

SKBF
KBS

TEKNISK
RAPPORT

83-03

Smectite alteration

Proceedings of a colloquium at State University of
New York at Buffalo, May 26–27 1982

Compiled by Duwayne M Anderson

State University of New York at Buffalo
February 15, 1983

SVENSK KÄRNBRÄNSLEFÖRSÖRJNING AB / AVDELNING KBS

POSTADRESS: Box 5864, 102 48 Stockholm, Telefon 08-67 95 40

SMECTITE ALTERATION

Proceedings of a colloquium at
State University of New York at Buffalo
May 26-27, 1982

Compiled by Duwayne M Anderson

State University of New York at Buffalo
February 15, 1983

This report concerns a study which was conducted for SKBF/KBS. The conclusions and viewpoints presented in the report are those of the author(s) and do not necessarily coincide with those of the client.

A list of other reports published in this series during 1983, is attached at the end of this report. Information on KBS technical reports from 1977-1978 (TR 121), 1979 (TR 79-28), 1980 (TR 80-26) and 1981 (TR 81-17) is available through SKBF/KBS.

PREFACE

The Swedish concept and plan for the long-term storage of high level and long-lived radioactive wastes from nuclear power generation involves a series of engineered barriers. Multibarrier designs of repositories for vitrified high-level waste (KBS-1) and for spent nuclear fuel (KBS-2) have been thoroughly investigated. The results of these investigations have been reported in a series of technical reports issued for the Swedish Nuclear Fuel Company by the KBS Company (Box 5864, 10248 Stockholm, Sweden). The basic scheme is illustrated in figure 1.

One of the barriers to be employed consists of highly compacted sodium bentonite surrounding a carefully engineered and constructed canister in a bore hole at a depth of approximately 500 meters. In Sweden, crystalline rock is available and probably will be selected as the host rock into which the bore holes will be sunk. Sodium bentonite has been selected as one of the barriers because when ground water enters at the walls of the bore hole, a swelling pressure results as water penetrates the bentonite. This creates a highly compacted colloidal mass with the following properties: 1. extremely low hydraulic conductivity to provide the second barrier in the multi-barrier design; 2. plasticity to accommodate to possible slow, minute deformation of the bore hole together with the ability to swell by imbibition of water and by generating high swelling pressures, exert an outward, balancing force on the walls of the bore hole; 3. long-term stability at the temperatures associated with this part of the repository.

There is no question that sodium bentonite will be completely satisfactory with respect to the first two properties. However, the third requirement raises some, as yet unresolved, questions regarding the degree to which sodium bentonite can be expected to maintain its favorable properties in the environment created by the buried nuclear materials over the very long time required for its decay to negligible levels.

It is known that under certain conditions smectite clays (a group that includes sodium bentonite) undergo diagenesis in nature. In other circumstances smectites have remained unaltered for millions of years. Recently, it has become recognized that elevated temperatures and pressures combined with circulating ground water can alter smectite to illite, a good, but less desirable, clay for this application.

This colloquium was convened to compose a summary of the most recent data and the best scientific appraisal of present knowledge on the process of smectite conversion to illite. The invited participants, in addition to each having devoted much time and energy in the study of this question, have also published original data and findings on the topic. The result of this colloquium is a brief account of a consensus view on the probable stability of smectite

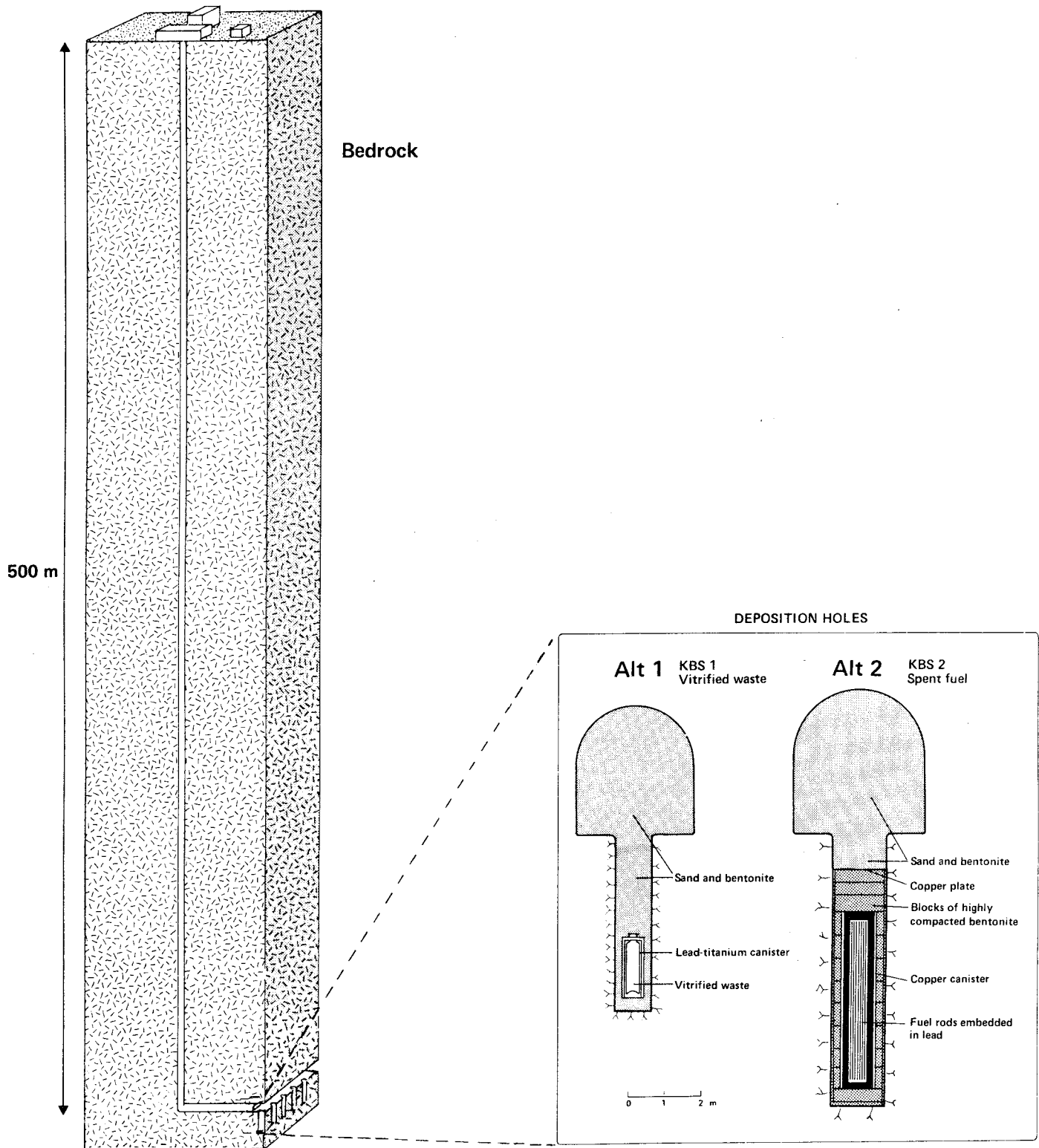


Figure 1 - Illustration of the basic features of the Swedish plan for the long-term, below ground storage of nuclear waste materials.

clays when employed as the buffer material in the Swedish Nuclear Fuel Storage System. This report is written in a manner to emphasize the informality of the colloquium, the wide ranging discussions, and the individual views of the participants. The report ends with a brief description of the illitization process and the conditions that are required for the conversion of sodium bentonite to the illite form. It is concluded that if the quantity of nuclear waste to be put in each bore hole is carefully limited, temperatures surrounding the cannister will not rise to an acceptable level and the clay buffer material can be relied upon to be effective throughout the life of the repository.

DUWAYNE M. ANDERSON
Colloquium Chairman

CONTENTS

	Page
Preface	i
Participants.	1
Agenda.	2
Informal Notes on Opening Remarks, D. M. Anderson . . .	3
Summary, C. V. Clemency	13
Summary, R. F. Giese, Jr.	15
Summary, J. J. Howard	16
Summary, J. A. Kittrick	21
Summary, H. E. Roberson	23
Summary, C. Waddell	26
Conclusion, D. M. Anderson.	28
References.	35
Appendix A.	37

COLLOQUIUM ON SMECTITE ALTERATION

May 26-27, 1982
State University of New York at Buffalo

PARTICIPANTS

Dr. Duwayne M. Anderson
Dean, Faculty of Natural
Sciences & Mathematics
State University of NY/Buffalo
732 Clemens Hall
Buffalo, NY 14260

Dr. James J. Howard
Schlumberger-Doll
Old Quarry Road
PO Box 307
Ridgefield, CT 06877

Ms. Patricia M. Costanzo
Dept. of Geological Sciences
State University of NY/Buffalo
4240 Ridge Lea
Buffalo, NY 14226

Dr. James A. Kittrick
Dept. of Agronomy
Washington State University
Pullman, Washington 99164

Dr. Charles V. Clemency
Dept. of Geological Sciences
State University of NY/Buffalo
4240 Ridge Lea
Buffalo, NY 14226

Dr. Herman E. Roberson
Dept. of Geology
State University of NY/
Binghamton
Vestal Parkway East
Binghamton, NY 13901

Dr. John C. Fountain
Dept. of Geological Sciences
State University of NY/Buffalo
4240 Ridge Lea
Buffalo, NY 14226

Ms. Carol Waddell
Dept. of Geological Sciences
State University of NY/Buffalo
4240 Ridge Lea
Buffalo, NY 14226

Dr. Rossman F. Giese, Jr.
Dept. of Geological Sciences
State University of NY/Buffalo
4240 Ridge Lea
Buffalo, NY 14226

AGENDA

Wednesday, May 26, 1982

- 9:00 a.m. Welcome and Opening Remarks - Duwayne Anderson
- 9:15-11:00 a.m. Opening Remarks - Dr. Howard
Dr. Kittrick
Dr. Roberson
Ms. Waddell
- 11:00-11:30 a.m. Presentation: "Energetics of Ordering in Mixed
Layer Systems" - Dr. Giese
- 2:00-2:30 p.m. Adoption of Continuing Discussions Agenda
- 2:30-4:30 p.m. Discussions

Thursday, May 27, 1982

- 9:00-12:00 a.m. Discussions (continued)
- 2:00-3:30 p.m. Discussions (continued)
- 3:30-4:30 p.m. Summary, Conclusions and Recommendations
- 4:30 p.m. Adjournment

James Howard

There are two basic approaches: (1) equilibrium model (Weaver): smectite unstable under repository conditions transforms to illite. Temperature of 100°C or more required. (2) Kinetic model: reaction goes even at 40°C, but very slowly.

