SKB KBS TECHNICAL REPORT 84-11

Smectite alteration

Proceedings of a Workshop Convened at The
Shoreham Hotel, Washington, D.C., December
8–9, 1993
Compiled by Duwayne M Anderson
Texas A&M University

November 1984

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A list of other reports published in this series during 1984 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), 1981 (TR 81-17), 1982 (TR 82-28) and 1983 TR 83-77) is available through SKB.

ABSTRACT

This report contains the proceedings of a second workshop in Washington DC December 8-9, 1983 on the alteration of smectites intended for use as buffer materials in the long-term containment of nuclear wastes. It includes extended summaries of all presentations and a transcript of the detailed scientific discussion.

The discussions centered on three main questions:

- What is the prerequisite for and what is the precise mechanism by which smectite clays may be altered to illite?
- What are likely sources of potassium with respect to the KBS project?
- 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?

The workshop was convened to review considerations and conclusions in connection to these questions and also to broaden the discussion to consider the use of smectite clays as buffer materials for similar applications in different geographical and geological settings.

SKBF/KBS technical report 83-03 contain the proceedings from the first workshop on these matters that was held at the State University of New York, Buffalo May 26-27, 1982.

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PREFACE

This is the second informal but detailed scientific discussion of the alteration of smectite clays as it pertains to the use of smectites as buffer materials in the long-term containment of nuclear waste materials. The first of these discussions was held at the State University of New York at Buffalo on May 26 and 27, 1982. The proceedings of this colloquium was published locally and distributed to the participants and to the Swedish Nuclear Fuel Supply Company (KBS), the sponsor of the colloquium. The proceedings of this first discussion eventually were published by the Swedish Nuclear Fuel Supply Company as SKBF/KBS technical report number 83-03.

The discussions centered on three main questions:

- What is the prerequisite for and what is the precise mechanism by which smectite clays may be altered to illite?
- What are likely sources of potassium with respect to the KBS project?
- 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 course of the colloquium, a general concensus emerged. It was agreed that the mechanism for the smectite-illite conversion probably involves three 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 concommitant 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 was thought to be 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. Both laboratory and field evidence was cited 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 was agreed, however, that the process probably begins when temperatures exceed about 60°C; but at the lower temperatures, rates of conversion are so slow, as to be almost negligible.

Under laboratory conditions a relatively pure smectite saturated with potassium ions can convert to illite in approximately 10^4 years. The temperature to which the smectite is subjected initiates the production of a high lattice charge through the exchange of silica for alumina, etc. This 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 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. Thus, it was concluded that it is the environmental temperature that is critical in determining whether or not 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 probably will be present as a result of solution of potassium-bearing feldspar, micas, and other potassium-bearing minerals in crystalline rocks. Potassium in the circulating ground water at sites selected as possible disposal sites in Sweden has been measured. 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.

Calculations based on these considerations indicate that the time required for the smectite-illite conversion under conditions existing in the bedrock at sites selected for the underground storage of nuclear wastes in Sweden exceed the 10^5 to 10^6 years regarded as necessary to insure their safe containment.

This workshop was convened to review these considerations and conclusions and to broaden the discussion to consider the use of smectite clays as buffer materials for similar applications in other geographical and geological settings.

Duwayne M. Anderson

ACKNOWLEDGEMENTS

This project was supported by a grant from the United States Department of Energy to the University of Buffalo Foundation through the Weston Corporation, Rockville, Maryland. Partial support for the European participants was provided by the Swedish Nuclear Fuel Company. The State University of New York sponsored the workshop and the manuscript was completed at Texas A&M University. Grateful thanks are expressed to June B. Anderson, conference secretary, and to Mrs. Joan Smith (SUNY, Buffalo, New York), Catherine Meyer, Ilene Gentry, Teresa Vinzant and Kay Parish (Texas A&M University, College Station, Texas) for their assistance in completing the manuscript.

