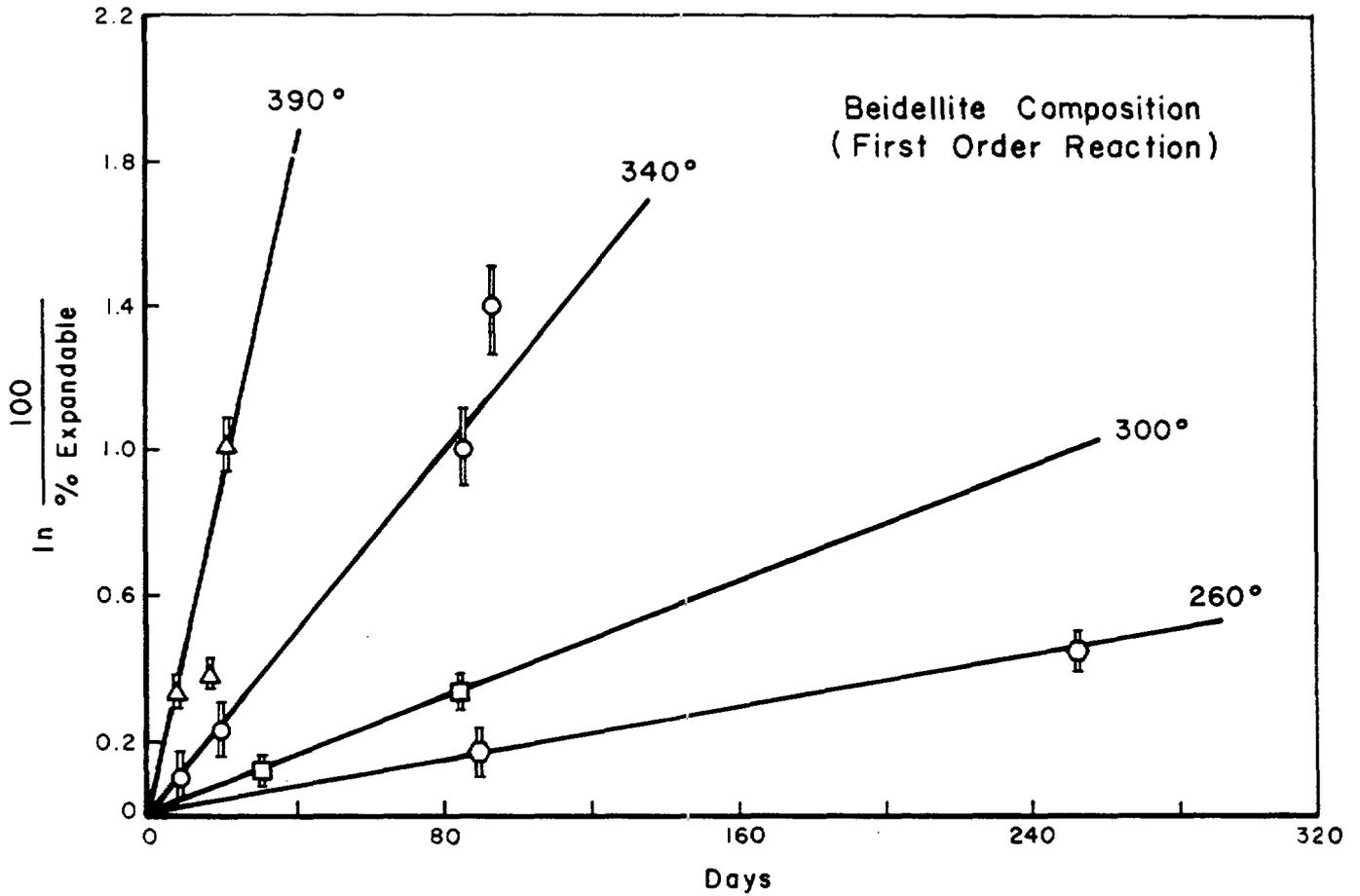


REFERENCE: HOWARD, 1980

Figure 4-7. Illite/Smectite Expandabilities for Selected Gulf Coast Shales as Related to Age

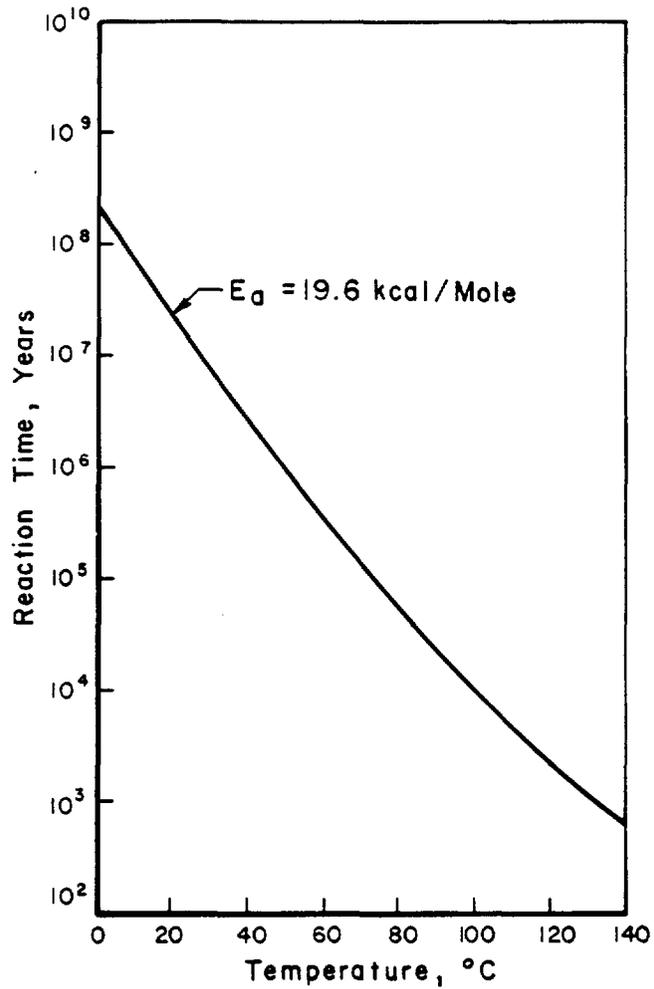
The transformation of smectite to a non-expandable illite is also the subject of many experimental studies. Results from this work reveal that the extent of reaction, or the percentage of illite layers intergrown in the smectite, is dependent upon temperature, duration of run, the nature of the interlayer cation, and fluid composition (Eberl and Hower, 1976; Eberl, 1978). A K-beidellite glass formed from standard Ludox gel procedures and reacted at temperatures between 250° and 400°C for up to nine months was altered to a mixed-layer illite/smectite clay. The extent of reaction as a function of time was identified on a series of first-order-kinetic plots, so that the slopes of the various isothermal lines are equal to rate constants for the illitization reaction (Figure 4-8). An Arrhenius plot of these rate constants against the inverse of temperature also produces a straight line, the slope of which is a function of the activation energy. For a K-beidellite reacting to illite, an activation energy of 19.4 kcal/mole is obtained, large enough to suggest that breaking of Si-Al-O bonds within the lattice is a necessary step in the illitization process (Eberl and Hower, 1976). This high activation energy probably represents the energy required to break bonds in the tetrahedral layers so that  $Al^{3+}$  can substitute for  $Si^{4+}$  and increase the negative structural charge.

The high temperature rate constants obtained in this experimental study can be extrapolated to lower temperatures; consequently "run durations" measured in years can be obtained by means of the calculated activation energies and the first order Arrhenius equation (Figure 4-9). The rates thus obtained are significantly faster than those observed in nature, i.e., at 90°C a smectite would collapse to 20 percent expandable I/S clay in less than one million years. By contrast, the Gulf Coast Miocene sediments at 80°C have reacted only to 50 percent expandable I/S clay in 25 million years. This contradiction led the authors and many subsequent investigators to conclude that the degree of I/S expandability is determined by prevailing P-T conditions rather than the length of time the clay had to react (Eberl and Hower, 1976; Weaver, 1979).



REFERENCE: EBERL AND HOWER, 1976

Figure 4-8. Extent of Reaction for a Beidellite Composition Glass Reacting to Illite as a Function of Time (Slope of Each Isotherm Provides a Rate Constant for the Illitization Reaction), at 200 MPa (29000 psi)



REFERENCE: EBERL AND HOWER, 1976

Figure 4-9. Relationship Between Temperature and the Time for the Illitization Reaction of a Beidellite Composition Glass Calculated from Experimentally Determined Rate Constants (Figure 4-6), at 200 MPa (29000 psi)

Eberl and Hower (1976) also recognize that the presence of  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{+2}$  in the interstitial fluids all have the effect of retarding reaction rates, which would permit their results to be consistent with either a kinetic or equilibrium interpretation. The effect of additional  $\text{Na}^+$  in the interstitial fluids on reducing the rate of silica removal from smectites illustrates the effect interstitial water chemistry can have on illitization reactions (Lahann and Roberson, 1980).

The energy required to dehydrate the interlayer cations found in smectites is inversely correlated with rates of illitization in hydrothermal studies (Eberl, 1978). The dehydration energy available to a clay corresponds to the negative structural charge created by substitution within primarily the tetrahedral sheet; therefore, the low charge deficiency associated with smectites is insufficient to dehydrate any interlayer cations and the layer remains completely expanded. As the layer charge is increased by lattice substitution, cations with low dehydration energies (e.g., potassium) are dehydrated, and the layer collapses forming an illite. The presence of other alkali and alkaline earth cations with higher hydration energies in the interlayer positions requires greater layer charge deficiencies, or higher temperatures to collapse the expandable smectite layers. The implication for natural clay assemblages is that the presence of these high hydration energy cations can effectively retard any illitization reaction when compared to a smectite with  $\text{K}^+$  already in the interlayer positions.

Thermodynamic calculations indicate that smectites like other clays are stable at surface conditions when compared to their component oxides in solution (Tardy and Garrels, 1974). However, when compared to free energies calculated for illite, smectite is the unstable phase at surface conditions, and at elevated temperatures. The implication is that smectites will eventually alter to illite under diagenetic conditions even though the rates at which the reaction proceeds cannot be determined from thermodynamic data.

Like illites, the variable composition of smectites results in a fairly diffuse and uncertain stability field on various activity-activity diagrams. Smectites generally inhabit a field close to amorphous silica saturation extending over a fairly wide alkali/ $H^+$  ratio (Figure 4-5).

Smectites are ubiquitous at and near the earth's surface in soil zones, on the ocean floors; as an authigenic cement in shallow-buried sandstones and shales, and even in certain hydrothermal zones. However, in many of these cases, the smectites under consideration are not phase pure, but contain a small percentage of other clay layers interstratified within the smectite packet. Closer investigation of many soil and diagenetic smectites indicates that they contain a small percentage of nonexpandable layers. The only phase pure smectites appear to be associated with freshly devitrified volcanic glass in recent bentonites, recent authigenic cement in very porous sandstones, and recent hydrothermal alteration products. Given enough time it is likely that even these examples would begin to incorporate other layers within the smectite clay.

At this time there is no overall kinetic expression to explain the illitization reaction; at best there are several elementary expressions which focus on individual steps, e.g., the release of  $Si^{4+}$ , and the diffusion of  $K^+$ . Despite the lack of consensus on whether illitization is a kinetic or equilibrium phenomenon, the expected response of smectite clay to the elevated temperatures anticipated in a repository is for it to partially collapse to an I/S clay. The extent of this collapse and the rate at which it does this will be dependent on whether rates or equilibrium exert the greater influence.

In summary, therefore, the longevity of smectite clays appears to be dependent upon several factors. Smectite stability is enhanced in silica-rich environments and low temperatures. Assuming that the kinetic model is correct, and utilizing the kinetic diagrams produced by Eberl and Hower (1976), a smectite would collapse to a virtually all-illite I/S clay at temperatures below  $100^\circ C$  within  $10^4$ - $10^5$  years. The

presence of interstitial fluids high in alkali and alkaline earth cations other than  $K^+$ , and interlayer, or exchange, cations other than  $K^+$  reduce the rate and extent of illitization of smectites. The magnitude of the retarding effect of other interstitial cations in the pore fluids is uncertain at this time. For example, a first-order kinetic model appears to fit Gulf Coast data relating the extent of illitization with the age of sediments. This model predicts only about 10 percent collapsed layers would occur in smectites at  $110^\circ\text{C}$  at the end of  $10^6$  years. Apparently, many environmental factors (heating rates, maximum temperature and fluid chemistry) strongly affect the illitization reaction under natural circumstances and could control the stability of smectite clay minerals under repository conditions. Of concern, though, is the recognition that many of the physical and chemical properties of even a slightly illitic I/S clay may vary from those associated with a pure Na-Wyoming bentonite.

#### 4.3 EFFECTS OF RADIATION ON CLAYS

Incorporation of clays in backfills that are intended to contact and sorb long-lived radionuclides requires that the clays remain stable and functional for long time periods. The exposure of the clays to ionizing radiation, particularly the radiation from sorbed radionuclides, may also decrease their long term stability.