Questions: 1.) Is the equilibrium approach or kinetic approach best?

2.) What are the mechanisms and rates?

Steps: 1.) Creation of lattice charge.

2.) Exchange of ions, supply of material.

James Kittrick

Says he concurs in the above. But not enough is known yet about smectite to make the equilibrium approach feasible.

Illite is also a controversial topic because it is hard to define precisely. In the common equation: smectite → illite, both are poorly defined and not homogenous. This is too crude an approach.

Potassium doesn't behave as a common ion. Usually it is a smectite to mixed-layer smectite conversion with a resultant change in properties.

Equilibrium calculations are extremely uncertain. They cannot be a reliable basis for stability criteria in a repository.

The kinetic approach is the only feasible approach.

Herman Roberson

Has concentrated on kinetics of the smectite → illite/smectite reaction.

Does know of some experimental data of value.

Smectite + random interstratified I/S + ordered I/S + illite are steps we could consider.

Kinetics is the most important topic for us today. In this he agrees with Howard and Kittrick.

The Effect of Ca, Mg, Na ions on rates should be a consideration; these are competing ions in the system.

Carol Waddell

From previous studies, it is apparent that many factors may affect the rate of the smectite to illite transformation. These can be divided into several general groups from which the most important can be determined and then discussed in more detail.

- I. Reaction Mechanism for Smectite-Illite Transformation
 1. Thermal Effects 0-200°C
 2. Amount of K⁺ necessary to insure sufficient exchange to bring about collapse.
 3. Does amorphous SiO₂ formation affect further reaction by inhibiting H₂O and ion migration?
 4. Can Si(OH)₄ migrate through the interlayer spaces? (Fyfe, May KBS Meeting 1982)
 5. Does the state of the H₂O on the interlayers affect ion migration?

- II. Establish the importance of diffusion in the control of this reaction and what may affect it
 1. Permeability (e.g. 10⁻¹⁴ m/sec in compacted bentonite)
 2. CEC
 3. Amount of water present
 4. Interlayer spacing
 5. Ca diffusion data, and KBS report
 6. Kinetics

- III. Establish critical reactions for: (KBS Meeting at Buffalo, N.Y. May 1982)
 - a. Smectite: Granite
 - b. Smectite:Illite:Kspar:Qtz
 - c. Smectite:Mafics (Olivine)
 1. OH acting as a possible SiO₂ and O₂ buffer
 2. Affects of Fe introduced to the system
 3. Thermodynamic feasibility of the reactions
 4. General kinetics of the smectite-illite transformation (note the stability of non-marine clays in marine environments).

- IV. General stability of smectites under conditions of interest to KBS: (May 1982 Meeting at Buffalo, N.Y.)
1. pH 7-10
 2. P H₂O of 1-1000 m
 3. T 0-200°C
 4. Electrolyte composition from ocean water
- V. Effects of stress imposed on thermal regime

Charles Clemency

Eberl & Hower (GSA Bull. 87:1326-1330, 1976) have written a paper on kinetics of the reaction. If there is no K present, there can be no reaction. This is an important paper and idea. This paper gives rates. Roberson, on the other hand, says these data are totally unrealistic because small amounts of Ca⁺⁺ will alter these numbers.

Rossmann Giese

The data on potential energy calculations of mixed-layer illite/smectite systems may not be of great use in the present problem because, like thermodynamics, one can only say which state of a specified set is most stable. We can't say anything about the rate(s) at which equilibrium will be reached or whether it will be reached under specified conditions.

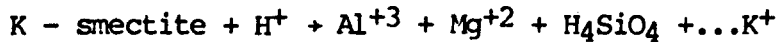
For the 2:1 phyllosilicates, one must treat the di- and tri-octahedral structures separately. For illite/smectite (di-octahedral) hydroxyl orientation has been suggested as the mechanism for forming ordered mixed-layer sequences as opposed to random stacking of illite and smectite layers. Our calculations of the relative stabilities of these two situations indicate at least a 5/1 preference for order over disorder. The existence of ordered mixed-layer phyllosilicates as an alteration of original smectite used as a diffusion barrier for nuclear waste disposal may be important. Diffusion of ions, water and heat transfer may be very different for an ordered as opposed to disordered mixed-layer product.

Lithostatic pressure probably would favor order over disorder while higher temperatures would probably not favor order. I use the qualifier "probably" because we have not done the calculations necessary to decide. These are my feelings about the two conditions.

GENERAL AGENDA FOR SUBSEQUENT DISCUSSIONS

- A. Equilibria and kinetic models/approaches
- B. Possible transformation sequences and mechanisms
- C. Observations/evidence

James Kittrick - On stability for the reaction:



$$K_{eq} = \frac{[K^+]^x [Al^{+3}]^y [] \dots}{[H^+]^2} \quad \text{vs} \quad K_{eq} = \frac{[Al^{+3}]^y [] \dots}{[H^+]^2}$$

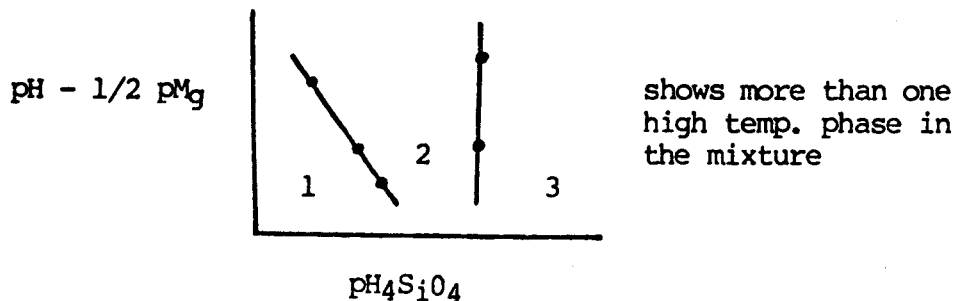
If the exchangeable K^+ is removed then K_{eq} doesn't depend any longer on the exchange ions. Kittrick thinks this is the way it must be dealt with. This is controversial as of now, however.

This flaws the equilibrium approach to the analysis of the problem for now. Jim thinks the controversial K_{eq} written by Garrels, etc. is wrong.

What most people call illite is really a smectite (room temp. variety) \rightarrow K-smectite (high temp.). This is not the mica-like material commonly known as illite.

The change in room temp. to high temp. smectite as seen by x-ray diffraction is extreme, much more so than the real change in the mineral itself. This has been very misleading. One concludes that stability of smectite is very high.

From solubility measurements on high temperature smectite.



1 is equivalent with 2
2 is equivalent with 3 (but not in equivalent units)
but 1 is not equivalent to 3

There may be more than one phase in room temp. smectite as well.

Anderson asked if one could approach the KBS problem as follows:

P 10-50 atm

Given:

A. Flowing Granitic H₂O → Na clay → Concrete → Na Clay → Granite

T < 100°C

B. $K_{\text{hyd}} \sim 10^{-10}$ m/sec → (hydraulic conductivity)

1. Calculate total CEC of unit.
2. Calculate time to saturation with K⁺ to obtain a conservative estimate of most rapid possible conversion.

Consensus: Yes, no one sees a basic flaw, but remember this is the minimum time to alteration.

Sequence would be:

(very slow)
Na Smectite → Na Smectite H.T + K → K-smectite illite; (10 Å material)
R.T

High charge lattice achieved by Al⁺³ replacing Si⁺⁴ in the tetrahedral layer with silica being removed at step 2.

Can one calculate rate of Si egress and from the quantity required to make the high charge lattice, deduce the time to alteration? Yes, but with qualification; Si may be precipitated and not require removal.

Refer to stability diagram from Dr. Kittrick on next page.

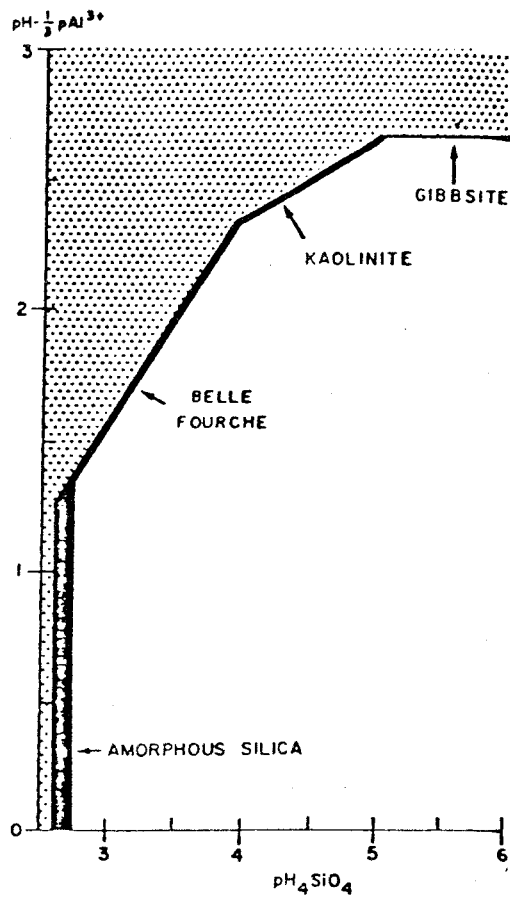


Fig. 1—Solubility lines for several minerals at pH of 6, pMg^{2+} of 3.7, and $\text{pH} - 1/3 \text{pFe}^{3+}$ of -0.32 (hematite). Line width corresponds to estimated error in the mineral stabilities. The shaded portion represents solution compositions supersaturated with respect to one or more of the minerals.

Thursday, May 27, 1982

(Resumption of talks on kinetics.)

Cited Eberl's assertion that he could observe first order kinetics for Na-smectite + K → (illite) K-smectite.