WORKSHOP ON SMECTITE ALTERATION

December 8-9, 1983
Shoreham Hotel, Washington, D. C.

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AGENDA

Thursday, December 8, 1983

SESSION I

The Smectite Minerals; Formation/Alteration; Properties

Chairman: Duwayne M. Anderson

8:30 a.m.	Introduction of Participants and Adoption of Workshop Agenda	
	Repository Design Criteria (Near field conditions)	A. Bergström R. Pusch F. Karlsson
	Remarks on Smectite Alteration	R. Johnston R. Ewing
10:15	Intermission	
10:30	Remarks on Clay-Water Interaction	D. Anderson J. J. Fripiat
	Nuclear Magnetic Resonance Investigation of Bentonite	D. Eberl T. Carlsson
12:00	Lunch	

SESSION II

Alteration Mechanisms, Rates and Effects on the Physical Properties of the Clay Overpack

Chairman: James K. Mitchell

1:30	Long-Term Stability of Smectites	A. Weiss
	Thermal Effects and Effects of Adsorbed Ions on Free Swelling in Smectites	A. Banin
	Smectite-Illite Transformation Rates and Mechanisms	A. M. Brusewitz
	Diffusion-Governed Smectite-Illite Transformation	A. Altaner
3:15	Intermission	

3:30	Thermodynamic Aspects of Smectite Alteration	B. Fritz
	Smectite Alteration Scenarios from Stochiometric and Geological Points of View	A. Gustafsson
4:45	Adjourn	
5:15-7:15	Reception -- CLUB ROOM B	

Friday, December 9, 1983

SESSION II (Continued)

8:30 a.m.	Physical, Chemical and Rheological Properties of Smectites and Alteration Products	J. K. Mitchell
	General Discussion	
10:15	Intermission	
10:30	Practical Consequences of Heating and Heat-Associated Alteration of Bentonite	R. Pusch
	General Discussion	
12:00	LUNCH	

SESSION III

Summary and Conclusions; Recommendations
Chairman: Neil Chapman

1:30	The Use of Clay as Overpack	N. Chapman
	General Discussion	
3:15	Intermission	
3:30	General Aspects of Clay-Based Overpacks	M. Wood
	General Discussion	
4:30	Adjourn	

Summary

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Zoned K-bentonites: Evidence for the Effect of Solution Chemistry on the Smectite to Illite Reaction

Smectite bentonite has been suggested as a buffer material surrounding canisters containing nuclear waste. An effective buffer material should have the following properties: low permeability and diffusivity for aqueous chemical species and water, long-term stability for the hydro-thermal and radioactive conditions present at the site, high thermal conductivity and sufficient strength to support the canister. I will address the first two properties (diffusivity and long-term stability) in this report.

Smectite bentonite has a low permeability and diffusivity because of its swelling ability and plasticity (1). Smectite bentonites in rocks which have experienced a low grade metamorphic event (T = 100-250°C) react to form an illite-rich (K-) bentonite, (2,3) where a generalized form of the reaction may be written in the following manner:

$$K^{+} + Al^{+3} + \text{Na-Smectite} \rightleftarrows \text{Illite} + Si^{+4} + NA^{+} + H_{2}0$$

The reaction to form illite has been observed to pass through a mixed-layered clay series (Illite/Smectite or I/S) where the proportion of illite layers in Illite/Smectite is a measure of reaction extent.

Formation of illite from smectite involves the increase in the negative layer charge on the silicate structure (Al^{+3} substitution for Si^{+4}), fixation of K^{+} and expulsion of the interlayer cation (here written as Na^{+}) and interlayer water. Since most smectite bentonites contain very little potassium stored in phenocrysts, such as sanidine and biotite, potassium for illite formation must be externally derived. Illite has a much lower cation exchange capacity than smectite and does not swell, therefore, the formation of illite in a bentonite would tend to increase porosity and degrade the integrity of the backfill material. Workers have noticed that illite forms with increased reaction temperature and time (4.5). The present study investigates a field example in which the smectite to illite reaction in a bentonite is controlled by the availability of potassium.