A study by Haire and Beall (1979) was restricted to the morphologic effect on kaolinite and palygorskite (attapulgitite) by a strong alpha radiation source\* sorbed on the clays. Morphologic effects (porosity, pitting, fragmentation of plates, and clumping of rods) were evident, and the rate and severity at which they appeared were directly related to the strength of the alpha source. Clays loaded to only a small

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\*Es-253,  $6 \times 10^{10}$  alpha/minute-microgram or 6.6MeV alpha radiation; this alpha source is very high with respect to decay energy of individual radionuclides in waste inventories, but not large with respect to the decay energy of the entire waste inventories.

fraction of their sorptive capacity remained apparently unchanged after several weeks, but with radionuclides sorbed to capacity, the clays rapidly showed evidence of disruption. In addition, the palygorskite which has a far greater sorptive capacity, showed much greater radiation damage in a given time. An important conclusion of this work was that the sorption of Es-253, as measured from the radionuclide concentration in brine carrier fluids, remained unaffected by the disruption of the sorbent. It must be noted, however, that the sorption mechanism under these conditions was not determined. The Es may be retained on the clay, or may occur in an unknown insoluble and centrifugeable phase. The experiment provides no evidence for either possibility, and the relevance of this result to other clays and radionuclides is unknown.

The potential for crystallographic, and thereby behavioral changes in clays due to irradiation by sorbed sources may be estimated by exposure of clay materials to radiation from external sources. The morphological effects of an electron beam and gamma irradiation on quartz and kaolinite have been investigated (Spitsyn et al, 1980). The radiation treatment (Co-60, 2.6 Mrad gamma/hr) resulted in the formation of clumps from an initially evenly dispersed and evenly size-distributed kaolinite sample. The electron beam (accelerating voltage,  $E_0 = 100$  kev, time =?) caused surficial pitting of the kaolinite crystals, and the clay crystals became anhedral. Nonetheless, no structural changes were apparent in the X-ray diffraction of the sample. A volume increase in the surface layers of the kaolinite may have occurred due to irradiation, although the causative mechanism for this phenomenon was not determined. Krumhansl (1982) also showed no crystallographic changes occurred in smectite (from bentonite) exposed to  $10^{10}$  rads of  $^{60}\text{Co}$  gamma radiation.

No firm conclusions can be made based upon existing data for the irradiation effects on clays. Apparently, clays are not immune to crystallographic disruption from strong radiation sources. Long term effects due to irradiation by nuclides in a repository and the effects on the functional properties of a clay seal or backfill are currently unknown.

## 5.0 EMPLACEMENT CONSIDERATIONS

Emplacement feasibility and quality control of the emplaced seals are critical to the design of repository seals. The optimum emplacement methodology depends on the type of seal (shaft, tunnel, or borehole seals, or room backfill) as well as on the intended function of the seal, including radionuclide migration retardation. Three emplacement methods may be considered for clay seals.

- In-place compaction
- Precompaction
- Slurries

Major considerations in evaluating emplacement methods include the following:

- Control of fabric anisotropy if fabric strongly controls seal performance
- Adequate compaction near the walls of penetrations, particularly in boreholes and near the ceiling of horizontal openings
- Optimization of consolidation of the seal without damage (crushing and fracturing) to the host rock or adjacent seal components
- Quality control of compacted clay seals particularly those that are remotely emplaced.

## 5.1 IN-PLACE COMPACTION

In shafts and tunnels clay seals may be compacted in place using standard methods currently employed in engineering practice. For example, Taylor et al (1980) describe seal emplacement using earth rollers, small compacters, and hand-held tampers. These methods appear feasible but additional attention must be given to the degree of compaction required (in terms of optimum permeability and porosity) and to the adequacy of methods for backfilling close to the ceilings of tunnels. Consideration must be given also to anisotropy. For example, if materials are placed horizontally in a tunnel and compacted, there will be a horizontal preferred orientation of clay particles which would be undesirable from the point of view of retarding flow along the tunnel. Remote compaction

methods which must be employed in boreholes may require further technical development (McGowan et al, 1976) in order to develop methods which will produce the required degree of compaction without damage to the host rock or abutting seals.

## 5.2 PRECOMPACTION

Precompacted clays or clay composites may be emplaced in seal zones as pellets or shaped bricks. Swelling clays (bentonite) are generally proposed with the assumption that the precompacted material will swell on contact with water forming a tight seal. For shafts or tunnels, for example, Taylor et al (1980) illustrate a concept for placing a seal in the form of bentonite blocks with the joints mortared with cement or powdered bentonite. Taylor et al also describe schemes for borehole sealing using either soil cartridges which are compacted by a wireline downhole hammer, or using bentonite pellets mixed with gravel placed in a slurry. Pusch and Bergstrom (1980) also describe a placement method for borehole sealing using a perforated, thin-walled copper pipe which is filled with highly compacted bentonite and permanently emplaced in the seal zone. Upon contact with water the bentonite swells and extrudes through the perforations to form a homogeneous, low permeability seal. An advantage of precompaction, compared with in-place compaction, is that it should be possible to achieve much higher densities. Precompaction will result in lower permeability and also higher swelling pressure.

## 5.3 SLURRY EMPLACEMENT

Bentonite slurry cutoff trenches are a viable method for retarding ground water flow in soils. Also, bentonite slurries have been used for grouting fractures in rock. For penetration sealing, the use of slurries appears to be suitable only where the introduction of additional water to the seal zone does not jeopardize repository or seal performance, such as in aquifers or other permeable (fractured or porous) zones in shafts and boreholes. The use of slurries for large volume emplacements, such as backfilling, may be unsuitable due to settling or

consolidation with drying, and the subsequent formation of void space or fractures. It should be noted that a swelling clay emplaced as an aqueous slurry has swollen before emplacement, and has little or no capacity to swell into a larger volume after emplacement.

The major application for bentonite slurries might be to grout fractures in the host rock. In pressure grouting operations in fractured rock, groutability is determined by fracture width and by the particle size of the grouting fluid. Tests with cement grouts have shown that the ratio of fracture width (aperture) to particle size should be at least 1.7:1 and preferably 3:1 or greater (Waterways Experiment Station, 1956). Mean particle sizes for various types of grout are given by Cambefort (1977) and can be related to groutability - in terms of the minimum permeability which can be treated - by means of relationships among fracture aperture, spacing and permeability given by Hoek and Bray (1977). Assuming a fracture spacing in the range 0.1 to 1.0 m, a ratio of fracture aperture to maximum grout particle size of 3:1, and a mean particle size for bentonite of 6 microns, the minimum rock mass permeability which can be treated with bentonite appears to be in the range  $10^{-6}$  to  $10^{-7}$  cm/sec. This permeability is approximately two to three orders of magnitude lower than the minimum which can be treated with cement grouts.

A different technique which might be considered for injecting bentonite into rock fractures is electrophoresis, where the bentonite is introduced into fractures by means of a difference in electrical potential. The method has been demonstrated in the laboratory (Pusch, 1978c) but not in the field. A possible configuration for treatment of the disturbed zone in boreholes involves inducing an electric potential across a packer in a disturbed region of rock (Figure 5-1). Bentonite may be induced to migrate into connected fractures and thereby reduce disturbed zone permeability. A possible advantage of this method compared to conventional grouting is that it does not involve high-pressure injection which can tend to open fractures.

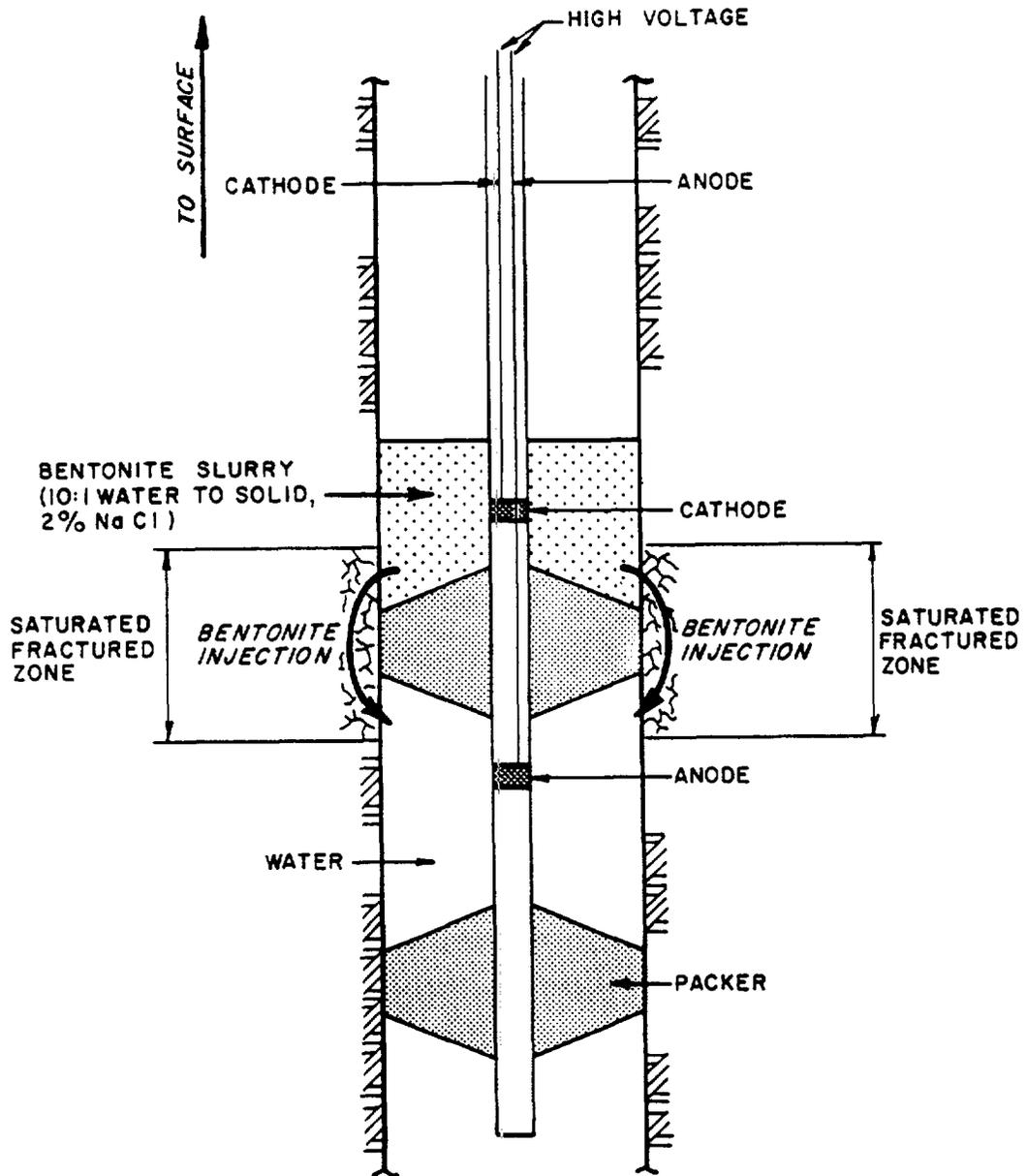


Figure 5-1. Conceptual Design to Seal Host Rock Fractures ("Disturbed Zones") in Boreholes by Electrophoresis

## 6.0 CONCLUSIONS AND RECOMMENDATIONS

### 6.1 CONCLUSIONS

The ability of clays to serve major seal functions, reduction of fluid flow and/or radionuclide migration, has been demonstrated in several research programs reviewed herein. Under the range of possible repository seal environments, however, the stability of many clay species is not certain. The long term stability of materials used in seals and backfills depends on the specific individual sealing environments. Consequently, the longevity of clays and seal functions can be reasonably assured only with completion of stability studies relevant to specific candidate sites.

#### 6.1.1 Material Selection

The swelling clays, smectites, appear to be effective in reducing the internal hydraulic conductivities of seals to values of  $10^{-9}$  cm/sec or less. Further, expansive clays require less energy input to achieve low permeability by compaction than is necessary for materials high in non-swelling clays. They may, however, require energy input for drying. Smectite clays can be used in mixtures of clay or non-clay materials to reduce permeability of the bulk material. Permeability, density, swelling pressure and capacity, and physical/mechanical properties can be adjusted and tailored to specific requirements by pretreatment, compaction methods, additives, and water content. Model seals using clay materials low in swelling clays showed that fluid flow through the seal may concentrate at or near the interface with the host. The swelling capacity of smectite clays may help prevent interface flow, although model tests must be performed to confirm this. In spite of highly desirable properties, swelling clays cannot be considered as the only candidate materials for clay seals. Economically, it may be preferable to use clay materials available at candidate repository sites. Also, the stability of swelling clays under the range of possible sealing conditions remains to be demonstrated. Thus, a range of clay materials must be considered viable candidate seal materials, as discussed in section 6.2.1.