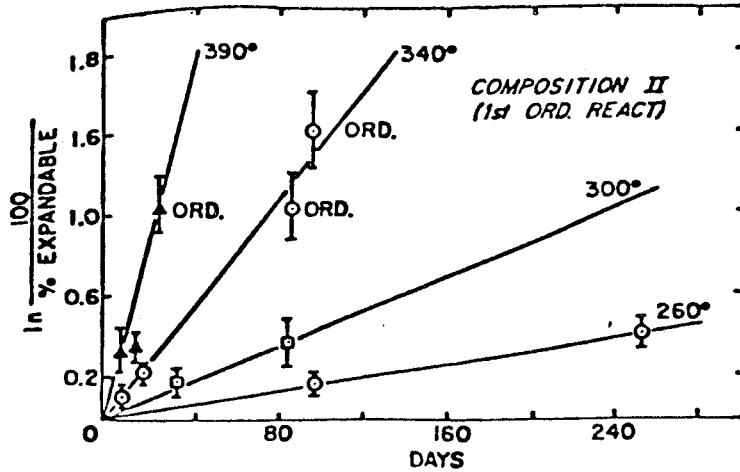


Figure 2. First-order kinetic plots of data found in Table 2 for the reaction of composition II. Error is maximum error.

(Eberl and Hower, 1976)

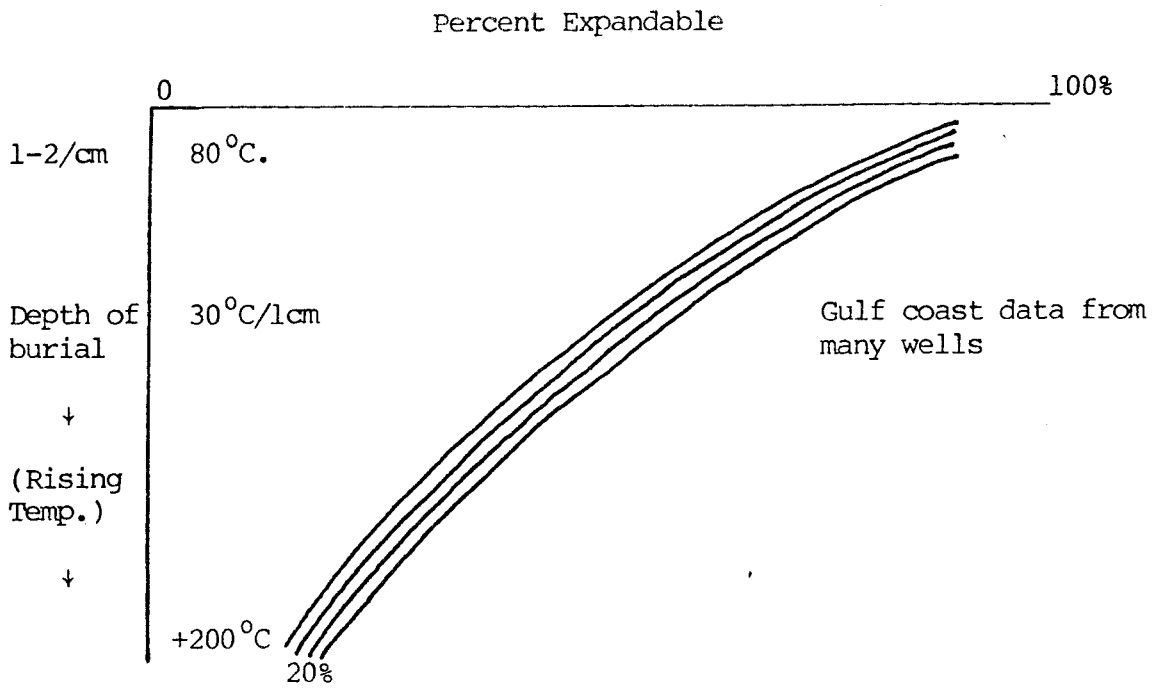
They calculated reaction rate constants - These rates were pretty fast, 10^4 years for 100% alteration. But, these were pure systems - when Ca_{+2} K_{+2} are present, these rates slow very much.

Jim Howard writes
$$\frac{dP}{dt} = \left. \frac{\partial P}{\partial t} \right|_x + \left. \frac{\partial P}{\partial x} \right|_t \omega + R(x,t)$$
 to describe heat flow

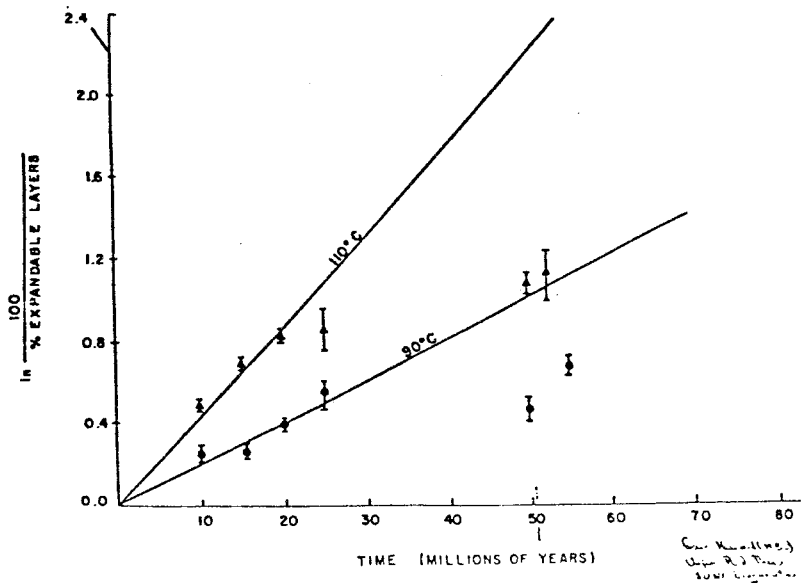
This yields an alteration rate of $\frac{2.5 \text{ expandable layers}}{100 \text{ layer}}$ million years.

$\approx 2.5\%$ altered/ 10^6 years assumes the K already in the system, only heat is required.

Complete alteration would take 40×10^6 years.



From the data available from this source one can infer



Summary:

It seems that we have the following essential steps:

- A. Formation of H_4SiO_4 (amorphous) and simultaneous substitution Al^{+3} into tetrahedral layer from ubiquitous $Al_3(OH)_3$.
- B. Na Smectite + heat \rightarrow Na - smectite (high lattice charge) + K \rightarrow K-smectite (10A collapsed condition)
1. Heat is required to form the high lattice charge.
 2. K supply is required for collapse.

Mg^{+2} slows the illitization reaction - Mg^{+2} is adsorbed preferentially - blocks some exchange sites from K and because it is hydrated it keeps the lattice open.

Mg^{+2} could be supplied by olivine (as per Fyfe's suggestion) but also from dolomite concrete. Mg^{+2} from ground water also is a good bet. In the Swedish circumstance, Mg^{+2} is three times more abundant than K. (KBS document TR-90).

Effect of Mg in retarding conversion rate is discussed in a paper by Roberson and Lahanne and thesis by Blatter (Clays and Clay Minerals, 29:129-135 (1981)).

James Howard did the calculation I suggested yesterday with the following rough, tentative result:

For the volume element Volume = $10^{-4} m^3$ 250 g, 2.5 equiv.s	$1 cm^2$ element of area	+ 1 m +	2.5 g/cm ³ 10% pore space 10 mg/l K ⁺ CEC = 1 equiv/ 100 g Na-smectite
--	-----------------------------------	---------	---

This is 2.5×10^{-5} equiv/l pore volume; thus one must pass 10^5 pore volumes.

Assume 10^{-14} m/sec for hyd. cond. or $1 \text{ m}^2/1000 \text{ yr}$.

Thus, 1 pore volume moves through in 1000 years.

Time = $(10^5)(10^3) \approx 10^8$ years to supply sufficient K_+ to convert all the smectite to K form.

SUMMARY

C. V. Clemency

The comment was made that it is planned to use quartz sand mixed with the bentonite to help conduct away the heat generated by the nuclear waste. Attached is a table of CEC values for various minerals and rocks. Quartz, of course, has a very low CEC (0.6 meg/100g). The materials showing the highest CEC values are the feldspathoidal minerals such as sodalite and cancrinite, which have values of about 1,000, and the zeolites which have values of about 230-620. Why not use these materials instead of quartz? If their thermal conductivity is anywhere near that of quartz, one could use material which has a higher CEC than the bentonite itself. These materials should not be any worse than quartz in so far as increasing the permeability is concerned. Even if their thermal conductivity were only half that of quartz, I think more might be gained in having a high CEC material. I could not find any information on thermal conductivity of these materials. However, they are all tectosilicates as is quartz and perhaps their thermal conductivity may not be too different. Perhaps it is even higher

Copper fins could be applied to the copper containment vessel to help conduct the heat away so that the "spike" temperature might be kept lower. Vertical fins along the length of the cylinder would be best, something like fins on a bomb. However it would probably be difficult to pack the bentonite tightly around vertical fins. Jim Kittrick has suggested using horizontal rings (like washers) of copper spaced perhaps a foot apart and with bentonite between them. With such a configuration, the bentonite could be packed firmly by pressure from above.

Further work on refining the XRD method of determining the smectite/illite ratio is needed. Many of the conclusions about the reaction depend on the S/I ratio determined by XRD. This seems to be one of the weakest links in the whole chain of reasoning and therefore in the conclusions reached. I know that Bob Reynolds has done a lot of work on this and his method is the standard used. But Jim Howard has said that some criticisms have been made (by someone named Srodon who worked with Howard). I do not know exactly what the criticisms are as I have not read the papers and Jim did not go into detail.

Jim Kittrick said that he believes that there may be more than one smectite present after the low-charged material has been converted to the high-charged material. Some additional work on this could be profitable. Perhaps the Greene-Kelly or some similar test could be developed to check this out or to identify or distinguish between these two materials.

More studies are needed on the kinetics of the S/I conversion using Roberson's and Eberl's work as a basis. Effects of the other ions on the rates, etc., for example. How one might slow down or even completely inhibit the reaction is an important question.

One should try to get samples from Pompeii (which I visited last September during the International Clay Conference). Pompeii was destroyed in 79 A.D. and is built completely of brick and cement. In addition, many of the brick walls were coated with a plaster stucco of about 3-4" thick. This stucco can be found both on indoor and outdoor walls and columns. They would provide samples that were exposed to water (rain) saturation periodically, and also samples from indoor walls of houses which were not exposed to water drenchings. Also other samples from Roman temples, buildings, aqueducts and monuments must also be well-dated and would provide specimens of both wet and dry exposures of cemented bricks.