Thirty-five K-bentonites and the enclosing black shale from the Late Cretaceous Marias River Formation in the disturbed belt of Montana were studied mineralogically to delineate clay mineralogical reactions in K-bentonites enclosed by shale. The bentonites were metamorphosed to temperatures between 100° and 200°C (2) caused by burial under thick thrust slabs during the Laramide Orogency.

A 2.5 m K-bentonite was found to be zoned mineralogically and chemically, relatively illite-rich (K-rich) near the contacts with the shale and more smectite-rich (K-poor) in the middle of the bed. The I/S near the contacts of the shale is of the same composition (given in % illite layers) as I/S in the shale and most other thinner bentonites in the area. This composition is interpreted as representing maximum reaction extent (illite formation) for the metamorphic conditions these rocks have experienced. The middle of the bentonite is more smectite-rich because of the deficient supply of potassium, which is interpreted as being derived from mineral breakdown in the enclosing shale. K/Ar ages of the I/S from the 2.5 m bed (50-55 m.y.) are 30 m.y. younger than the age of deposition for the bentonite, indicating the general time that maximum temperatures were achieved in the strata during the Laramide Orogeny. In addition, I/S from the middle of the 2.5 m bentonite is about 3 m.y. younger than I/S near the contact of the shale. This age difference reflects the slow rate of potassium transport into the bentonite and gives a measure of minimum reaction time to form illite in the bentonite. The 3 m.y. age difference also indicates diffusion, rather than advection, is the dominant transport process.

Using the K_2O and K/Ar age zonations across the bentonite, we can calculate a diffusion coefficient for potassium in a deeply buried bentonite. The equations model diffusion in aqueous solution with a constant potassium concentration outside the bentonite and a build-up of potassium in the bentonite caused by the reaction to form illite. The following equations were solved:

$$\frac{\partial C_s}{\partial t} = D\,\frac{\partial^2 C_s}{\partial x^2} - \frac{\rho_b(1-\phi)}{\rho_s\,\phi}\ \text{[Chemical Reaction Term]}$$

where

C_s = concentration of potassium in solution
D = diffusion coefficient for potassium
ρ_b = density of the bentonite
ρ_s = density of the solution
ϕ = porosity

$$\text{Chemical Reaction Term} = -\frac{\partial C_b^{\,sm}}{\partial t} = K(C_b^{\,sm})^a\ (C_s^{\,k}/C_o^{\,k})^b$$

where

C_b^{sm} = fraction of smectite in I/S in the bentonite
K = rate constant for the smectite to illite reaction
C_s^k/C_o^k = potassium concentration in solution within the bentonite divided by a constant potassium concentration present outside the bentonite (in the shale)
$a + b$ = constants which added together equal the reaction order

The second equation can just as easily be represented in terms of potassium concentration. Probably the best study to date on the kinetics of the smectite to illite transition is from work on dike-intruded shale (6). Pytte's kinetic parameters were used and diffusion coefficients of around $10^{-7} - 10^{-8}$ cm^2/s with reaction temperatures of around 100°C were calculated. These D values are in agreement with published results on diffusion of Sr^{+2} and Cs^+ through compacted bentonite (7) and diffusion through the layer of water immediately surrounding smectite particles (8). A simple calculation of this kind was made to model diffusion of potassium and reaction to form illite in a repository surrounded by Na-bentonite. For reaction temperatures of 100°C and a reaction time of 1 million years and a solution chemistry in which the combined molalities of Na, Mg and Ca are one hundred times greater than K, then insignificant amounts of illite will form (<10%). If the molality ratios of (Na + Mg + Ca)/K are significantly less than 100, then much greater amounts of illite may form.

REFERENCES

1. Bryant, W. R., Thompson, L. and Chiou, 1981, Permeability and microfabric of clayey sediments: Gulf Coast Assoc. Geol. Soc., v. 31, p. 238.