### 6.1.2 Emplacement Methods

Clay materials may be emplaced in granular form and compacted in place, or they may be precompacted prior to emplacement, or they may be emplaced as a slurry. In-place compaction can be applied to shaft and tunnel backfilling and sealing using familiar technologies, provided that inhomogeneities in compaction, particularly at the host rock interface and at the roofs of tunnels and rooms, can be minimized. Barriers may be necessary to restrain movement with clay expansion. Remote in-place compaction methods for boreholes require further technical development particularly with respect to quality control, suggesting that the priority might be given to hydraulic cement based materials for this application. Precompacted clay materials, especially those containing swelling clays, may be particularly useful in some seal components when high density is essential. Clay slurries may be considered for grouting in waterbearing and disturbed rock zones.

### 6.1.3 Sorption

Several clay minerals appear to perform relatively well as sorptive media, particularly for cations. However, most sorption studies and experimentally determined  $K_d$  values are of questionable value for the design of seals and backfills. Few studies realistically duplicate repository conditions of Eh, pH, temperature, fluid composition, radionuclide concentration, or fluid:sorbent ratio. The results obtained, therefore, are difficult to apply rigorously to the design and assessment of repository seals or backfills. The available body of data for clay sorption is useful as an indication of trends in clay sorptivity due to environmental effects (pH, temperature, and radionuclide concentration), and as a relative measure of the sorptivity of clay species; for example, smectites, vermiculite, and attapulgite appear to be more effective sorbers than kaolinite, illite and chlorite, under most experimental conditions. Illite and vermiculite may be most effective in fixing certain cations. Clays do not appear to sorb anions significantly. Seal designs requiring high sorptivity may necessitate the use of zeolites in certain mixes or in certain seal components.

Additional work is required to define sorptive properties in rigorously controlled, simulated repository conditions.

#### 6.1.4 Longevity

Clay longevity remains an important issue, and one which cannot be clearly resolved using existing information. Under dry conditions, reversible dehydration of many clays occurs at temperatures up to 300°C, while partial collapse of smectites and vermiculite may take place with prolonged time at temperatures below 100°C (i.e., at temperatures likely to be experienced in seal zones) and more rapidly at higher temperatures. Dehydration of clays occurs at higher temperatures under hydrothermal conditions. Low temperature (<300°C) equilibrium phase transformation appears to be more applicable to smectites and kaolinite than to illite and chlorite. Smectite may transform to mixed layer clays which will reduce the swelling capacity of the clay and may decrease the volume of the clay body. Furthermore, the sorption capacity of the clay material will diminish. The kinetics of phase transformations at low temperatures appear to be controlled by fluid composition, grain size, and temperature; among smectites, the interlayer cation is a further control. The likelihood of these transformations and the hydraulic, chemical, and physical consequences to the integrity of a repository seal system have not been investigated and will undoubtedly depend on seal emplacement conditions.

## 6.2 RECOMMENDATIONS FOR ADDITIONAL RESEARCH

Some observations and recommendations that may be used to guide research efforts in support of repository sealing follow below.

1. The continued research on clays should include only a select group of clays and clay-bearing materials. The selection of this candidate group may be based upon promising results from existing studies, or site-specific considerations. The latter might include investigation of clays or shales occurring at candidate repository sites, to assess their value as sealing materials.

2. Sorption experiments require standardization of materials, procedures, and experimental conditions. Careful control of experimental parameters is required, including Eh, pH, fluid composition, radionuclide concentration, and temperature. All variables should realistically reflect repository site conditions, and only a minimum number should be varied in any one set of experiments.
3. Chemical and thermodynamic data must be collected on selected clays and clay-bearing materials. This data will be critical to the assessment of the long-term stability of clays.

Research recommendations are summarized in Table 6-1. The following sections briefly describe recommendations with respect to each performance characteristic. Recommendations for performance testing are not necessarily appropriate to all candidate materials.

#### 6.2.1 Candidate Materials

Ideally, priority clay materials for repository sealing applications should be readily available near candidate sites. High volumes of material may be required in backfills in rooms, shafts and tunnels. The applicability of any locally derived materials to sealing requires further study, including precise mineralogic composition (and uniformity), physical properties, chemical stability in repository seal environments, and perhaps sorptivity. Candidate sites, with appropriate clays include:

- Columbia River Basalts
  - Ringold D Clay and Nontronite
- Nevada Test Site
  - Eleana Argillite
- Bedded or Dome Salt Site (to be determined)
  - associated illitic or smectite-bearing shales or clays

Oregon (Ca-) and Wyoming (Na-) bentonites should also be evaluated, both as materials to be used alone in seal components and as additives to the

Table 6-1. Data Needs and Research Recommendations for Candidate Clay-Bearing Seal Materials

Performance Property	Performance Objective	Research Need	Research Recommendations
1. Permeability	Seal zone permeability approaching undisturbed host rock	Internal permeability; Interface permeability; Permeability as f(temperature, and cyclic heating.	Water permeability, using appropriate groundwater; Material compressed at lithostatic pressure (up to 1.4 MPa) during test; Achieve steady state in tests, for long term study; Test seal and model seal-host interface; Test @35°, 100°, 300°C; cyclic heating regimes accompanied by gas (N <sub>2</sub> ) fringe.
2. Strength, stress/strain properties	Non-brittle response to stress	Ductility, deformability, shear strength and elastic properties as f(water content, degree of compaction, emplacement); Response to cyclic stress.	Ductility as f(initial degree of compaction, and water content); Deformability (same); Response to cyclic stress; Shear strength and friction angle of model seal in salt host.
3. Compressibility	Physical support through volume stability	Compressibility as emplaced; Compressibility after dehydration.	Compressibility as f(initial degree of compaction), 35°C; Compressibility of swollen and subsequently dehydrated seal as f(swell volume); Compressibility during cyclic compression.
4. Swelling/shrinkage	Fracture/void space filling; minimal and recoverable shrinkage	Swelling pressure; Minimum width of fractures that can be filled, and controls; Maximum volume loss as f(temperature, time).	Swell pressure as f(emplacment or degree of compaction, initial water content) in groundwater; Volume loss as f(temperature) for various montmorillonite contents; Volume loss as f(time) to steady state at constant temperature; Minimum fracture width which can be filled as f(swell pressure, grain size of material).
5. Erodability	Freedom from erosion in seepage water	Piping and dispersion potential.	Model tests of materials as emplaced, maximum hydraulic gradient for specific site, temperature 35°, vary fracture width 0.1-200mm; Determine pore water composition as emplaced, and % Na in pore water.
6. Thermal properties	Compatible with host rock(?)	Thermal expansion coefficient; Thermal conductivity; Heat capacity.	Standard thermal testing at 35°, 100°, 300°C; Materials as emplaced; specify water content; Test water saturated seal materials and steady state water content at test temperature
7. Sorption of radionuclides	High sorption of radionuclides (high K <sub>d</sub> , cation exchange capacity)	K <sub>d</sub> as f(temperature, radionuclide loading, pH, Eh, water composition, surface area of sorbent).	Study key radionuclides (Barney & Wood, 1980; Moody, 1982) using groundwater or brine carrier fluids; Radionuclide loadings expressed as ratio to major exchange cation; temperatures = 35°, 100°, 200°C; Eh = air, HM, QFM as appropriate Test bulk material and material as emplaced (compacted); measure surface area by ethylene glycol method
8. Longevity	Thermochemical stability; mechanical durability	Free energy of formation, all phases; Free energy of reactions as f(temperature); Volume change with reactions; Solubility, reactivity in groundwater as f(temperature); Radiation effects Long-term natural mineralogic changes as f(groundwater composition, temperature).	Determine by means of K <sub>sp</sub> , calculation or calorimetry (clays dissolve incongruently); DTA or cold seal for steady state phase change determination; lithostatic pressure; Long term (Dickson autoclave or equivalent) groundwater-seal material reactions; lithostatic pressure, 100°, 300°C, monitor pH; note phase changes, exchange cation changes, breakdown of clay structure; Use external radiation sources and sorbed radiation sources studied as f(dose, temperature); determine structural, density, K <sub>d</sub> changes; temperature = 35°, 100°, 300°; observe annealing; Detailed diagenetic studies.
9. Interaction with adjacent seals/host	Inert with respect to adjacent seals/host	Dehydration of adjacent components; Reaction with adjacent components.	Model tests of wet concrete-clay interface; Cold seal or Dickson autoclave tests of clay + concrete powder, run to steady state @ 100°, 300°C.

above materials. Bentonite (or smectite clay group) properties may be desirable in repository sealing, but questions remain of their long-term stability in repository environments. For example some degree of smectite to illite conversion may occur in the seal zone. In order to evaluate the effects of this conversion on seal properties, particularly permeability and mechanical properties, mixed-layer (e.t., illite-smectite) clays and illite (or paragonite) should also be examined.

These clay minerals are the products of the smectite-illite conversion and their properties may provide important information regarding the consequences of the conversion, if it were to occur during the life of the seal.

#### 6.2.2 Performance Testing

Permeability. Research should emphasize the internal permeability of clay bearing seals and of the interface between a clay seal and shaft walls. Permeability at elevated temperatures (e.g., 35°, 100°, and 300°C) and under cyclic heating-cooling and wetting-drying regimes should be determined.

Strength-Stress/Strain Properties. Mechanical properties of clay materials, including deformability (strain to failure), should be investigated in candidate materials at various compaction densities and water contents. Model tests of clay plug-host systems under shear stress may elucidate shear behavior of emplaced materials. Constant static and cyclic stress effects should be evaluated.

Compressibility. The compressibility of candidate materials should be related to the emplacement method used and to the density of the material as emplaced. Compressibility may be altered by dehydration of the material as well as by cyclic compression.

Swelling/Shrinkage. Maximum swelling pressures and total volume changes should be determined for candidate seal materials and related to initial

density and water content. Appropriate site-specific ground waters must be used in swelling pressure studies. Shrinkage should be determined with respect to the time required to achieve a constant volume at various temperatures. Swelling behavior and fracture healing on rehydration must also be investigated.

#### Fracture Filling

Testing is required to better define the fracture filling ability of various clays, particularly bentonite slurries, in candidate host rocks. Initially, tests should be conducted in the laboratory for examination of the relationships among swelling capacity, grain size distributions, and fracture aperture and depth which can be filled by a swelling clay seal. Field tests would be required at a later stage.

Erodability. Erosion of a clay material seal or backfill by piping will be a major concern only if fairly wide fractures occur in host rocks or adjacent seals, and a flowing ground water under a hydraulic gradient impinges on the seal material. Seals could be designed to minimize dispersion and erosion, in given host environments. Model testing to determine the fracture width which will permit piping of candidate clay material seals under hydraulic gradients occurring at, or likely to occur at, candidate repository sites may be initiated. Based on local geology, rock and seal behavior, and tectonics, the likelihood of fractures opening in the host rock or adjacent seals, to the width indicated by the model tests, may be related to the likelihood of seal piping.

The potential for dispersion may be estimated by means such as the pin hole test, or by analysis of pore fluid composition (TDS and percent Na) of the clay material as emplaced, and estimating the propensity for dispersion knowing ground water composition (the eroding fluid) at candidate repository sites (Sherard et al, 1976).

Thermal Properties. Thermal properties that will be important in determining seal performance include thermal expansion, thermal conductivity,

and heat capacity. As noted earlier, these properties are strongly dependent on water content. Standard thermal testing should examine materials in "as-placed" conditions (water content, density/porosity), through a range of temperatures and water contents which the seal components are likely to experience after repository closure.

Sorption of Radionuclides. Sorption coefficients for key radionuclides must be determined under controlled experimental conditions which match specific repository environments. In planning tests, consideration should be given to the following:

1. Use of materials keyed to specific candidate repository sites.

Water chemistry obviously is a major control on sorption, the effects of which appear to require empirical determination. Therefore, the use of water compositions similar to specific site ground water is extremely significant to the relevance of sorption coefficients ( $K_d$ 's) to actual repository performance. Distilled water experiments are of little value in meeting the needs of repository sealing and backfill designers. Solids should be compacted to the range of densities expected in backfills, and the permeability of these materials in experimental studies should duplicate the repository seal design.

2. Control of chemical parameters.

It is critical that major chemical parameters be controlled in all sorption experiments, and that these conditions be completely reported. Included among these parameters are Eh (or oxygen fugacity), pH, temperature, pressure, and fluid and sorbent composition. Redox potential (Eh) may be controlled by the atmosphere, or by rock-water interactions. All parameters should be representative of the repository environment. Experiments should be conducted using fluid and sorbent compositions which represent the initial and anticipated phases that will occur at different stages of repository history.

3. Appropriate radionuclide concentration and inventory.

The appropriate concentration(s) of radionuclides for use in experimental systems requires knowledge of waste type, waste form, and waste solubility under repository conditions. Unfortunately, these criteria are largely undefined for candidate repositories. Experimentation with individual radionuclides or with limited groups of radionuclides is more practical than studying a complete radionuclide inventory of a given repository experimentally. Nevertheless, results from tests with individual nuclides should be supported by some more encompassing experiments in order to evaluate

competing ion effects, or other effects that may give misleading results in the simpler systems. Studies such as Barney and Wood (1980) which define key radionuclides based on hazard, quantity and release rate for a given repository scenario, would be useful in determining high priority sorption studies.