SUMMARY

R. F. Giese, Jr.

When dealing with mixed-layer structures, as in smectite-micas, one commonly distinguishes three situations; 1) fully disordered, 2) partially ordered and 3) completely ordered. In natural materials the disordered situation is most common but partially and fully ordered phyllosilicates are well known and may be more abundant than previously thought. The simplest type of ordering is an alternation of the two types of structure present in the clay as in the pattern ABABAB. More complex types are known. Such an alternation implies the existence of long range forces in the clay layers or some means of transferring information from one part of the structure to another. Two mechanisms have been proposed; 1) charge polarity of the 2:1 layers and 2) hydroxyl reorientation.

Polarity of the layers refers to the situation where high charge on some T sites (principally due to Al for Si replacement) causes dehydration and layer collapse (as in the change smectite to illite) while adjoining layers remain low charge and hydrated.

Various authors have appealed to the hydroxyl orientation mechanism. Assume that one begins with a completely collapsed dioctahedral structure (this doesn't work for trioctahedral clays). Hydration of a single layer allows neighboring OHs to reorient towards the hydrated cation because the cation-hydrogen distance has increased (because of the water now present). This is due to the decreased electrostatic repulsion between the hydrogen and the interlayer cation. The reorientation affects OHs in the next sheets which, in turn, reorient in such a way that the neighboring interlayer cations are more strongly bonded to the 2:1 layers. These interlayer cations have a smaller probability of hydration. This begins the ABABAB pattern.

Our theoretical models of OH reorientation which were patterned after a low-charge Na-smectite indicate that the energy difference between a random stacking and an ordered one is about 1 kcal/mole. This gives a probability (based on the Boltzman distribution) of about 5:1 in favor of ordering of the type ABABAB. One would expect in any natural system of dioctahedral smectites to find ordered mixed-layer intermediates (during heating or dehydration). Ordering may change the thermal properties of the clay greatly. The case for trioctahedral clays is not as clear nor do we know much about the polar charged layer mechanism.

SUMMARY

J. J. Howard

It does not appear possible to apply chemical equilibrium arguments to predict the extent of smectite transformation in mixed-layer clays under diagenetic conditions despite the efforts of many previous workers to utilize I/S expandability as a geothermometer. Actually their argument is somewhat misplaced since they only attempted to equate temperature with reaction extent ignoring solution chemistry effects which are central to the argument. A major conclusion from these "equilibrium" arguments is the generalization that smectite transformation does not initiate until temperatures in excess of 100°C are attained and that an appreciable percentage of smectite layers persist to about 200°C. (Weaver, 1979) "Equilibrium" arguments are weakened by the observation in many natural examples at diagenetic temperatures and by hydrothermal experiments at higher temperatures of a wide range of I/S expandabilities at any given temperature within a sedimentary basin. Further problems in the "equilibrium" approach arise from a model that must imply instantaneous reaction as smectite layers transform to illite and a reversible nature to the reaction, which has not been documented to the satisfaction of many.

The problem of constructing a chemical equilibrium model for the smectite to illite transformation using solubility data to calculate an array of equilibrium constants appears to be too complex to be solved at this time. A key problem appears to be the compositional heterogeneity of the two end members, exacerbated by the wide range of materials termed "illite". More important for this subject is the wide range of layer charge distribution observed in many smectites, values ranging from ~0.1 - 0.6 equiv./unit cell (Smectite generally defined as 0.33 equiv./unit cell) along with distribution in both octahedral sheets (Lagaly and Weiss; work dating back to 1970). Even within individual packets (stacking of 2:1 layers into a diffraction unit "~10 or so layers) there is often a wide range of charge distribution. This obviously creates problems in characterizing smectites, but also in identifying the origin of the layer charge increase which is necessary for illite layers to be formed. Hence the heterogeneity of smectite composition limits the application of chemical equilibrium studies. It also inhibits the specification of reaction rate expressions.

A key point that was made in our discussions is that subsequent studies on equilibrium constants for smectites are going to have to differentiate between the effect of the silicate layer structure and the exchangeable cation. The application of ΔG values for component oxides determined by computational methods may provide some insight here (see Tardy and Garrels, 1974, 1976). ΔG estimates based upon average compositions indicate that illite is more stable even at

relatively low temperatures than smectite. These same calculations also suggest that a beidellitic smectite (tetrahedral Al substitution) is somewhat more stable than a "normal" smectite with mostly octahedral charge deficiency. This may be useful in predicting the relative stability of low-charged smectite and the expandable higher-charged precursor to illite.

If the smectite transformation cannot be satisfactorily modeled by any current equilibrium approaches the other means is to apply a kinetic argument, a procedure that until fairly recently has met some resistance. The essence of a kinetic interpretation is that the extent of reaction is dependent upon an overall rate constant (which in turn may be defined by elementary rate expressions) and the time available for reactions. Factors that influence these rate expressions include temperature, the supply of material, and the inhibiting effect of competing ions.

Early workers were discouraged in applying any kinetic arguments to explain observed I/S contents in natural environments due to the lack of a clear time-related phenomena, often older samples were less reacted than younger in seemingly similar environments.

A set of laboratory experiments first put a kinetic interpretation upon firmer footing by determining rate constants for a fairly simple system (Na-smectite and Na-beidellite glass with sufficient K^+ to saturate). Plots of reaction extent versus time result in linear isotherms suggestive of first-order kinetics, from which rate constants and an activation energy were produced (Eberl and Hower, 1976). While the activation energy of 20kcal/mole agreed favorably with values obtained for the breaking of Si-O, Al-O bonds in silicates, the calculated reaction rates at diagenetic temperatures were much too fast to account for the high percentage of expandable layers in natural sediments. This lack of agreement was enough for the authors to waver from their kinetic approach. However, this example represents a maximum rate, in that they used highly reactive glasses, and did not include any inhibiting cations that would effectively compete with the potassium for available exchange sites. Later studies which have included the effect of other cations, particularly Mg^{2+} , upon reaction rates reveal a significant reduction in reaction rates that are more in agreement with observed rates (Blatter, 1974; Lahann and Roberson, 1980). The effect of these inhibiting cations is illustrated by the reduction of the pre-exponential A factor in the Arrhenius equation from 3200 in Eberl and Hower's experiments to ~0.2-3.0 in many of the later runs; a change in rate constants of several orders of magnitude.

The importance of the chemical contribution to the smectite transformation rate is illustrated by another calculation where

temperature distribution in a compacting basin was modeled with reaction extent: where,

$$\frac{dP}{dt} = \left. \frac{\partial P}{\partial t} \right|_x + \left. \frac{\partial P}{\partial x} \right|_t \omega + R(x,t)$$

where P = any property, in this case % smectite layers,
 $\left. \frac{\partial P}{\partial t} \right|_x$ is a rate at a given depth,
 $\left. \frac{\partial P}{\partial x} \right|_t$ is a present day gradient
 ω = the sedimentation rate, which determines the heat distribution and $R(x,t)$ = a chemical effects term.

When one evaluates the total derivative for just the first two temperature-dependent terms an alteration rate of ~2.5 expandable layers per 100 layers in an I/S mixture are transformed to illite every million years. This is an order of magnitude greater than the observed rates for the sediments from which this data is derived. This suggests that the chemical effects term, R, has a tremendous influence on the rate of smectite transformation. At this time we appear able to only qualitatively estimate that influence, quantitative efforts are still down the road.

Addition thermal modeling is being done by Reynolds and students in the diagenetically altered shales around an igneous intrusion. At this time his results are in good agreement with the above studies. The advantage of his work is that it is a closer natural analog to repository behavior, while providing a single-event thermal pulse for the modelers who then need not worry about the complications found in slowly subsiding basins.

Note: First-order kinetic plots do not fit many natural assemblages, older I/S clays are more expandable than predicted.

Kinetic interpretations are by nature (definition?) very mechanistically inclined, in the case of the smectite transformation to illite there appear to be at least two separate steps, each of which could be rate-limiting. The first step is the creation of sufficiently high layer charge, primarily in the tetrahedral sheet, so that any interlayer potassium is dehydrated by the attractive forces between layer and naked cation; the water is driven off and the layer collapses irreversibly to an illite basal spacing. The second rate-limiting step in the mechanism is the supply of potassium to high-charged interlayers. The dissolution of feldspar and other K-bearing minerals provides a source for potassium which is in turn transported by either advective flow, or especially by diffusion once within the interlayer spaces.

The more interesting step is the actual development of layer charge in the smectites, creating a reaction intermediate. This intermediate step, termed high-temperature smectite by Kittrick, proto-illite or vermiculite-like by Roberson and high-charged expandable layer by Howard has only recently been recognized in natural samples. Along with the obvious implication of having an identifiable intermediate step which can be useful in increasing the sensitivity of reaction-extent measurements, you have a 2-component system enlarged to three. Most importantly this would influence the I/S measurement techniques of Reynolds and Hower (1970) which only deal with two components, though the errors are probably not too major.

This reaction intermediate can be identified by K^+ -saturating the I/S clay and comparing it with an unsaturated specimen by XRD. The difference in measured expandabilities can be attributed to high-charged expandable layers (Howard, 1981).

It appears that the increased layer charge is developed by Al for Si substitution in the tetrahedral sheets which provides the source of charge as close to the interlayer as possible. The source of the Al and how it enters the tetrahedral sheet is essentially the unsolved question. In short... I believe that Al may be derived from the cannibalization of smectite edges; as Si is released and floats away, the Al complexes and finds itself intercalated in the interlayer. Hence an outside sources of Al, such as feldspar dissolution, is not required, and in as much is supported by the hydrothermal experiments that utilize only clay. (Eberl, 1977, 1978) Chemical analysis of natural I/S clays also indicate that Al is not simply redistributed by diffusion from octahedral to tetrahedral sheet, but that tetrahedral Al increases during progressive illitization while octahedral Al remains constant (Howard, 1981).

The experiments that Roberson reported of decreasing CEC with progressive reaction also support the idea of Al-hydroxides finding themselves in the interlayer.

The actual transfer of Al in the interlayer with Si in the tetrahedral sheets requires a little imagination and faith. Quite simply the bond strengths are quite high, 20kcal/mole, but if there is a certain amount of disorder in the lattice due to the poor fit of the "ideal" tetrahedral sheet on octahedral sheet, the resultant rotation in the lattice may produce sufficient strain so that it becomes relatively easier for an individual Si to "pop-out" and Al to "jump-in" and relieve some of the excess energy. I am hard pressed to come up with some means of testing this.

Regardless of actual mechanism, it appears that the creation of layer charge in the smectites is solely dependent upon temperature.

The rate of Al substitution must increase with increased temperature though we do not have an elementary rate expression at this time. Solution chemistry does not appear to affect this step.

The second rate-limiting step is the supply of K^+ to the high-charged sites. In smectites of low layer charge K^+ is the least preferred interlayer cation compared to Mg^{2+} , Ca^{2+} , and Na^+ , such that any potassium in the system is severely inhibited in occupying interlayer sites by the competing cations. However, the easily dehydratable K^+ is suddenly preferred over the other cations when layer charge is sufficiently high enough to overcome hydration energy, drive off the water, collapse the interlayer and result in a lower energy state.

The maximum smectite transformation rate is therefore defined by Eberl & Hower's experiments (1976) which did not have any competing ions, and included only sufficient K^+ to occupy all the sites. Later experiments which yielded slower reaction rates illustrate the influence the cation inhibition of K^+ migration to available sites.

The proposed K^+ migration scenario in a granite-clay barrier design illustrates how effective the compacted clay will act as a barrier for K^+ supply to the smectite. Conclusion is that despite whatever worst-case scenario one might envision it would require a large number of pore volumes of K-bearing groundwater moving at whatever rate to satisfy all the available sites. An interesting perturbation would be to estimate the minimum amount of K^+ on the exchange sites that would significantly affect the physical properties, e.g. 25% sites filled... .

The natural analog of the altered bentonite bed in the disturbed belt of Montana (Altaner, et al, 1981) indicates that K^+ migration there occurred at a rate of 1 meter/million years. This may represent a maximum in that K^+ -migration probably was not significant until almost complete compaction of the bentonite by burial occurred.

The Ca-migration studies in archeological clays appears to be rather promising, though I feel additional information is needed. This includes a Sr^{+2} profile to correlate with the Ca, and more ancient examples that come from water-saturated samples, eg. cisterns and aqueducts. Also, that these studies must distinguish between diffusion through a static medium and advective flow that transports the species under consideration.

SUMMARY

J. A. Kittrick

Without going into who contributed what, this seems to be the situation and our conclusions.

THE PROBLEM

Na-Bentonite is desirable as a backfill surrounding radioactive waste containers because of the low water transmission and high cation retention properties of smectites. Both of these desirable physical properties may be seriously degraded by the conversion of smectite to illite. Assuming that the repository requires desirable smectite physical properties over a time span of 10^2 to 10^4 years it is necessary to determine if the illite conversion will take place during this time span.

WHAT HAPPENS

Various studies, including thermodynamic studies based upon solution solubilities, indicate that smectites formed at earth surface temperatures are unstable at higher temperatures where other smectites form. The higher temperature (HT) smectites with greater tetrahedral charge are much more K^+ selective. When K^+ is available these smectites contract, effectively decreasing CEC and expandability. In the K- contracted state these HT smectites are identified as illites by x-ray diffraction analysis. The energy states, and hence the probability, of various ways of distributing K^+ throughout the HT smectite can be calculated. However, the degradation of desirable smectite physical properties is probably proportional to total K^+ content as a first approximation, so that it is probably unnecessary to know the exact way in which the K^+ is distributed.

CONVERSION RATE VS EQUILIBRIA

Equilibrium thermodynamic calculations would establish the conditions of T, P, and ion activities where various HT smectite phases can be stable. Unfortunately, the necessary data for these calculations is not yet available and in some respects the method of calculation is also uncertain. Experimental evidence indicates that the formation times of HT smectites may be long, relative to repository requirements, so that kinetics appear to be much more important than equilibria. This is a fortunate situation because at present usable rate data is much more abundant than usable equilibrium data.

CONVERSION RATE MEASUREMENTS

Conversion of smectite to illite increases rapidly with temperature above approximately 100°C . Conversion may take place at

temperatures as low as 60°C, but the rate is so slow that estimates of conversion times are very unreliable. For relatively pure K⁺ systems in the laboratory at approximately 100°C, conversion of smectite to illite requires about 10⁴ years. It is unclear whether the Mg²⁺, for example, slows the conversion of smectite to HT smectite or whether it slows the conversion of HT smectite to illite. In any event, it is the ultimate formation of illite that is expected to degrade bentonite backfill performance. Natural systems appear to agree best with laboratory experiments where Na, Ca, or Mg are present requiring approximately 10⁷ years for illite formation at 100°C.

CONVERSION RATES FROM K⁺ FLOW ESTIMATES

Considering the K⁺ content of granitic ground waters and a diffusion rate of 10⁻¹⁴ cm²/sec for compacted bentonite, it can be estimated that the amount of K⁺ required to convert HT smectite to illite would take about 10⁸ years to accumulate, assuming no K⁺ from a breached waste container. If the diffusion rate of 10⁻¹⁴ cm²/sec does not alter appreciably with time, the estimate of 10⁸ years appears conservative because not all smectite may be converted to HT smectite in that time, and not all K⁺ will be effective in converting HT smectite to illite. There is some evidence from natural systems indicating that the diffusion rate of 10⁻¹⁴ cm²/sec may actually decrease to approximately 10⁻¹⁶ cm²/sec. This suggests K⁺ flow conversion estimates of approximately 10¹⁰ years.

CONCLUSIONS

There appears to be sufficient data available from laboratory and field experiments to estimate approximate conversion rates of illite to smectite. Estimated time range from 10⁷ to 10¹⁰ years. These are sufficiently large compared to repository requirements of 10² to 10⁴ years that more detailed calculations seem warranted. The degradation of necessary physical properties of bentonite backfill below repository requirements may be a nonproblem.

SUMMARY

H. E. Roberson

Bentonite, which is primarily composed of smectite, is seriously being considered as barrier or backfill material in the "permanent" disposal of radioactive waste. Compacted smectite, itself, has many properties that make it an attractive candidate for use. These properties include its high adsorptive capacity, its ability to flow rather than fracture under stress, and its extremely low permeability (in the "dry" or "wet" state). However, one has to consider the possibility that smectite may not be stable under the temperature, pressure, and chemical conditions that can be expected to exist in the immediate environment at the canister burial site. The questions we have primarily concentrated on during our discussion at the "Buffalo Meeting" have been.

1. Can smectite be expected to retain the desirable properties mentioned above under peak temperatures ($\sim 80^{\circ}\text{C}$) at an actual burial site?
2. If smectite, itself, changes in composition and/or structure over time (under burial site conditions) what can be predicted about possible changes that may occur?
3. Will mixed-layer illite smectite, in appreciable amounts, form, and if so, under what conditions?
4. Will other phases form and what effect might these have on porosity permeability, etc.?

Experimental and observational data suggest that smectite will stay fully expanded (i.e. retain 2 molecular layers of crystalline water per unit cell) at 80°C (and probably up to $\sim 250^{\circ}\text{C}$) for extremely long periods of time (millions of years) as long as no K^+ becomes exchanged on the smectite interlayer surfaces. Studies by Roberson and Lahanne, Howard, and Roberson and Sass indicate that the original smectite composition can be altered in saline solutions at elevated temperatures even when no K^+ is present. The data these investigators have obtained indicate that a more highly charged (higher charge density) smectite can be expected to form when smectite comes into contact with solutions containing Na^+ , Ca^{++} , and/or Mg^{++} . Even though smectite altered by hot saline solutions (with no K^+) will develop a higher charge (become more like a K- depleted illite) it may go through an intermediate state when much of the charge is satisfied by Al (hydroxyl) species if pH conditions are low (say between 3-6) (Roberson and Sass, unpublished).

If smectite is treated with K^+ solutions, smectite may be transformed to a mixed-hydrate system consisting of nonexpanding layers (those layers which have adsorbed K^+ and become dehydrated to a 10 Å "irreversibly" collapsed state) and expanding layers (with one or two molecular layers of water). Whether or not this transformation will occur depends on the composition of the original smectite (including the exchange composition), the concentration of K^+ in solution, the type and concentration of other ions present, and the temperature. Based on a small number of observations pressure is thought to play a minor role.

Thus, any consideration of a transformation of smectite to mixed-layer illite/smectite ultimately focuses on the availability and concentration of K^+ . The limiting step in illitization is seen to be the availability of K^+ . If no K^+ is present in the solution in contact with smectite over a temperature range of 25° - 250°C and pH range of 3-4 to 9-10, then smectite should be quite stable for millions of years. However, if K^+ is present in solutions that can be expected to interact with smectite then one needs to estimate the amount of K^+ that would be available for exchange over a given period of time. "Rough calculations" discussed at our meeting indicate that at the low flow rates to be expected and for conditions of anticipated K^+ concentrations (~ 10ppm) it would take millions of years to even have enough K^+ to satisfy all the exchange sites for typical smectite (100meg/100g clay). Obviously, one would want to calculate carefully for a variety of conditions (assuming higher permeability values, higher K^+ concentrations, etc.) to arrive at a total K^+ value that would represent the amount for exchange (and potential interlayer dehydration and collapse (illitization)). This, of course, would be the fastest possible illitization rate. This follows because much of the K^+ that would be available for exchange would not actually exchange. And, some of the exchanged K^+ would not cause dehydration and layer collapse (eg. low-charged smectite layers would probably behave this way even at temperatures of 80°C). Any Mg^{++} , Ca^{++} , and Na^+ in the interacting K^+ solutions would be selectively adsorbed in the interlayer position and would be expected to stay hydrated over the temperature range (~80°C) being considered. Roberson and Lahanne have shown that Mg , Ca^{++} and Na^+ (in that order) will significantly impede or inhibit the reaction rate of smectite-illite/smectite.