Additional tests are required to evaluate appropriate admixtures (probably containing copper or other metals) for retarding anion migration. These admixtures must be compatible with the clay sealing materials and must be designed to be non-detrimental to seal functions and material stability.

#### 4. Emplacement considerations.

Because sorption is a surface area phenomenon, emplacement (as it affects porosity) may be an important consideration. Tests must be designed to determine any optimum combination of porosity and permeability, and to evaluate any effects of fabric anisotropy.

Longevity. Thermodynamic modeling will require determination of thermodynamic properties of clays and non-clay constituents in candidate materials. Long-term experimental studies will be required, particularly because reaction kinetics may play an important part in phase transformation in clay materials at low temperatures. Site-specific ground waters from candidate sites should be used in experiments. Additional studies of natural diagenesis can yield important information.

Determination of long-term radiation effects on clays should incorporate the use of both external and sorbed radiation sources. Dose, dose rate, and temperature (perhaps an annealing effect may obscure morphologic changes at high temperatures) are critical parameters to examine.

Interactions with Adjacent Materials. Model tests may be important to assess the ability of clay materials to alter portland cement based concrete properties by juxtaposition of these materials. Dehydration of the concrete (or concrete phases) by hydrophilic clays or the dehydration of clays by cementitious phases should be examined in greater detail. Long term cold seal or autoclave testing of clay and concrete powders in hydrothermal regimes may be needed to assess the reactivity of these sealing materials in specific repository environment.

## REFERENCES

- Allard, B., J. Rydberg, H. Kipatsi, and B. Torstenfelt, 1979. "Disposal of Radioactive Waste in Granite Bedrock," in Radioactive Waste in Geologic Storage, S. Fried, ed., American Chemical Society, Washington, D.C., pp. 47-73.
- Allard, B., B. Torstenfelt, K. Anderson, and J. Rydberg, 1980. "Possible Retention of Iodine in the Ground," in Scientific Basis for Nuclear Waste Management, Vol. 2, C. J. M. Northrup, Jr., ed., Plenum Press, New York, New York, pp. 673-680.
- Almon, W. R., L. B. Fullerton, and D. K. Davies, 1976. "Pore Space Reduction in Cretaceous Sandstones Through Chemical Precipitation of Clay Minerals," Journal of Sedimentary Petrology, Vol. 46, pp. 89-96.
- Ames, L. L., and J. E. McGarrah, 1979. Lower Temperature (23°C, 60°C) Radionuclide Solid-Liquid Distribution Measurement Methodology, PNL-3103, Battelle Northwest Laboratory, Richland, Washington.
- Ames, L. L., and J. E. McGarrah, 1980a. Investigation of Basalt-Radionuclide Distribution Coefficients: Fiscal Year 1980 Annual Report, RHO-BWI-C-108, Rockwell Hanford Operations, Richland, Washington.
- Ames, L. L., and J. E. McGarrah, 1980b. High Temperature Determination of Radionuclide Distribution Coefficients for Columbia River Basalt, RHO-BWI-C-111, Rockwell Hanford Operations, Richland, Washington.
- Arulanandan, K., P. Loganathan, and R. B. Krone, 1975. "Pore and Eroding Fluid Influences on Surface Erosion of Soil," Journal of the ASCE Geotechnical Engineering Division, Vol. 100, pp. 51-66.
- Barney, G. S., and B. J. Wood, 1980. Identification of Key Radionuclides in a Nuclear Waste Repository in Basalt, RHO-BWI-ST-97, Rockwell Hanford Operations, Richland, Washington.
- Barrer, R. M., 1978. Zeolite and Clay Minerals as Sorbents and Molecular Sieves, Academic Press, New York, New York.
- Beall, G. W., B. H. Ketelle, R. G. Haire, and G. D. O'Kelley, 1979. "Sorption Behavior of Trivalent Actinides and Rare Earths on Clay Minerals," in Radioactive Waste in Geologic Storage, S. Fried, ed., American Chemical Society, Washington, D.C., pp. 201-213.
- Berner, R. A., 1971. Chemical Sedimentology, McGraw-Hill Book Co., New York, New York.
- Bird, G. W., and V. J. Lopata, 1980. "Solution Interaction of Nuclear Waste Anions With Selected Geological Materials," in Scientific Basis for Nuclear Waste Management, Vol. 2, C. J. M. Northrup, Jr., ed., Plenum Press, New York, New York, pp. 419-426.

- Blatter, C. L., H. E. Roberson, and G. R. Thompson, 1973. "Regularly Stratified Chlorite-Dioctahedral Smectite in Dike-Intruded Shales, Montana," Clays and Clay Minerals, Vol. 21, pp. 207-212.
- Boles, J. R., and S. G. Franks, 1979. "Clay Diagenesis in Wilcox Sandstones of Southwest Texas: Implications of Smectite Diagenesis on Sandstone Cementation," Journal of Sedimentary Petrology, Vol. 49, pp. 55-70.
- Brindley, G. W., 1981. "Structures and Chemical Compositions of Clay Minerals," in Clays and the Resource Geologist, F. J. Longstaffe, ed., Mineralogical Association of Canada, Calgary, Alberta, pp. 1-21.
- Burst, J. F., 1969. "Diagenesis of Gulf Coast Clayey Sediments and its Possible Relation to Petroleum Migration," American Association of Petroleum Geologists Bulletin, Vol. 53, pp. 73-93.
- Cambefort, H., 1977. "The Principles and Applications of Grouting," Quarterly Journal of Engineering Geology, Vol. 10, pp. 57-95.
- Chen, F. H., 1975. Foundations on Expansive Soils, Elsevier Scientific Publishing Co., New York, New York.
- Churchman, G. J., and M. L. Jackson, 1976. "Reaction of Montmorillonite With Acid Aqueous Solutions: Solute Activity Control by a Secondary Phase," Geochimica et Cosmochimica Acta, Vol. 40, pp. 1251-1259.
- Claasen, H. C., and A. F. White, 1978. "Application of Geochemical Kinetic Data to Groundwater Systems," in Chemical Modeling in Aqueous Systems, E. A. Jenne, ed., American Chemical Society, Washington, D.C., pp. 771-793.
- D'Appolonia Consulting Engineers, Inc., 1979. Repository Sealing Design Approach - 1979, ONWI-55, prepared for Office of Nuclear Waste Isolation, Battelle Memorial Institute, Columbus, Ohio.
- D'Appolonia Consulting Engineers, Inc., 1980. Repository Sealing: Evaluation of Materials Research Objectives and Requirements 1980, ONWI-108, prepared for Office of Nuclear Waste Isolation, Battelle Memorial Institute, Columbus, Ohio.
- Davis, S. N., and R. J. M. DeWiest, 1966. Hydrology, John Wiley and Sons, New York, New York.
- Dayal, R., 1977. "Kinetics of Silica Sorption and Clay Dissolution Reaction at 1 and 670 atm," Geochimica et Cosmochimica Acta, Vol. 41, pp. 135-141.
- Deer, W. A., R. A. Howie, and J. Zussman, 1966. An Introduction to the Rock Forming Minerals, Longman, London.

Diamond, S., 1970. "Pore Size Distributions in Clays," Clays and Clay Minerals, Vol.18, pp.7-23.

Dosch, R. G., and A. W. Lynch, 1978. Interaction of Radionuclides with Geomedia Associated with The Waste Isolation Pilot Plant (WIPP) Site in New Mexico, SAND78-0297, Sandia National Laboratories, Albuquerque, New Mexico.

Dunoyer, G., 1970. "The Transformation of Clay Minerals During Diagenesis and Low-grade Metamorphism, a Review," Sedimentology, Vol. 15, pp. 281-346.

Eberl, D., 1978. "The Reaction of Montmorillonite to Mixed-Layer Clay: the Effect of Interlayer Alkali and Alkaline Earth Cations," Geochimica et Cosmochimica Acta, Vol. 42, pp. 1-7.

Eberl, D. and J. Hower, 1976. "Kinetics of Illite Formation". Geological Society of America Bulletin, Vol. 87, pp. 1326-1330.

Eberl, D., G. Whitney, and H. Khoury, 1978. "Hydrothermal Reactivity of Smectite," American Mineralogist, Vol. 63, pp. 401-409.

Erdal, B. R., B. P. Bayhurst, B. M. Crowe, W. R. Daniels, D. C. Hoffman, F. O. Lawrence, J. R. Smyth, J. L. Thompson, and K. Wolfsberg, 1979. Laboratory Studies of Radionuclide Transport in Geologic Media, IAEA-SM-243/37, presented at OECD International Symposium, Helsinki.

Erickson, K. L., 1979. "Radionuclide Sorption Studies on Abyssal Red Clays," in Radioactive Waste in Geologic Storage, S. Fried, ed., American Chemical Society, Washington, D.C., pp. 267-290.

Erickson, K. L., 1980. "Radionuclide Sorption Studies on Abyssal Red Clays," in Scientific Basis for Nuclear Waste Management, Vol. 2, C. J. M. Northrup, Jr., ed., Plenum Press, New York, New York, pp. 641-646.

Fagerstrom, H., and B. L. Lundahl, 1977. Handling of Buffer Material Quartz-Bentonite, KBS Teknisk Rapport 37, Karnbranslesakerhet, Stockholm.

Foscolos, A. E., and H. Kodoma, 1974. "Diagenesis of Clay Minerals from Lower Cretaceous Shales of Northeastern British Columbia," Clays and Clay Minerals, Vol. 22, pp. 319-336.

Fuchtbauer, H., 1974. Sedimentary Petrology--II. Sediments and Sedimentary Rocks 1, John Wiley and Sons, New York, New York.

Garrels, R. M., and C. L. Christ, 1965. Solutions, Minerals, and Equilibria, Freeman, Cooper, and Co., San Francisco, California.

- Grim, R. E., 1962. Applied Clay Mineralogy, McGraw-Hill Book Co., New York, New York.
- Grim, R. E., 1968. Clay Mineralogy, McGraw-Hill Book Co., New York, New York.
- Grimshaw, R. W., 1971. The Chemistry and Physics of Clays, 4th ed., John Wiley and Sons, New York, New York.
- Güven, N., W. F. Hower, and D. K. Davies, 1980. "Nature of Authigenic Illite in Sandstone Reservoirs," Journal of Sedimentary Petrology, Vol. 50, pp. 761-766.
- Haire, R. G., and G. W. Beall, 1979. "Consequences of Radiation From Sorbed Transplutonium Elements on Clays Selected for Waste Isolation," in Radioactive Waste in Geologic Storage, S. Fried, ed., American Chemical Society, Washington, D.C., pp. 291-295.
- Harder, H., 1974. "Illite Mineral Synthesis at Surface Temperatures," Chemical Geology, Vol. 14, 241-254.
- Hayes, J. B., 1970. "Polytypism of Chlorite in Sedimentary Rocks," Clays and Clay Minerals, Vol. 18, pp. 285-306.
- Helgeson, H. C., J. M. Delany, H. W. Nesbitt, and D. K. Bird, 1978. "Summary and Critique of the Thermodynamic Properties of Rock-forming Minerals," American Journal of Science, Vol. 278-A, pp. 1-229.
- Heling, D., 1974. "Diagenetic Alteration of Smectite in Argillaceous Sediments of the Rhinegraben (SW Germany)," Sedimentology, Vol. 21, pp. 463-472.
- Hemley, J. J., 1959. "Some Mineralogical Equilibria in the System  $K_2O-Al_2O_3-SiO_2-H_2O$ ," American Journal of Science, Vol. 257, pp. 241-270.
- Hemley, J. J., C. Meyer, and D. H. Richter, 1961. Some Alteration Reactions in the System  $Na_2O-Al_2O_3-SiO_2-H_2O$ , Professional Paper 424-D, U.S. Geological Survey, pp. 338-340.
- Hoek, E., and J. Bray, 1977. Rock Slope Engineering, Institution of Mining and Metallurgy, London.
- Howard, J. J., 1980. Diagenesis of Mixed-Layer Illite-Smectite in Interlaminated Shales and Sandstones, Ph.D. Dissertation, State University of New York at Binghamton, Binghamton, New York.
- Howard, J. J., 1981. "Lithium and Potassium Saturation of Illite/Smectite Clays from Interlaminated Shales and Sandstones," Clays and Clay Minerals, Vol. 29, pp. 136-147.

Hower, J., E. V. Eslinger, M. E. Hower, and E. A. Perry, 1976. "Mechanisms of Burial Metamorphism of Argillaceous Sediment: 1. Mineralogical and Chemical Evidence," Geological Society of America Bulletin, Vol. 87, pp. 725-737.

Kelsall, P. C., J. B. Case, W. E. Coons, and D. Meyer, 1982. Schematic Designs for Penetration Seals for a Reference Repository in Bedded Salt, ONWI-405, prepared by D'Appolonia Consulting Engineers, Inc. for Office of Nuclear Waste Isolation, Battelle Memorial Institute, Columbus, Ohio.