Item #4 above was not considered earlier in great detail because we were focusing primarily on the smectite-illite transformation. However, it was brought up from time to time, and a few words are probably called for here. Clearly, silica will be leached from the smectite as hot saline solutions interact with it. Depending on the flow rates of the solution, the concentration of the solutions (including pH), and temperature, a whole range of possibilities exist. At normal pH range (3 or 4 to around 9) and for dilute solutions smectite should probably be quite stable for millions of

years. If flow rates are low through the bentonite, then dissolved silica would be expected to reach saturation levels and silica will become precipitated. Fine grained silica such as this, might tend to make the bentonite even less permeable than in its original condition.

If pH conditions become very active Al will dissolve and we might expect Al-hydroxide complexed smectite + Al(OH) precipitated material + new Al-silicate phases. The composition of the system and the temperature obviously would dictate phases (metastable and stable) that might be expected to form. High pH conditions would cause hydroxides to form and possibly chlorite or smectite-chlorite mixed-layer clays. This subject should be explored in more detail, in my opinion, because should these phases form, the permeability of the material might be considerably altered.

Returning to the original question posed - will smectite retain its desirable properties after burial at moderately high temperatures (up to 80°C) over long periods of time (millions of years)? The answer is a qualified yes. Under conditions that we expect will obtain - low flow rates through the compacted bentonite, relatively dilute solutions (with concentration levels of 10-100ppm K^+ , and with accompanying Na^+ , Ca^{++} and/or Mg^{++} at concentrations summing to roughly equal that of the K^+ concentrations, and with a pH range of 4 to ~9, one could feel quite confident in predicting smectite stability for an extremely long period of time. If drastic deviations away from these conditions become the case, then care should be taken in predicting behavior.

SUMMARY

C. Waddell

Calculation of the Effect of K^+ Migration on the Smectite-Illite Transformation.

Experimental kinetics by Eberl (1978) established that in a simplified system the smectite-illite reaction was a first-order reaction. He calculated a rate of approximately one expandable smectite layer altering to illite per 10^4 years. Devoid of any inhibiting cations and utilizing highly reactive glasses, this clearly represents a maximum rate. Field evidence indicates that the rate is considerably slower in natural systems. A rate of approximately 2.5 expandable layers converting to illite per million years was calculated using the P-T regime from compacting basins in the Gulf Coast (Howard, J.J., 1981). Although at closer approximation, it is still too large to account for the number of expanded layers still remaining. This discrepancy indicates that other factors must be considered to make an adequate estimate of the reaction rate. One factor which may play an important role in such a rate determination is the availability of the K^+ .

Experimental studies by Eberl and Hower (1977), Howard (1981), and Roberson and Lahanne (1981) indicate that the exchange of K^+ on the smectite triggers the collapse of the smectite to an illitic form. These studies show that at temperatures below 200°C , expanded highly-charged smectites may remain stable if no K^+ is present. However, with the addition of K^+ , the smectite collapses to form illite. Examination of a Cretaceous bentonite from Montana which had been heated to between 100 - 200°C , revealed such a relationship between the presence of K^+ and the illite in the mixed-layered clay (Altaner, et al., 1981). They observed that as K^+ decreased regularly away from the contacts, the illite mimicked the same regular decrease.

These studies imply that the availability of the K^+ to the exchange sites is crucial to the determination of the final reaction rate. The availability of the K^+ is determined by the mobility of the K^+ within the clay. The penetration of the K^+ into the clay is thus a function of the permeability of the clay to groundwater and the diffusion rate of the K^+ . If the permeability and diffusion coefficients are sufficiently low, the ability of the K^+ to reach the exchange sites will be severely restricted. If the penetration of the K^+ is slow enough the smectite-illite reaction will not occur over most of the bentonitic body. Therefore, the smectite-illite reaction would not be a great danger to the long-term efficiency of the smectite barrier.

The rate at which the K^+ can penetrate the clay may be calculated from the amount of K^+ present in the groundwater and from the permeability and diffusivity of the clay. Using $10\text{mg/l } K^+$ (KBS TR-90, Appendix A) and a permeability of approximately 10^{-14} m/sec an alteration rate of 1.48×10^{11} years/meter of clay may be calculated. Using diffusion coefficients of 10^{-11} m^2/sec and 10^{-20} m^2/sec , rates of 1.48×10^8 y/m^2 and 1.48×10^{17} y/m^2 were calculated respectively. These diffusion rate estimates also represent a maximum because the rate of diffusion generally tends to decrease with time as the chemical gradient decreases.

These calculations indicate that the K^+ penetration rate is so slow that the amount of K^+ will be severely restricted in most of the system. Hence, the rate of smectite-illite transformation would be negligible if the temperature remains below 200°C and if the chemistry of the groundwater does not alter appreciably from its present state. Thus this reaction should not pose a significant threat to the efficiency and longevity of the smectite barrier as proposed by KBS.

CONCLUSION

D. M. Anderson

The Colloquium on Smectite Alteration was scheduled over a two-day period with opportunities for individual interaction at several times each day. At the conclusion of the colloquium, participants were invited to summarize their views and provide whatever comments or suggestions that, in their judgment, might prove to be useful to the KBS organization. Some time was allowed for this for participants, who had in the meantime returned to their home institutions. During the month of August informal telephone conversations and correspondence between the colloquium chairman and Drs. Anders Bergstrom and Roland Pusch of the KBS organization took place. As a result of these exchanges the following questions were identified as of prime interest and importance, answers to which might be included in the conference proceedings then in preparation. These questions can be summarized as follows:

1. What is the prerequisite for and what is the precise mechanism by which smectite clays may be altered to illite?
2. What are likely sources of potassium with respect to the KBS project?
3. Is it likely that the conversion of smectite to illite will be of importance in the 10^5 to the 10^6 year time frame?

During the discussions held at this colloquium a general consensus based upon quite reliable and definitive laboratory and field evidence has emerged. The consensus can be discerned in part or in whole in the individual summaries of the participants. The colloquium has served a highly useful purpose in formulating, and also to a large degree, in validating reliable answers to the three questions posed long before such a consensus could have been expected to emerge in the normal course of events involving the presentation of individual views in scientific journals, presentations at society meetings, etc..

With regard to the first question, after the presentation and subsequent discussion of preliminary views on the subject, there remained little doubt in the minds of the participants that the mechanism for the smectite-illite conversion involves three fundamental steps:

1. The creation of a high lattice charge by the removal of silicon atoms, precipitation of silica in various forms at locations adjacent to the clay lattices, the concomitant replacement of silica in the lattice by aluminum, magnesium, etc., locally available from the dissolution of accessory minerals, or the exchangeable ion complex, etc..

2. Influx of potassium ions derived from local dissolution of potassium-bearing minerals, percolating ground water, etc. to saturate the exchange capacity of the now highly charged smectite intermediate.
3. Irreversible collapse of the high lattice charge, smectite intermediate to the typical nonexpanding illite lattice.

The most critical, rate-limiting step is the production of a highly charged smectite lattice by the progressive substitution of aluminum, etc. for the silica in the smectite lattice referred to in step one. The most important prerequisite to the exchange of lattice silicon for aluminum, etc., is an environmental temperature sufficiently high to allow passage of these ions out of and into the lattice, respectively. There is both laboratory and field evidence to substantiate the conclusion that at temperatures above about 100°C the exchange of silicon and aluminum is relatively rapid and the conversion of smectite to illite, other conditions being favorable, therefore can proceed quite rapidly. It is very likely, however, that the process begins when temperatures exceed about 60°C; but at the lower temperatures, rates of conversion are so slow, as to be almost negligible.

As Dr. Kittrick has pointed out, under laboratory conditions a relatively pure smectite saturated with potassium ions can convert to illite in approximately 10^4 years. Clearly, it is the temperature to which the smectite is subjected that initiates the production of a high lattice charge through the exchange of silica for alumina, etc. and sets the stage for conversion to illite when sufficient potassium is present to bring about lattice collapse. The aluminum required for substitution for silica is sufficiently ubiquitous, available for instance at the corner edges of the smectite sheets, that its availability cannot be regarded as a rate limiting step. Silica removed from the lattice is immediately precipitated and removed from active involvement. Therefore, this process cannot be rate limiting. It is the environmental temperature that is critical in determining whether the smectite-illite conversion is possible and the rate at which it will proceed.

With regard to the source and role of potassium ions in circumstances characteristic of the KBS application, this ion will be present as a result of solution of potassium-bearing feldspar, micas, and other potassium-bearing minerals common in crystalline rocks. The presence of potassium in the circulating ground water at sites selected as possible disposal sites in Sweden has been determined. In the absence of any additional potassium-bearing materials used in the construction of the KBS facility, the main source of potassium then must be the minerals just mentioned and potassium ions would be brought to reaction sites in the compacted smectite buffer material by percolating ground water or by diffusion. Since irreversible lattice

collapse of the smectite to form a potassium-bearing illite requires the presence of a sufficient quantity of potassium ions to nearly saturate the exchangeable ion complex and to penetrate all the interlayer space, the rate at which potassium is supplied by hydraulic permeation or by diffusion is very important. This process too has the possibility of being the rate limiting step.

To summarize and recapitulate the smectite-illite conversion involves the processes of solution, ground water flow and ion diffusion, smectite lattice alteration and mineral reconstitution. The most essential steps are the creation of a high tetrahedral lattice charge brought about by the removal of silica and its replacement by aluminum, or other divalent cations, followed by the uptake and incorporation of potassium ions brought to the appropriate sites by ground water percolation or by ion diffusion. The removal of silica from the tetrahedral sheet and its replacement by aluminum, etc. has been shown to proceed at extremely low rates at temperatures below about 60°C. Above 60°C the rate at which this process can proceed continually increases. At temperatures above 100°C the exchange of silica for the aluminum or certain divalent cations to produce the high lattice charge proceeds quite rapidly and may no longer be the rate limiting step.

The quantity of potassium required to saturate the smectite exchange complex in its state of high lattice charge prior to irreversible lattice collapse is sufficiently great that a plentiful source must be available. In impure smectites the source of potassium may actually be dispersed throughout the clay in the form of silt-sized, potassium-bearing mineral particles such as feldspar, mica, chlorite, etc.. In purified smectites an external source of potassium must be available. In this case potassium ions must be brought to individual reaction sites sequentially, by percolating pore fluids or by the diffusion of potassium ions. At temperatures above 100°C it is very likely that for relatively pure smectite the rate limiting process is the transport of potassium ions by hydraulic flow or ion diffusion from its outer boundary inward.