Kisch, H., 1966. "Chlorite-Illite Tonstein in High-rank Coals from Queensland, Australia: Notes on Regional Grade and Coal Rank," American Journal of Sciences, Vol. 264, pp. 386-397.

Kisch, H., 1974. "Anthracite and Meta-anthracite Coal Ranks Associated with 'Anchimetamorphism' and 'Very-low-stage' Metamorphism. I.," Proceedings, Koninkl. Nederl. Akademie Van Wetenschappen-Amsterdam 77, Series B, pp. 81-118.

Kittrick, J. A., 1966. "Free energy of formation of kaolinite from solubility measurements," American Mineralogist, Vol. 51, pp. 1457-1466.

Kittrick, J. A., 1971a. "Stability of Montmorillonites. I. Belle Fourche and Clay Spin Montmorillonites," Soil Science Society of America Proceedings, Vol. 35, pp. 820-823.

Kittrick, J. A., 1971b. "Stability of Montmorillonites. II. Aberdeen Montmorillonite," Soil Science Society of America Proceedings, Vol. 35, pp. 820-823.

Knutsson, S., 1977. Thermal Conductivity Tests on Buffer Material of Compacted Bentonite, KBS Teknisk Rapport 72, Karnbranslesakerhet, Stockholm.

Komarneni, S. and D. M. Roy, 1978. "Effect of Layer Charge and Heat Treatment on Cs Fixation by Layer Silicate Minerals," Journal of Inorganic Nuclear Chemistry, Vol. 40, pp. 893-896.

Komarneni, S., and D. Roy, 1979. "Shale as a Radioactive Waste Repository: The Importance of Vermiculite," Journal of Inorganic Nuclear Chemistry, Vol. 41, pp. 1793-1796.

Komarneni, S., and D. M. Roy, 1980. "Hydrothermal Effects on Cesium Sorption and Fixation by Clay Minerals and Shales," Clays and Clay Minerals, Vol. 28, pp. 142-148.

Komarneni, S., and R. Roy, 1980. "Superoverpack: Tailor-Made Mixtures of Zeolites and Clays," in Scientific Basis for Nuclear Waste Management, Vol. 2, C. J. M. Northrup, Jr., ed., Plenum Press, New York, New York, pp. 411-418.

- Komarneni, S., and W. B. White, 1981. "Hydrothermal Reactions of Clay Minerals and Shales with Cesium Phases from Spent Fuel Elements," Clays and Clay Minerals, Vol. 29, pp. 299-308.
- Koster van Groos, A. F., 1981. Determination of Dehydration Temperature of a Secondary Vug-Filling Mineral (Smectite Clay) Using Differential Thermal Analysis at Various Pressures, RHO-BWI-C-102, Rockwell Hanford Operations, Richland, Washington.
- Krumhansl, J. L., 1982. "Mineralogic Stability of a Bentonite Backfill in a Bedded Salt Repository Environment," Abstracts With Programs, 1982, Vol. 14, Geological Society of America, Boulder, Colorado, P. 536.
- Lahann, R. W., and H. E. Roberson, 1980. "Dissolution of Silica from Montmorillonite: Effect of Solution Chemistry," Geochimica et Cosmochimica Acta, Vol. 44, pp. 1937-1944.
- Lambe, T. W., and R. V. Whitman, 1969. Soil Mechanics, John Wiley and Sons, New York, New York.
- Lynch, A. W., and R. G. Dosch, 1980. "Interaction of Radionuclides with Geomedia from the Nevada Test Site," in Scientific Basis for Nuclear Waste Management, Vol. 2, C. J. M. Northrup, Jr., ed., Plenum Press, New York, New York.
- Martin, R. T., 1975. Feasibility of Sealing Borehole with Compacted Natural Earthern Materials, Vols. 1 and 2, MIT Research Report 75-28, ORNL/SUB-3960/2, Office of Waste Isolation, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- Mason, B., and L. G. Berry, 1968. Elements of Mineralogy, W. H. Freeman and Co., San Francisco, California.
- McGowan, C., E. Nolan, R. Morey, and A. Palty, 1976. Borehole Plugging by Compaction Process, Y-OWI-SUB-7087-1, Office of Waste Isolation, Oak Ridge, Tennessee.
- Mesri, G., and R. E. Olson, 1971. "Mechanisms Controlling the Permeability of Clays," Clays and Clay Minerals, Vol. 19, pp. 151-158.
- Miller, S. E., G. E. Heath, and R. D. Gonzales, 1982. "Effects of temperature on the sorption of lanthanides by montmorillonite," Clays and Clay Minerals, Vol. 30, pp. 111-122.
- Millot, G., 1970. Geology of Clays, Springer-Verlag, New York, New York.
- Mitchell, J. K., 1976. Fundamentals of Soil Behavior, John Wiley and Sons, New York, New York.

- Moody, J. B., 1982. Radionuclide Migration/Retardation Research and Development Technology Status Report, ONWI-321, Office of Nuclear Waste Isolation, Battelle Memorial Institute, Columbus, Ohio, 71 pp.
- Moody, J. B., D. Meyer, and E. Jenkins, 1983. "Experimental Characterization of the Greenschist/Amphibolite Boundary in Mafic Systems," American Journal of Science, Vol. 283, pp. 48-92.
- Muffler, L. J. P., and D. E. White, 1969. "Active Metamorphism of Upper Cenozoic Sediments in the Salton Sea Geothermal Field and the Salton Trough, Southeastern California," Geological Society of America Bulletin, Vol. 30, pp. 157-182.
- Neretnieks, I., 1979. Transport Mechanism and Rates of Transport of Radionuclides in the Geosphere as Related to the Swedish KBS Concept, IAEA-SM-234/108, presented at OECD International Symposium, Helsinki.
- Niagu, J. O., 1975. "Thermochemical Approximations for Clay Minerals," American Mineralogist, Vol. 60, pp. 834-839.
- Nowak, E. J., 1980a. Radionuclide Sorption and Migration Studies of Getters for Backfill Barriers, SAND 79-1110, Sandia National Laboratory, Albuquerque, New Mexico.
- Nowak, E. J., 1980b. "The Backfill as an Engineered Barrier for Nuclear Waste Management," in Scientific Basis for Nuclear Waste Management, Vol. 2, C. J. M. Northrup, Jr., ed., Plenum Press, New York, New York.
- Office of Nuclear Waste Isolation, 1979. Technical Progress Report for the Quarter 1 October - 31 December, 1979, ONWI-9 (1), Battelle Memorial Institute, Office of Nuclear Waste Isolation, Columbus, Ohio, pp. 274-280.
- Office of Nuclear Waste Isolation, 1981a. Technical Progress Report for the Quarter 1 October - 31 December, 1980, ONWI-9 (81-1), Battelle Memorial Institute, Office of Nuclear Waste Isolation, Columbus, Ohio, pp. 76-80.
- Office of Nuclear Waste Isolation, 1981b. Technical Progress Report for the Quarter 1 October - 31 December, 1980, ONWI-9 (81-1), Battelle Memorial Institute, Office of Nuclear Waste Isolation, Columbus, Ohio, pp. 111-128.
- Office of Nuclear Waste Isolation, 1982a. Technical Progress Report for the Quarter 1 April-30 June, 1982, ONWI-9 (82-3), Battelle Memorial Institute, Office of Nuclear Waste Isolation, Columbus, Ohio, pp. 41-46.
- Office of Nuclear Waste Isolation, 1982b. Technical Progress Report for the Quarter 1 January-31 March, 1982, ONWI-9 (82-2), Battelle Memorial Institute, Office of Nuclear Waste Isolation, Columbus, Ohio, pp. 45-48.

Office of Nuclear Waste Isolation, 1982c. Technical Progress Report for the Quarter 1 April-30 June, 1982, ONWI-9 (82-3), Battelle Memorial Institute, Office of Nuclear Waste Isolation, Columbus, Ohio, pp. 136-138.

Olsen, J. M., and R. J. Martin, 1976. Feasibility of Sealing Boreholes with Compacted Natural Earthen Materials, Vol. 3, MIT Research Report R76-26, ORNL/SUB-3960, Office of Waste Isolation, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Olsen, J. M., and R. T. Martin, 1980. Feasibility of Sealing Boreholes with Compacted Earth to Protect Underground Nuclear Waste Repositories, ASCE Preprint 80-166, presented at American Society of Civil Engineers Convention and Exposition, Portland, Oregon.

Olson, R. E., and G. Mesri, 1970. "Mechanisms Controlling Compressibility of Clays," Journal of Soil Mechanics, Vol. 96, pp. 1863-1878.

ONWI, see Office of Nuclear Waste Isolation.

Perry, E. A., and J. Hower, 1970. "Burial Diagenesis in Gulf Coast Pelitic Sediments," Clays and Clay Minerals, Vol. 18. 165-178.

Powers, D. W., S. J. Lambert, S-E. Shaffer, L. R. Hill, and W. D. Weart, 1978. Geological Characterization Report, Waste Isolation Pilot Plant (WIPP) Site, Southeastern New Mexico, SAND 78-1596 (2 Vols.), Sandia National Laboratories, Albuquerque, New Mexico.

Pusch, R., 1978a. Self-Injection of Highly Compacted Bentonite into Rock Joints, KBS Teknisk Rapport 73, Karnbranslesakerhet, Stockholm.

Pusch, R., 1978b. Highly Compacted Na-Bentonite as Buffer Substance, KBS Teknisk Rapport 74, Karnbranslesakerhet, Stockholm.

Pusch, R., 1978c. Small Scale Bentonite Injection Test on Rock, KBS Teknisk Rapport 75, Karnbranslesakerhet, Stockholm.

Pusch, R., 1979. Water Percolation Effects on Clay-Poor Bentonite Quartz Buffer Material at High Hydraulic Gradients, KBS-19, Karnbranslesakerhet, Stockholm, Sweden.

Pusch, R., and A. Bergstrom, 1980. Highly Compacted Bentonite for Borehole and Shaft Plugging, presented at OECD/ONWI Workshop on Borehole and Shaft Plugging, Columbus, Ohio.

Pusch, R., A. Jacobson, and A. Bergstrom, 1979. "Bentonite-Based Buffer Substances for Isolating Radioactive Waste Products at Great Depth in Rock, and Discussion," in Underground Disposal of Radioactive Wastes, Vol. 1, Proceedings of a Symposium held at Otaniemi, Finland, July 2-6, 1979, published by the International Atomic Energy Agency, Vienna, Austria, 1980. pp. 487-502.

- Rieke, H. H., III, and G. V. Chilingarian, 1974. Compaction of Argillaceous Sediments, Vol. 16 in Developments in Sedimentology, Elsevier Publishing Co., Amsterdam.
- Rose, A. W., and D. M. Burt, 1979. "Hydrothermal Alteration," in Geochemistry of Hydrothermal Ore Deposits, H. L. Barnes, ed., John Wiley and Sons, New York, New York, pp. 173-235.
- Roy, D. M., 1981. "Progress in Repository Sealing Materials Studies in 1981," Proceedings of the 1981 National Waste Terminal Storage Program Information Meeting, USDOE/NWTS-15, pp. 55-64.
- Roy, D. M., M. W. Grutzeck, and L. D. Wakeley, 1982. Selection and Durability of Seal Materials for a Bedded Salt Repository: Preliminary Studies, ONWI-479, Office of Nuclear Waste Isolation, Battelle Memorial Institute, Columbus, Ohio, 157 pp.
- Salter, P. F., L. L. Ames, and J. E. McGarrah, 1981a. Sorption of Selected Radionuclides on Secondary Minerals Associated with the Columbia River Basalt, RHO-BWI-LD-43, Rockwell Hanford Operations, Richland, Washington.
- Salter, P.F., L. L. Ames, and J. E. McGarrah, 1981b. The Sorption Behavior of Selected Radionuclides on Columbia River Basalts, RHO-BWI-LD-48, Rockwell Hanford Operations, Richland, Washington.
- Sasaki, N., S. Komarneni, B. E. Scheetz, and R. Roy, 1982, "Backfill-Waste Interactions in Repository Simulating Tests," in Scientific Basis for Nuclear Waste Management, Materials Research Society Symposia Proceedings, Vol. 6, S. V. Topp, ed., North-Holland, New York, pp. 397-404.
- Seed, H. B., J. K. Mitchell, and C. K. Chan, 1961. "The Strength of Compacted Cohesive Soils," in Research Conference on Shear Strength of Cohesive Soils, American Society of Civil Engineers, New York, New York, pp. 877-964.
- Serne, R. J., D. Rai, M. J. Mason, and M. A. Molecke, 1977. Batch Kd Measurements of Nuclides to Estimate Migration Potential as the Proposed Waste Isolation Pilot Plant in New Mexico, PNL-2448, Battelle Northwest Laboratories, Richland, Washington.
- Sherard, J. L., L. P. Dunnigan, and R. S. Decker, 1976. "Identification and Nature of Dispersive Soil," Journal of the ASCE Geotechnical Engineering Division, Vol. 102, pp. 287-301.
- Shiao, S. Y., P. Rafferty, R. E. Meyer, and W. J. Rogers, 1979. "Ion Exchange Equilibria Between Montmorillonite and Solutions of Moderate-to High Ionic Strength," in Radioactive Waste in Geologic Storage, S. Fried, ed., American Chemical Society, Washington, D.C., pp. 299-324.
- Seed, H. B., R. J. Woodward, and R. Lundgren, 1962, "Prediction of Swelling Potential for Compacted Clays," Journal of the Soil Mechanics and Foundations Division, ASCE, Vol. 88.

Silva, R. J., L. V. Benson, and J. A. Apps, 1979a. "Studies of Actinide Sorption on Selected Geologic Materials," in Radioactive Waste in Geologic Storage, S. Fried, ed., American Chemical Society, Washington, D.C., pp. 215-240.

Silva, R. J., L. V. Benson, A. W. Yee, and G. A. Parks, 1979b. Waste Isolation Safety Assessment Program Task 4: Collection and Generation of Transport Data, Theoretical and Experimental Evaluation of Waste Transport in Selected Rocks, Annual Progress Report, October 1, 1978-September 30, 1979, LBL-9946, Lawrence Berkeley Laboratory, Berkeley, California.

Smith, M. J. (principal author), 1980. Engineered Barrier Development for a Nuclear Waste Repository in Basalt: An Integration of Current Knowledge, RHO-BWI-ST-7, Rockwell Hanford Operations, Richland, Washington.

Spitsyn, V. I., V. D. Balukova, I. M. Kosareva, and E. I. Evko, 1980. "Influence of Ionizing Irradiation on the Properties of Aluminosilicate Mineral Rock Repositories of Radioactive Waste," in Scientific Basis for Nuclear Waste Management, Vol. 2, C. J. M. Northrup, Jr., ed., Plenum Press, New York, New York, pp. 593-599.

Srodon, J., 1979. "Correlation between Coal and Clay Diagenesis in the Carboniferous of the Upper Silesian Coal Basin," in International Clay Conference-1978, Vol. 27 in Developments in Sedimentology, M. M. Mortland and V. C. Farmer, eds., Elsevier Scientific Publishing Co., New York, New York, pp. 337-347.

Steiner, A., 1968. "Clay Minerals in Hydrothermally Altered Rocks in Wairakei, New Zealand," Clays and Clay Minerals, Vol. 16, pp. 193-213.

Stumm, W., and J. J. Morgan, 1970. Aquatic Chemistry, John Wiley and Sons, New York, 583 pp.

Sucheckí, R. K., E. A. Perry, Jr., and J. F. Hubert, 1977. "Clay Petrology of Cambro-Ordovician Continental Margin, Cow Head Klippe, Western Newfoundland," Clays and Clay Minerals, Vol. 25, pp. 163-170.

Tamura, T., 1972. "Sorptions Phenomena Significant in Radioactive Waste Disposal," in Symposium on Underground Waste Management and Environmental Implications, American Association Petroleum Geologists Memoir 18, American Association of Petroleum Geologists, Tulsa, Oklahoma, pp. 318-329.

Tardy, Y., and R. M. Garrels, 1974. "A Method of Estimating the Gibbs Energies of Formation of Layer Silicates," Geochimica et Cosmochimica Acta, Vol. 38, pp. 1101-1116.

Taylor, C. L., G. J. Anttonen, J. E. O'Rourke, and D. Alliot, 1980. Preliminary Geochemical and Physical Testing of Materials for Plugging for Man-Made Accesses to a Repository in Basalt, RHO-BW1-C-66, Rockwell Hanford Operations, Richland, Washington.

Terzaghi, K., and R. B. Peck, 1967. Soil Mechanics in Engineering Practice, John Wiley and Sons, Inc., New York, New York.

United States Nuclear Regulatory Commission, 1982. "Disposal of High-Level Radioactive Wastes in Geologic Repositories: Technical Criteria," 10 CFR Part 60, Final Rule, U. S. Nuclear Regulatory Commission, Washington, D. C.

USNRC, see United States Nuclear Regulatory Commission.

van Moort, J. E., 1971. "A Comparative Study of the Diagenetic Alteration of Clay Minerals in Mesozoic Shales from Papua, New Guinea, and Tertiary Shales from Louisiana, USA," Clays and Clay Minerals, Vol. 19, 1-20.

Velde, B., 1977. Clays and Clay Minerals in Natural and Synthetic Systems, Vol. 21 in Developments in Sedimentology, Elsevier Scientific Publishing Co., New York, New York.

Waterways Experiment Station, 1956. Pressure Grouting Fine Fissures, Technical Report No. 6-437, Waterways Experiment Station, U.S. Army Corps of Engineers, Vicksburg, Mississippi.

Weaver, C. E., 1976. Thermal Properties of Clays, Y/OW1/SUB-4496/2, Office of Waste Isolation, Union Carbide, Nuclear Division, Oak Ridge, Tennessee.

Weaver, C. E., 1979. Geothermal Alteration of Clay Minerals and Shales: Diagenesis, ONWI-21, Office of Nuclear Waste Isolation, Battelle Memorial Institute, Columbus, Ohio.

Weaver, C. E., 1980. Use of K-Ar Dating and Oxygen Isotopes for Determining the Thermal History of Shales, ONWI-107, Office of Nuclear Waste Isolation, Battelle Memorial Institute, Columbus, Ohio.

Weaver, C. E., and K. C. Beck, 1971. Clay Water Diagenesis During Burial: How Mud Becomes Gneiss, Special Paper 134, Geological Society of America, pp. 1-78.

Weaver, C. E., and L. D. Pollard, 1973. The Chemistry of Clay Minerals, Vol. 15 in Developments in Sedimentology, Elsevier Scientific Publishing Co., Amsterdam.

Wheelwright, E. J., F. N. Hodges, L. A. Bray, J. H. Westic, and D. H. Lester, 1981. Development of Backfill Material as an Engineered Barrier in the Waste Package System - Interim Topical Report, PNL-3873, Pacific Northwest Laboratory, Richland, Washington.

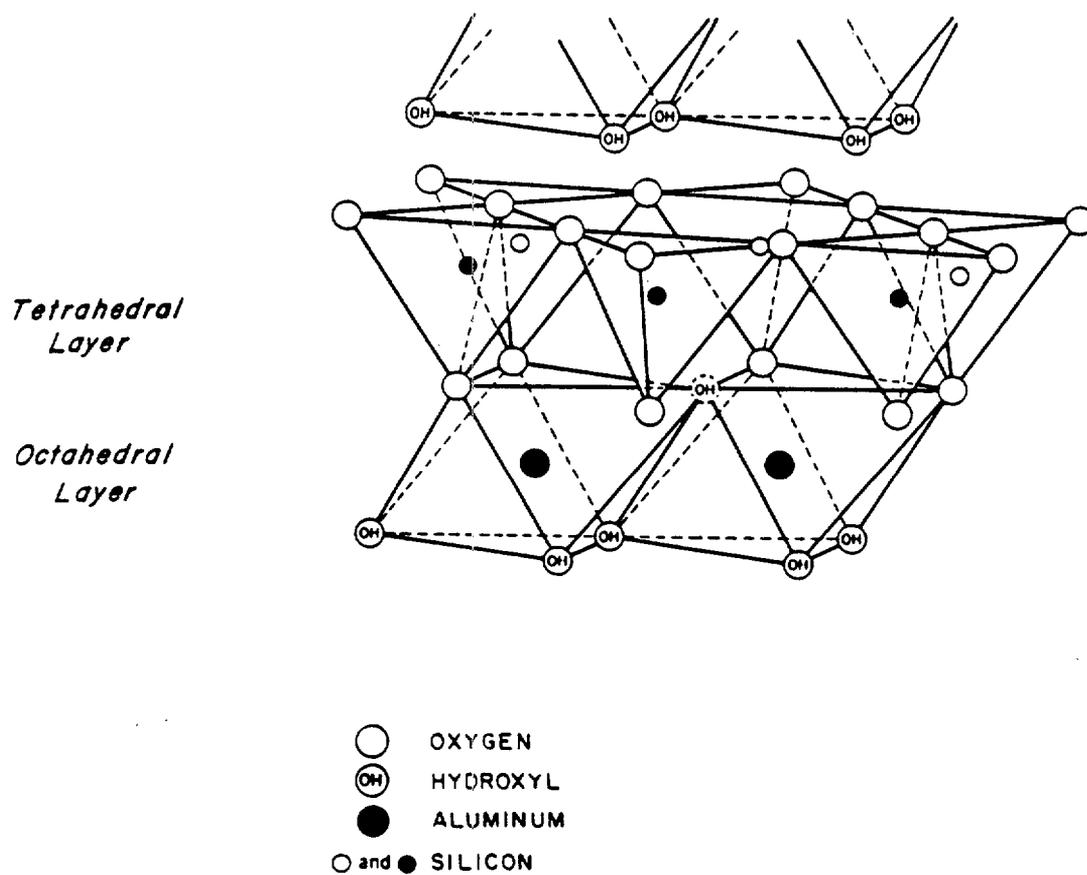
Wilson, M. D., and E. D. Pittman, 1977. "Authigenic Clays in Sandstones. Recognition and Influence on Reservoir Properties and Paleoenvironmental Analysis," Journal of Sedimentary Petrology, Vol. 47, pp. 3-31.

Young, A., P. J. Low, and A. S. McLatchie, 1964. "Permeability Studies of Argillaceous Rocks," Journal of Geophysical Research, Vol. 68, pp. 4237-4245.

APPENDIX A  
CLAY MINERAL STRUCTURE

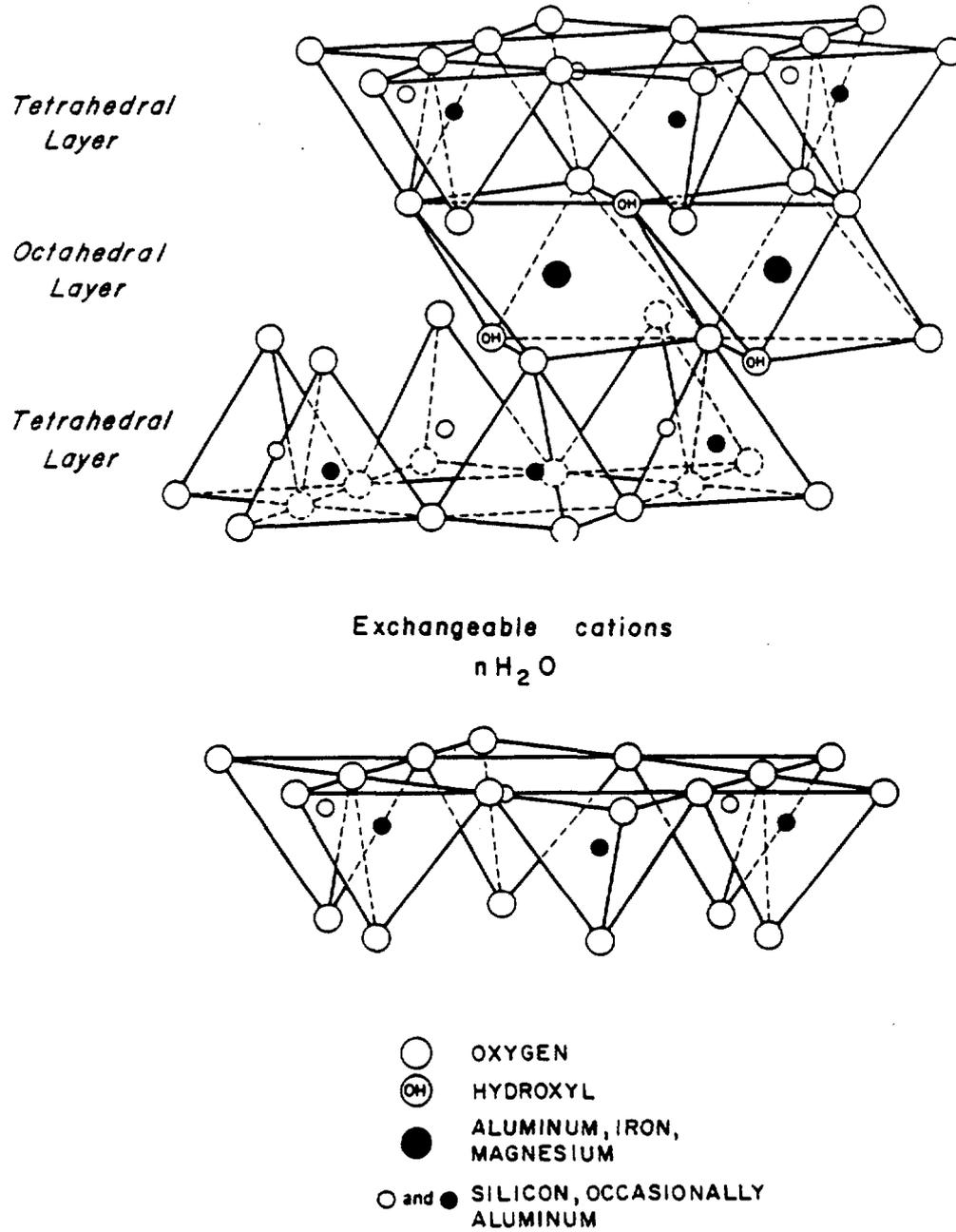
Clay minerals belong in the phyllosilicate subclass of silicate minerals, and are usually characterized by sheet or fibrous habits. In all phyllosilicates,  $\text{SiO}_4$  tetrahedra are linked in a plane. Three of each four oxygens are shared (see Figure A-1), forming hexagonal structure in this silica or tetrahedral sheet. The sheet composition  $(\text{Si}_4\text{O}_{10})^{-4}$  may be altered by  $\text{Al}^{+3}$  substitution for up to half the  $\text{Si}^{+4}$ , with commensurate increase of the negative charge on the sheet. In clay minerals, the tetrahedral layer is bonded to an "octahedral" layer in which  $\text{Al}^{+3}$  and/or  $\text{Mg}^{+2}$ , and less commonly other cations, such as  $\text{Fe}^{+2}$ ,  $\text{Fe}^{+3}$  are octahedrally coordinated with oxygen or hydroxyls (OH). Because of the larger charge on  $\text{Al}^{+3}$  (or  $\text{Fe}^{+3}$ ) relative to  $\text{Mg}^{+2}$  ( $\text{Fe}^{+2}$ , etc.), only 2/3 as many trivalent cations are required for charge balance of the octahedral layer as divalent cations. This is the basis for the distinction in phyllosilicates, including clays, between dioctahedral phyllosilicates and trioctahedral phyllosilicates; the former, with octahedral cations such as  $\text{Al}^{+3}$  require only two trivalent ions to each octahedron of hydroxyl ions, whereas the latter requires three divalent cations to each hydroxyl octahedron, to achieve charge balance.