The rate of probable smectite-illite conversion can be reliably estimated in the KBS application from the above considerations. Assuming that the environmental temperature of the stored nuclear waste and the surrounding buffer material never approaches 100°C. The most probable rate-limiting step in the smectite-illite conversion process is the rate at which potassium ions are transported into the buffer in quantities sufficient to saturate the exchange complex. Smectite-illite conversion thus, must proceed from an outer boundary inward, assuming that there are no sources of potassium ion within. This emphasizes the need for leak-free nuclear waste containers if potassium ions are a constituent and that the particular smectite clay employed as a buffer material be as nearly free as possible from potassium containing accessory minerals. This condition is necessary to assure that the only source of potassium ion is the surrounding

crystalline rock and that the potassium ions will be transported into the buffer material only at concentration levels characteristic of the circulating ground water.

Given these circumstances and conditions it is possible to derive an estimate of the probable stability of the smectite clay. The computations would proceed along the following lines: assume a smectite buffer material of unit thickness (one meter) placed between walls of massive crystalline rock on either side. Visualize a horizontal column of the smectite through which circulating ground water passes ($1 \text{ cm}^2 \times 1\text{m}$). Assume a typical value for the pore volume (a typical value would be in the range of 30 to 40% of the total volume of the element under consideration). To proceed further, it is necessary to assign values to the cation exchange capacity of the buffer material, the concentration of potassium ion in the percolating ground water, and the hydraulic conductivity and density of the compacted bentonite: reasonable values are 70 meq/100g clay, 10 mg/l potassium ion, 10^{-12}m/sec and 1.9 g/cm^3 , respectively.

The next step is to calculate the total quantity of potassium ion required to eventually bring about collapse of all the smectite lattices in the buffer to the illite configuration. Note that this assumes that the environmental temperature may at some time rise to sufficiently high levels to make the conversion possible. The quantity of potassium ion required is found by multiplying the cation exchange capacity of the smectite by the total quantity of smectite present in the volume element under consideration. Next, it is necessary to calculate the length of time required for this quantity of potassium to pass into the volume element at the flow rates that might be anticipated. This can be estimated from measured values of the hydraulic conductivity of the crystalline rocks typical of the potential KBS sites. If one assumes a unit hydraulic gradient the value of the hydraulic conductivity itself can be employed to roughly estimate the time required to fully saturate the smectite with potassium. This number, representing as it does the most rapid possible rate of conversion given the most unfavorable circumstances, is a highly conservative estimate of the minimum time required for total alteration of the smectite buffer to the nonexpansible illite form.

Calculations performed in this manner yield estimates of millions of years, estimates that greatly exceed the times required by the KBS plan to allow for the natural decline of radiation levels to acceptable levels long before there is any danger of the smectite failing to perform its functions as a buffer material. A sample computation and the resulting estimates are illustrated in Appendix A. Depending upon the degree to which one wishes to consider variations in cation exchange capacity, hydraulic conductivity, porosity, hydraulic gradients, etc., a range of estimates of the probable useful lifetime of the smectite buffer material may be obtained. In all reasonable cases the lifetimes greatly exceed the 10^5 to 10^6 year regarded as necessary in the KBS application.

Reliance on these estimates requires acceptance of the fact, unanimously agreed to by the participants of the colloquium, that in order to bring about the smectite-illite conversion, temperatures approaching or exceeding 100°C are an absolute necessity. Even though the smectite may eventually become fully saturated by potassium ion it cannot spontaneously convert to a nonexpanding illite clay unless the environmental temperatures approach or exceed about 100°C for quite a long period of time. When the exchange complex of a smectite clay is fully saturated with potassium but temperatures do not exceed about 60°C the replacement of silica by aluminum, etc., required to bring about the high lattice charge required for conversion to the illite form, the changes in the properties of the smectite are quite minor. Potassium saturated smectite retains its ability to swell and it is highly impermeable to water. Moreover, it retains the plasticity necessary to function effectively as a buffer material. Therefore, the mere saturation of smectite with potassium is not in itself a serious matter. It could become serious only if the temperature of the buffer material were to rise to about 100°C and remain there for an extended period of time.

Let us again review the basic process: If the environmental temperature rises to exceed 100°C, lattice expansion due to the increased energy of atomic vibrations permits the escape of silica from its tetrahedral location in the lattice and its replacement by aluminum or certain divalent cations if they are available. Aluminum ions generally are the most plentiful of these and are always in locations that permit almost instantaneous replacement in the tetrahedral sites vacated by silica atoms with these aluminum ions. The overall rate at which this exchange proceeds is known only in qualitative terms. At temperatures in the range of 60°C and below, this is relatively slow and the formation of the highly charged smectite lattice resulting from this process of the substitution of ions of different charges is sufficiently low to become rate limiting. At temperatures approaching the 100°C range, however, this process is sufficiently rapid that the supply of potassium ions regulates the rate at which individual lattice sheets collapse to the illite configuration and become nonexpanding. The proportion of nonexpanding to expanding layers increases as this process continues until all the smectite lattice layers are converted to the high negative charge form and have taken up quantities of potassium sufficient ultimately to bring about their irreversible collapse to the illite configuration. As this process proceeds, potassium ions in the percolating fluids penetrate ever deeper into the unaltered smectite and the zone of alteration advances inward. By viewing the matter in this way the governing role and the importance of the rate of influx of potassium ion can be fully appreciated. Even though the smectite might be fully converted to the highly charged lattice form by the substitution of aluminum for silicon in the tetrahedral positions, collapse does not occur until a sufficient quantity of potassium ion is present. Without the presence of potassium the high temperature form of the smectite clay would still perform effectively as a buffer material in the KBS application. Looking at the same

question from another point of view, in the absence of the high environmental temperatures which are required for the formation of a high lattice charge in the smectite and render it vulnerable to collapse, an influx of potassium ions merely converts the smectite to its potassium form and does not render it ineffective as a buffer. This, then, is the basis upon which it is firmly concluded that under the projected conditions of the KBS storage facility, smectite clays are expected to function effectively as a buffer material over times greatly in excess of the 10^5 to 10^6 years required in the KBS application.

In addition to the laboratory data referred to in the discussions of the colloquium participants, field evidence is at hand to confirm the conclusions derived from the forgoing arguments. Altaner et al. (1981) have identified a location in the State of Montana where a pure bentonite (smectite) bed lies between two rock strata that contain potassium-bearing minerals. These rocks were formerly buried and subject to ground water permeation. Hower et al., 1982 have fully characterized this interesting occurrence of bentonite and have studied the extent of alteration of the smectite bed. They have found that illitization is nearly complete at both contacts. The extent of conversion of smectite to illite was observed to diminish in a roughly exponential manner with distance inward. Independent isotope ratio measurements have established that this bed experienced environmental temperatures for a sustained period of time of 100° to 200°C . The time involved has been reliably estimated to be approximately 3×10^6 years. Alteration in whole or in part has affected roughly half of the smectite in the 2.5 meter thick smectite layer. Clearly the field evidence confirms the conclusion that the smectite-illite conversion, even when the temperatures rise to levels sufficient to create the high lattice charge smectite and K^+ is readily available, is very slow. Clearly it is limited by the rate at which potassium ion can saturate the exchange complex and lead to lattice collapse to the illite configuration. In the case of the Montana bentonite deposit potassium ion must have entered the bed by diffusion since alteration upward from the bottom of the bed almost exactly matches the alteration profile from the top of the bed downward.

Diffusion was considered in an earlier report (Anderson and Fountain 1981) and subsequently by Pusch and his co-workers in a report commenting on this work. Diffusion coefficients ranging from $6 \times 10^{-12} \text{ m}^2 / \text{sec}$ to an apparent diffusion coefficient of $1 \times 10^{-20} \text{ m}^2 / \text{sec}$ or less are quite possible. Anderson and Fountain (1981) derived very low values of the apparent diffusion coefficient from measurements of calcium ion penetration into various clay matrices. The larger values were derived from field tests in soft illitic clay using calcium hydroxide solution to inject a Ca^{++} tracer (Moum et al., 1968). The large range in values makes it difficult to perform computations that will be convincing to all. However, the conclusions, fully supported by the field evidence cited above, is that potassium permeation by diffusion also is very slow in

smectite clay. It is of the same order of magnitude as that which would result from hydraulic permeation.

To summarize, all available evidence is indicative of exceedingly slow permeation by ionic species that might bring about undesirable changes in properties of the smectite buffer material. If environmental temperatures can be kept substantially below 100°C it can confidently be concluded that alteration of the compacted smectite buffer material can be held to negligible levels and that it can be fully relied on to perform its essential functions.

REFERENCES

- Altaner, S., Whitney, G. and Hower, J., 1981, The Role of Potassium Metamorphism in the Origin of a Zoned K-Bentonite from the Disturbed Belt Montana, Abstr. 1981 Clay Minerals Conference No. 30 Urbana, Ill., Abst. p. 4.
- Altaner, S., Aronson, J.L., Whitney, G. and Hower, J., 1982, Diffusional Modeling of a Zoned K-Bentonite from the Disturbed Belt. Circum-Pacific CMS Hawaii, p. 38.
- Anderson, D. M. and Fountain, J., 1981, Investigation of the Chemical Stability of Clays employed as Buffer Materials in the Storage of Nuclear Waste Materials; Interim Rep. to SKBF-Project KBS.
- Blatter, C. F., 1974, Interactions of Clay Minerals with Saline Solutions at Elevated Temperatures, Abstr. Clay Minerals Conference 23, 1974, Abs. p. 18.
- Eberl, D. D., 1978, The Reaction of Montmorillonite to Mixed Layer Clay: The Effect of Interlayer Alkali and Alkaline Earth Cations, *Geochim. et Cosmochim. Acta.*, 42:1-7.
- Eberl, D. D. and Hower, J., 1977, The Hydrothermal Transformation of Sodium and Potassium Smectite into Mixed-Layer Clays, *Clays and Clay Minerals*, 25:215-228.
- Eberl, D. D. and Hower, J., 1976, Kinetics of Illite Formation, *GSA Bulletin* 87 : 1326-1330.
- Howard, J. J., 1981, Lithium and Potassium Saturation of Illite/Smectite Clays from Interlaminated Shales, *Clays and Clay Minerals* 29 : 136-142.
- Lagaly, G., 1981, Characterization of Clays by Organic Compounds, *Clay Minerals Conference*, 16:1-21.
- Lahann, R. W. and Roberson, H. E., 1980, Dissolution of Silica from Montmorillonite: Effect of Solution Chemistry, *Geochim. et Cosmochim. Acta.*, 44:1937-1944.
- Moore, D. M., Alcover, J. F., Giese, R.F. and Hower, J., Ordered Interstratification of Collapsed and Hydrated Na-Smectite, Abstr. 1981 Clay Minerals Conference 30, p. 35.
- Moum, J., Sopp, O. I. and Koken, T., 1968, Stabilization of Undisturbed Quick Clay by Salt Wells. *Vag- och vattenbyggaren* No. 8, 1968.
- Nadeau, P. H. and Reynolds, R. C., 1981, Burial and Contact Metamorphism in the Manchos Shale, *Clays and Clay Minerals* 29: 249-259.