Simple clays are composed of only one octahedral and one tetrahedral layer combined to form an electrically neutral sheet structure. Kaolinite, shown in Figure A-1, is such a clay. Other clays may combine two tetrahedral layers with an octahedral layer in a tetrahedral-octahedral-tetrahedral sheet structure. Smectite clays have this structure (Figure A-2). A small negative charge developed on the sheets, due to ion substitutions, is balanced by weakly bound hydrated interlayer cations. Illite clays, like micas, have a larger anionic charge on the sheet structures which are balanced by strongly bound interlayer cations ( $\text{K}^+$ , usually) in specific sites in the mineral structure. Chlorite minerals (Figure A-3) include similar anionic mica or illite sheets alternating with "brucite" sheets, trioctahedral  $(\text{Mg}, \text{Al})_6(\text{OH})_{12}$  sheets which include sufficient Al substitution for Mg to balance the negative charge on the mica sheets. In vermiculite, the anionic illite-mica



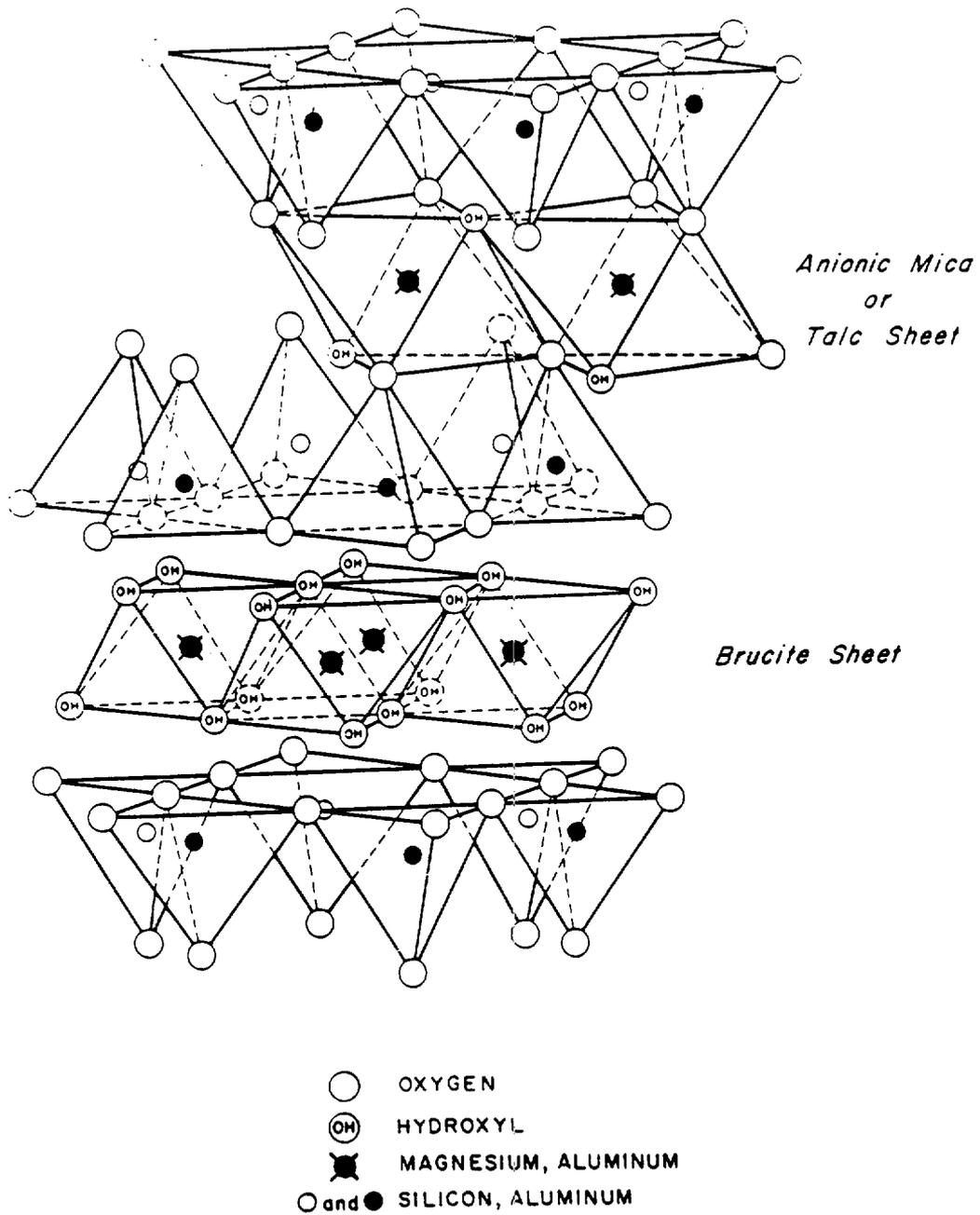
REFERENCE: GRIM, 1968

Figure A-1. Crystal Structure of Kaolinite



REFERENCE: GRIM, 1968

Figure A-2. Crystal Structure of Smectite

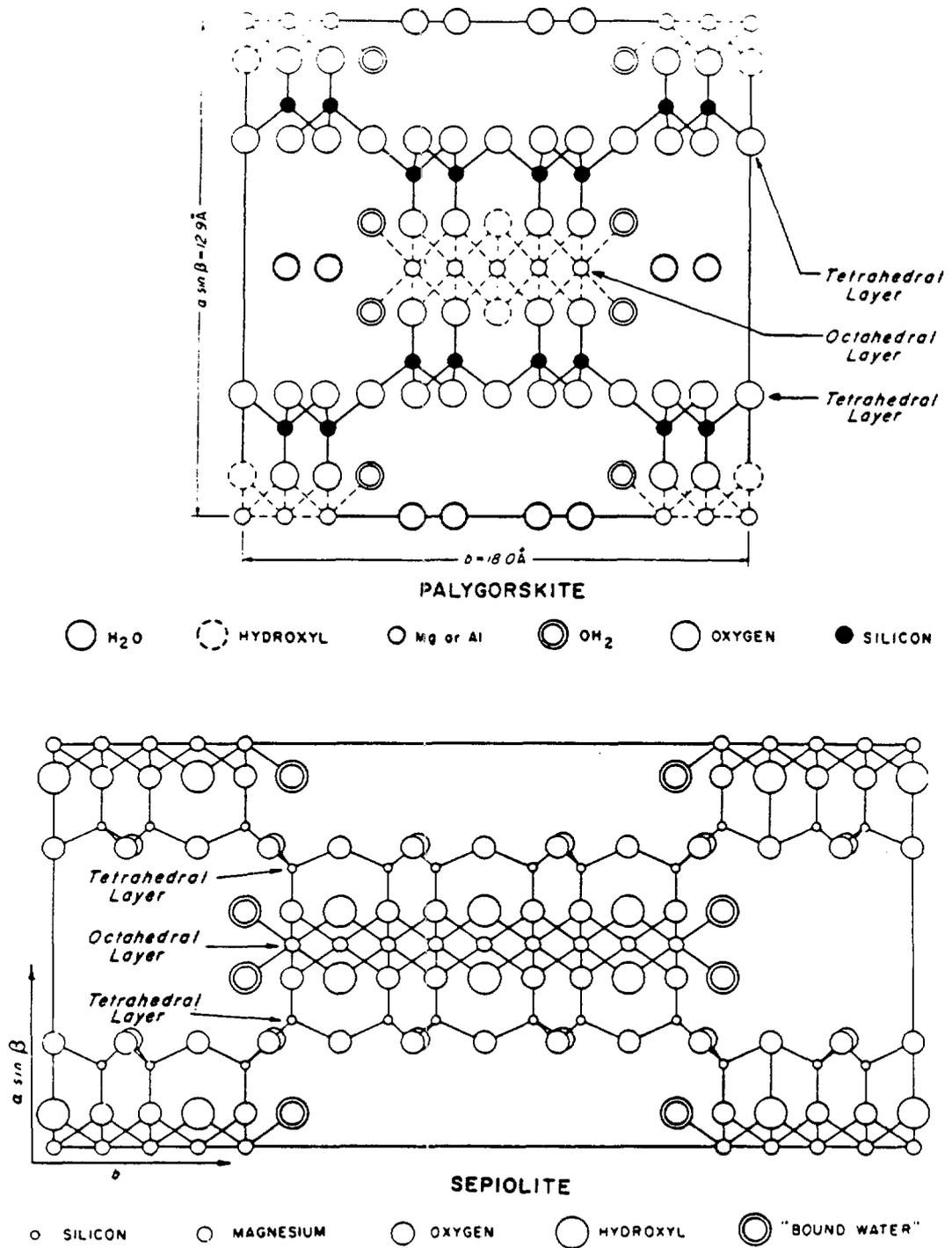


REFERENCE: GRIM, 1968

Figure A-3. Crystal Structure of Chlorite

sheet alternates with water interlayers, in which water molecules occupy specific sites in the structure. Charge balance is achieved by weakly bound cations in this interlayer.

Clay minerals which are structurally unlike the kaolinite-smectite-illite-vermiculite clays, in that tetrahedrally-and octahedrally coordinated layers do not occur stacked in regular alternating sequences, are anauxite and the fibrous clays. Anauxite is not especially important to the present discussion and may not often occur as a unique species, but as a silica rich composite with kaolinite. Grim (1968) cites evidence for a double silica sheet as a possible anauxite structure. More important is the palygorskite, or fibrous clay group, including sepiolite, and palygorskite (or attapulgite) (Figure A-4). Here, a tetrahedral (silica) - octahedral (Mg, Al) - tetrahedral structure forms chains rather than sheets. Adjacent chains share oxygens, and the resulting crystal structure has large water filled cavities. The major structural difference between palygorskite and sepiolite is the breadth of the tetrahedral-octahedral-tetrahedral chains. Attapulgite is synonymous with palygorskite.



REFERENCE GRIM, 1968

Figure A-4. Crystal Structure of the Palygorskite Group Minerals, Palygorskite and Sepiolite

APPENDIX B  
GLOSSARY

Adsorption - Adhesion of dissolved substances in fluids to surfaces (substrates) of associated solids. Substrates with large surface areas per unit mass, open crystallographic structures, or high, localized, unbalanced charge in crystals favor adsorption of dissolved material.

Bentonite - A weathering product of tuff or volcanic ash, composed largely of very fine-grained montmorillonite. Other phases are usually present. It is soft, plastic and greasy feeling. Upon application of water, bentonite swells greatly. The term is frequently applied to any impure montmorillonite. Ca montmorillonite occurs most commonly in natural bentonite, although the sodic form is found, particularly in Wyoming.

Chlorite - A clay mineral containing a sheet composed of octahedrally coordinated ions sandwiched between layers of tetrahedrally coordinated Si and Al linked in hexagonal patterns alternating with brucite-like layers containing octahedrally coordinated cations (often  $Mg^{+2}$ ). The charge on alternating sheets is greater than in other clays. Substitutions of cations in the crystal structure is common, particularly between  $Si^{+4} - Al^{+3}$ ,  $Mg^{+2} - Fe^{+2} - Mn^{+2}$ ,  $Mg^{+2} - Al^{+3}$ ,  $Fe^{+3} - Al^{+3}$ . Trace quantities of other metals are frequent in chlorites. Chlorite is usually green or blue-green. Chlorite does not expand upon application of water or organic fluid and has a relatively limited cation exchange capacity. Chlorite occurs in low grade metamorphic rocks, and in hydrothermally altered basic igneous rocks, or as authigenic or detrital constituents of sedimentary rocks.

Clay - Common usage in engineering and soil science, refers to any fine-grained (predominantly less than .002mm), earthen, more-or-less plastic material containing a substantial proportion of clay minerals.

Clay Mineral - Usually fine-grained, hydrous alumino or magnesium silicates with a platy or fibrous habit due to regular interlayers of octahedrally or tetrahedrally coordinated cations. Clays frequently absorb water and usually display compositional variability due to cation substitution and ion exchange. The layer charge on clay sheets is lower than in micas, frequently permitting ion substitution and expansion of the interlayer spacing. Heating tends to drive off adsorbed or interlayer water. Clay minerals are often found in fine-grained aggregates, which are plastic upon addition of water. Fibrous clays are less common than platy clays.

Desorption - The removal of a trace substance or minor component of interest from the surface of a solid material by an associated fluid.

Exchangeable Cation - In clays, a monovalent or divalent cation which is electrostatically bound between weakly negatively charged aluminosilicate sheets, and which can be substituted by other cations dissolved in associated fluids under certain physiochemical conditions. The cation exchange capacity of a clay is a measure of the ability of a clay to substitute its cations, and is usually measured in milliequivalents per unit mass of clay.

Filtration - Removal of particulate matter and colloidal-size particles from a fluid substance by a porous mesh of solid matter.

Hydraulic conductivity - Often used synonymously with permeability, the hydraulic conductivity is the flow volume of fluid

(usually water) through a unit cross-sectional area under a unit hydraulic gradient per time; measured in units of L/T (e.g., cm/sec). For water at 20°C, 1 cm/sec  $\approx 10^3$  darcy.

Illite - Dioctahedral (rarer trioctahedral), monoclinic clay mineral group, in which clay sheets of layers of octahedrally coordinated cations ( $Al^{3+}$ , usually) sandwiched between  $SiO_4$  tetrahedra linked in hexagonal networks. Like muscovite, illites contain interlayer potassium ions, although in illite these are coordinated to relatively weakly negatively charged clay layers. The presence of the bound interlayer potassium ions prevents significant expansion of the crystal structure and ion exchange capacity in illites. Illites dominate in sedimentary formations and hydrothermal environments. They may occur due to alteration of clays during diagenesis. Illite formation is favored by alkaline conditions when aluminum and potassium are available.

Ion Exchange - The substitution of ions in a fluid for specific ions in a structural site an associated solid, generally of equivalent charge and similar size.

Kaolinite - Triclinic or monoclinic dioctahedral clay, usually white in color, occurring in massive aggregates; each clay sheet is composed of gibbsite-like sheets composed of aluminum octahedrally coordinated with oxygen and (OH)- ions coordinated with  $SiO_4$  tetrahedra in a hexagonal array.

The chemistry of kaolinite  $[(Al_4(Si_4O_{10})(OH)_8)]$  shows little variation. There is little ion substitution in the clay structure. There is little or no layer charge on clay sheets, but kaolinite does not swell upon application of water, or have a large cation exchange capacity, as many other clay minerals do. Kaolinite occurs as a hydrothermal alteration or weathering product of feldspar and other silicates. Its

occurrence appears to be favored by alteration of siliceous rocks under acid (or non-alkaline) conditions (Grim, 1953; Deer et al, 1966). Polymorphs include dickite and nacrite. Halloysite is a hydrated form which displays swelling properties and a significant ion-exchange capacity.

Kd (Partition coefficient, distribution coefficient or constant) -

Strictly, a constant describing the distribution of a trace substance between two phases, at equilibrium; being a ratio of the concentration of the trace substance in each phase. In the present report, the distribution coefficient is measured in ml/g where:

$$\frac{\text{concentration of x in solid}}{\text{concentration of x in fluid}} = \frac{\frac{\text{mg x}}{\text{g solid}}}{\frac{\text{mg x}}{\text{ml fluid}}}, \text{ in } \frac{\text{ml}}{\text{g}}$$

For experiments determining the distribution of radionuclides between fine-grained solids and aqueous solutions, equilibrium is not proven (steady state is usually the criterion for the completion of reaction), in which case, the term  $R_d$ , denoting non-equilibrium, is frequently used.

Mixed Layer Clays - Clays which contain usually two different minerals which are randomly or regularly interstratified. The properties and behavior of mixed layer clays generally reflect the constituent minerals and their relative proportions. Mixed layer clays occur due to diagenetic effects or hydrothermal reactions. Illite-smectite, kaolinite-smectite, and chlorite-smectite commonly occur in mixed layers.

Palygorskite Group - Fibrous "chain-lattice" clays including palygorskite (attapulgite) and sepiolite.  $\text{SiO}_4$  tetrahedra are linked in hexagonal patterns, with each hexagon joined in strips parallel to the b-axis by an oxygen. Strips of tetrahedra are joined by

MgO<sub>6</sub> octahedra. The resultant structure contains channels parallel to the c-axis. The clays are absorbent, and sepiolite occurs in calcite veins and as a weathering product of serpentine bodies.

### Permeability

Intrinsic permeability - The capability of a solid medium to transmit fluid, usually measured in darcys (dimensions L<sup>2</sup>).

Permeant - Any fluid, including multiphase fluids, which occupies the pores of and is transmitted through a permeable substance.

Precipitation - Any reaction between sorbent and dissolved materials which results in the formation and deposition of insoluble species.

Smectite (montmorillonite group) - Monoclinic dioctahedral and trioctahedral clays. Principal dioctahedral smectites include montmorillonite (commonly  $1/2(\text{Ca}, \text{Na})_{0.7} (\text{Al}, \text{Mg}, \text{Fe})_4 [(\text{SiAl})_8 \text{O}_{20}] (\text{OH})_4 \times n\text{H}_2\text{O}$ ), beidellite (an aluminous (<sup>VI</sup>Al<sup>+3</sup> and <sup>IV</sup>Al<sup>+3</sup>) montmorillonite) and nontronite (a ferric iron-rich (<sup>IV</sup>Fe<sup>+3</sup>) montmorillonite. Trioctahedral smectites include saponite ( $1/2(\text{Ca}, \text{Na})_{0.7} (\text{Mg}, \text{Fe})_6 [(\text{SiAl})_8 \text{O}_{20}] \text{OH}_4 \times n\text{H}_2\text{O}$ , hectorite (a <sup>VI</sup>Li<sup>+</sup> - rich saponite), and sauconite (a <sup>VI</sup>Zn<sup>+2</sup> - rich saponite). All are so-called swelling clays, whose crystal structures expand to admit water and organic liquids. All have significant ion exchange capacities. Because the interlayer cation is frequently substituted, smectites may carry H, Li, Be, Mg, K, Rb, Sr, Cs, and Ba ions as well as Na<sup>+</sup> and Ca<sup>2+</sup> in the interlayer sites. There is a small anionic charge on the clay layers which is balanced by the interlayer cations. Water and organic liquids are readily absorbed between layers, the quantity of which is influenced somewhat by the interlayer cation species. Smectites occur as weathering and hydrothermal alteration products of acid

ash (bentonite). Calcium montmorillonite is more common than the sodic form. Smectites occur in hydrothermal assemblages also. The availability of Mg and Ca and alkaline conditions, and the absence of K during weathering of basic igneous rocks also favor smectite formation.

Sorption - The major emphasis in this report is upon radionuclide sorption. Common usage indicates sorption as any mechanism by which a solid (sorber or sorbent) removes species from associated fluids (liquids or gases). Mechanisms may include absorption, adsorption, ion exchange, chemical reactions (precipitation), and filtration. This common usage arose because the effects of individual mechanisms have not been regularly studied in experiments regarding radionuclide-clay interaction.

Vermiculite - Like trioctahedral smectite, vermiculite is a clay containing octahedrally coordinated (Mg, Fe) layers sandwiched between layers of  $\text{SiO}_4$ . Small anionic charges on the clay layers are balanced by interlayer cations, usually  $\text{Mg}^{+2}$ . Water occurs in the interlayers, as well, occupying regular sites between clay layers and the interlayer cations. The degree of hydration and the mineral structure are, therefore, readily affected by the exchangeable interlayer cation. The swelling capacity due to absorbed water or organic liquids is less pronounced than in smectites, but the cation exchange capacity is generally greater. Vermiculites exfoliate and expand upon heating to  $>300^\circ\text{C}$ , and produce a low density thermal insulator. They frequently occur as weathering or hydrothermal alteration products of biotite.

APPENDIX C  
SUMMARY OF MODEL TESTS

MATERIAL	SEAL PREPARATION	PERMEABILITY (MICRODARCY)	OTHER FACTORS	REFERENCE
Ninnescah Sh. Core	Static compaction @ 27.6 MPa	0.1-7100	*	Martin, 1975
Ninn Sh. Outcrop	Static comp. @27.6 MPa	0.12		
"	Impact Compaction	0.09	1.4" diam. plug; 15 lifts, 10 lb.-18" drop, 30 impacts/lift, 1.2" diam. tamper	"
"	"	1.5-1.9	same, except 5 impacts/lift	"
"	"	1.4	same, except 0.9" tamper	"
"	"	0.08-0.16	same, except 10 impacts/lift, 1.2" diam. tamper, measured sfter drying in air	"
Ninn. Sh. Core	Impact	0.18-0.47	same, except w/o air drying	"
Dewey Lake Sh. Outcrop	Static comp. @27.6 MPa	4.4		
DLS Core	Impact	0.13-1.9	1.4" diam. plug; 10 impacts/lift, 1.2" diam. tamper	"
"	"	2.9-4.2	same, except 2.5" diam. plug; 2.0" diam. tamper	"
Conasauga Sh. Outcrop	Static comp. @27.6 MPa	1.7		"

1 MPA = 145 psi.

\* all samples 2.5" long, except where noted

APPENDIX C  
SUMMARY OF MODEL TESTS (cont'd.)

MATERIAL	SEAL PREPARATION	PERMEABILITY (MICRODARCY)	OTHER FACTORS	REFERENCE
Dewey Lake Core	Static compaction @27.6 MPa	0.46-805	1 lift	Olsen & Martin, 1976
"	Static comp. @6.9 MPa	1670-10300	1 lift	"
"	"	564	3 lifts	"
"	"	248-2720	5 lifts	"
"	Gravity impact compaction	0.15-6.67	1.4" diam. plug, 1016-19" drop, 10 impact/lift (1 lift = 3 tap)	"
"	"	0.25-2.0	same, except 6.9 lb.	"
"	"	0.4-2.0	same, except 12" drop	"
"	"	28-131	same, except 1 impact/lift	"
"	"	0.67-1.04	2.5" diam. plug; 1016-19" drop, 10 impacts/lift	"
"	pneumatic impact	0.08	50 lb.- 5.5" drop, 5 impact/lift	"

**APPENDIX C  
SUMMARY OF MODEL TESTS (cont'd.)**

MATERIAL	SEAL PREPARATION	PERMEABILITY (MICRODARCY)	OTHER FACTORS	REFERENCE
0.8 Dewey Lk. Shale + 0.2 montmorillonite* (Mt)	Static compaction @ 6.9 MPa	0.25	1 lift, 1 minute	Olsen & Martin, 1976
0.9 DLS + 0.1 Mt	"	2.7		"
0.8 Gypsum + 0.2 Mt	"	0.74	1 lift	"
0.8 Anhydrite +0.2 Mt	"	3.5	"	"
0.65 Sand + 0.35 Mt	"	0.11	"	"
0.67 DLS + 0.33 Mt	Static	0.07	3 lifts, alternating DLS-Mt-DLS	"
0.8 DLS + 0.2 Mt	Gravity impact	0.05-0.10	10 lb.-19" drop, 5 impact/lift, 1 lift = 3 tsp	
0.9 DLS + 0.1 Mt	"	1.15	"	"
0.8 Gypsum + 0.2 Mt	"	0.06	"	"
0.9 Sand + 0.1 Ca-bentonite	Gravity impact	90	ASTM-D-1557 except 2.5" diam. plug; 2.0" tamper, 10 lb. tamper, 3.0" long	Taylor, et al., 1980
*weight %				

**APPENDIX C  
SUMMARY OF MODEL TESTS (cont'd.)**

MATERIAL	SEAL PREPARATION	PERMEABILITY (MICRODARCY)	OTHER FACTORS	REFERENCE
6% shurgel + 19% Ringold D clay + 25% crushed colite + 50% basalt aggregate	Slurry - 8 % solids consolidated at 0.45 MPa effective pressure	12	3.0" long	Taylor, et al., 1980
Mont- morillonite (Mt)	Static compaction @ 6.9 MPa	0.09		Martin, 1975
Mt	Static comp. @ 0.69 MPa	0.09-0.24	1 lift	Olsen & Martin, 1976
"	Static comp @ 2.1 MPa	0.05	1 lift	"
"	Static compaction @ 2.76	0.05	1 lift	"

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