- Pusch, R., 1982, Chemical Interaction of Clay Buffer Materials and Concrete. (Informal report to KBS.)
- Reynolds, R. C. and Hower, J., 1970, The Nature of Interlayering in Mixed Layer Illite-Montmorillonites, Clays and Clay Minerals, 18:25-36.
- Roberson, H. E. and Lahann, R. W., 1981, Smectite to Illite Conversion Rates: Effects of Solution Chemistry, Clays and Clay Minerals, 29:129-135.
- Tardy, Y. and Garrels, R. M., 1974, A Method of Estimating the Gibbs Energies of Formation of Layer Silicates, Geochim. et Cosmochim. Acta., 38:1101-1116.
- Tardy, Y. and Garrels, R.M., 1976, Prediction of Gibbs Energies of Formation: 1. Relationship Among Gibbs Energies of Formation of Hydroxide, Oxides and Aqueous Ions, Geochim. et Cosmochim. Acta., 40:1051-1056.
- Weaver, C. E., 1979, Geothermal Alteration of Clay Minerals and Shales: Diagenesis, Technical Report OnW1 - 21.

Appendix A

Sample Computation

- Assume:
- (1) Volume element $1 \text{ cm}^2 \times 1 \text{ m} = 1 \times 10^{-4} \text{ m}^3$
 $= 1 \times 10^2 \text{ cm}^3$
 - (2) Pore volume (assume 30% porosity) $= 3 \times 10^{-5} \text{ m}^3$
 $= 30 \text{ cm}^3$
 - (3) Volume of clay (assume 70% clay) $= 7 \times 10^{-5} \text{ m}^3$
 $= 70 \text{ cm}^3$

(refer to figure 1 for a schematic representation)

- Calculate: Total cation exchange capacity of volume element
(assuming 1.9 g clay/cm^3 and $70 \text{ meq/100 g clay}$)
- $$(1.9 \text{ g clay/cm}^3)(70 \text{ meq/100 g clay})(70 \text{ cm}^3 \text{ clay})$$
- $$= 93.1 \text{ meq} = 9.3 \times 10^{-2} \text{ eq}$$

- Given:
- (1) K^+ concentration of 10 mg/l (KBS TR-90 Appendix A)
 $= 0.256 \text{ meq/l} = 2.56 \times 10^{-4} \text{ eq/l} = 2.56 \times 10^{-7} \text{ eq/cm}^3$
 - (2) Hydraulic conductivity $5 \times 10^{-12} \text{ m/sec}$ (KBS TR-81-09)
 $= 5 \times 10^{-10} \text{ cm/sec}$

- Calculate: Time required to pass sufficient K^+ into the volume element of smectite to fully saturate its exchange capacity of 9.3×10^{-2} equivalents. Assuming Darcy's Law and unit hydraulic gradient, the flow rate is then

$$q = K = 5 \times 10^{-10} \text{ cm}^3/\text{cm}^2/\text{sec}$$

and the quantity of K^+ entering the volume element per unit of time is simply this rate times the concentration of K^+ :

$$\begin{aligned} & (2.56 \times 10^{-7} \text{ eq/cm}^3)(5 \times 10^{-10} \text{ cm}^3/\text{sec}) \\ & = 12.8 \times 10^{-17} \text{ eq/sec} \\ & = 4.03 \times 10^{-9} \text{ eq/yr} \\ & = 0.248 \times 10^9 \text{ yr/eq} \end{aligned}$$

Then the time required to accumulate 9.3×10^{-2} eq K^+ in the volume element is:

$$\begin{aligned} & (0.248 \times 10^9 \text{ yr/eq})(9.3 \times 10^{-2} \text{ eq}) \\ & = 2.3 \times 10^7 \text{ yr.} \end{aligned}$$

This is an estimate of the minimum possible time for complete alteration of a 1 meter thick mass of smectite kept always below 60°C in a granite through which ground water containing K^+ at a concentration of 2.56×10^{-7} eq/l is flowing at a rate of $5 \times 10^{-8} \text{ cm}^3/\text{cm}^2\text{-sec}$. It is a highly conservative estimate. Recall that this computation assumes a hydraulic gradient of one. This is far too high. A hydraulic gradient of 0.01 is a more reasonable figure.

Performing the same computation for a hydraulic gradient of 0.01 yields an estimate of

$$2.3 \times 10^9 \text{ yr}$$

as the minimum time for complete alteration. Many variations of this approach are possible. The possible thickness of the zone of alteration after a given time, for example, might be computed from a simplified schematic, but more

elaborate models might be employed. All will demonstrate the very slow rate of permeation of the buffer material and its fundamental impermeability.

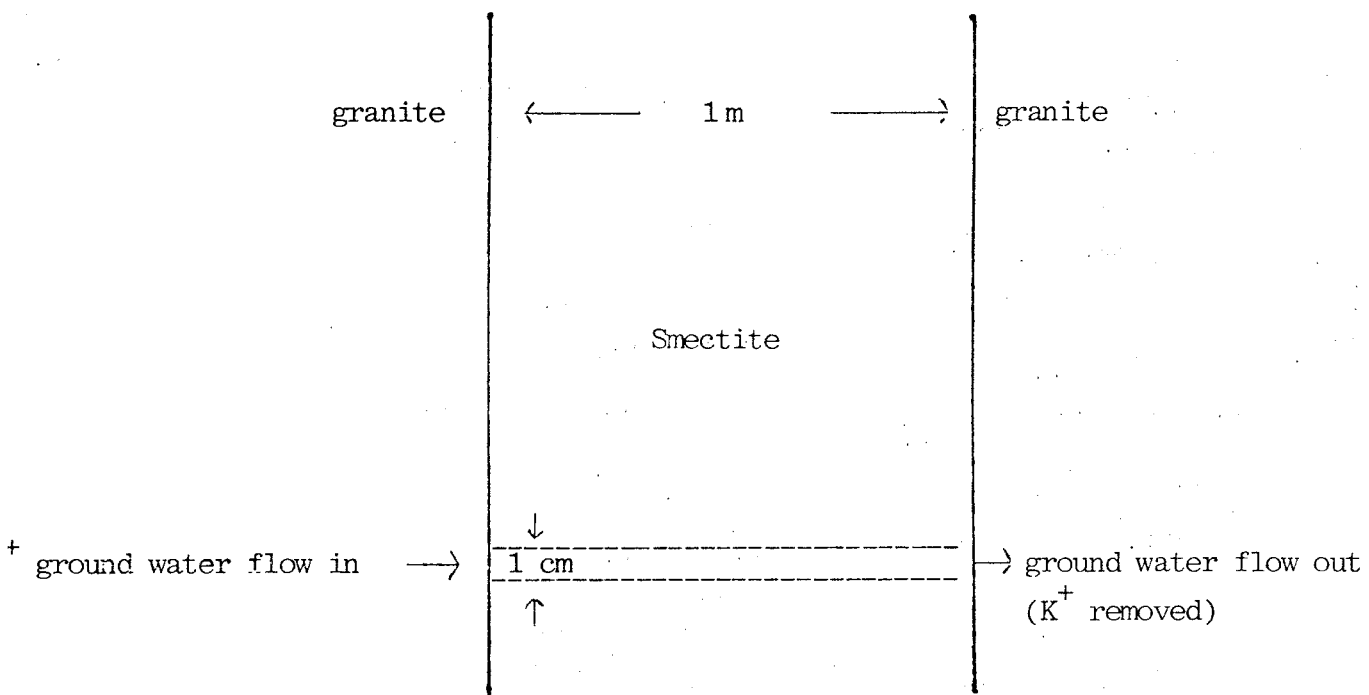


Figure 1

LIST OF KBS's TECHNICAL REPORTS

1977-78

TR 121 KBS Technical Reports 1 - 120.
Summaries. Stockholm, May 1979.

1979

TR 79-28 The KBS Annual Report 1979.
KBS Technical Reports 79-01--79-27.
Summaries. Stockholm, March 1980.

1980

TR 80-26 The KBS Annual Report 1980.
KBS Technical Reports 80-01--80-25.
Summaries. Stockholm, March 1981.

1981

TR 81-17 The KBS Annual Report 1981.
KBS Technical Reports 81-01--81-16
Summaries. Stockholm, April 1982.

1983

TR 83-01 Radionuclide transport in a single fissure
A laboratory study
Trygve E Eriksen
Department of Nuclear Chemistry
The Royal Institute of Technology
Stockholm, Sweden 1983-01-19

TR 83-02 The possible effects of alfa and beta radiolysis
on the matrix dissolution of spent nuclear fuel
I Grenthe
I Puigdomènech
J Bruno
Department of Inorganic Chemistry
Royal Institute of Technology
Stockholm, Sweden January 1983

- TR 83-03 Smectite alteration
Proceedings of a colloquium at State University of
New York at Buffalo, May 26-27, 1982
Compiled by Duwayne M Anderson
State University of New York at Buffalo
February 15, 1983
- TR 83-04 Stability of bentonite gels in crystalline rock -
Physical aspects
Roland Pusch
Division Soil Mechanics, University of Luleå
Luleå, Sweden, 1983-02-20