2. Hoffman, J. and Hower, J., 1979, Clay mineral assemblages as low grade metamorphic geothermometers: Applications to the thrust faulted disturbed belt of Montana, U.S.A.: SEPM Spec. Pub. 26, p. 55-79.

3. Velde, B. and Brusewitz, A. M., 1982, Metasomatic and non-metasomatic low-grade metamorphism of Ordovician meta-bentonites in Sweden: Geochim. et Cosmochim. Acta, v. 46, p. 447-452.

4. Hower, J., Eslinger, E. V., Hower, M. and Perry, E. A., 1976, Mechanism of burial metamorphism of argillaceous sediments: I. Mineralogical and chemical evidence: Geol. Soc. Am. Bull., v. 87, p. 725-737.

5. McCubbin, D. G. and Patton, J. W., 1981, Burial diagenesis of illite/smectite: The kinetic model: Ann. Mtg. Am. Assoc. Pet. Geol., San Francisco.

6. Pytte, A. M., 1982, The kinetics of the smectite to illite reaction in contact metamorphic shales: [M.S. thesis], Dartmouth College, 78 pp.

7. Eriksen, T. E. and Jacobsson, A., 1982, Ion diffusion in compacted sodium and calcium bentonites: KBS Technical Report TR81-12.

8. Fripiat, J. J., 1980, The application of NMR to the study of clay minerals, in: Advanced Chemical Methods for Soil and Clay Minerals Research, J. W. Stucki and W. L. Banwart, eds., Proc. of the NATO Advanced Study Institute, p. 245-315.

Summary

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The Implications of Alpha Radiation Damage For Bentonites Utilized In High-level Nuclear Waste Disposal

INTRODUCTION

The efforts in the United States to construct and operate a high-level nuclear waste disposal repository in deep geologic formations have been in accordance with the provisions of the Nuclear Waste Policy Act of 1982[1]. The ultimate goal of these efforts is to isolate high-level nuclear waste from the human environment. The geologic formation and the surrounding rocks chosen for the repository will be the principal barrier to the escape of radioactive material. In addition, several engineered barriers will complement the isolation characteristics of the host rock. These include the waste form, waste canister, overpack, and backfill material around the canister and in tunnels. Several requirements have been specified for the engineered barrier system by the Nuclear Regulatory Commission. Specifically, the waste canister must last between 300 to 1,000 years, and the engineered barrier system must not release more than 1 part in 100,000 per year of the radionuclide inventory present at 1,000 years.

The backfill material around the canisters and in the tunnels above the canister will ideally perform a multitude of functions which includes acting as:

- a barrier to limit water movement to diffusion type flow;
- a strong sorptive medium for radionuclides;
- a mechanical support and buffer for the canisters; and
- a chemical buffer for ingressing ground water to decrease the corrosion rate of the overpack and canister material.

The most common materials suggested for use as backfill material are crushed host rock[3], bentonite mixed with crushed host rock[4], or other minerals[5], or alone as compressed blocks[6]. Bentonite appears to be ideal for this application since it has a large swelling capacity when exposed to water and also sorbs many radionuclides very strongly due to its high cation exchange capacity.

There are, however, conditions in a repository, including elevated temperature and radiation field, that could adversely affect the bentonites' performance. A great deal of study has been conducted on thermal and chemical effects on bentonites. Under postulated repository conditions, bentonites appear to remain stable. However, the same is not true of all radiation effects. While there has been a reasonable amount of work on the effect of gamma-radiation on bentonites that indicate little effect, alpha-radiation appears to have a strong effect on bentonites. A study[7] of ^{253}Es sorbed onto three clay minerals (montmorillonite, kaolinite, and attapulgite) shows that total structural destruction of the clays within a few days can occur. The same results have been obtained on several other materials where the actinide is incorporated into the matrix of the compound[2]. As illustrated in Table 1, the rate of destruction of the minerals appeared to correlate well with the cation exchange capacity. That is, montmorillonite (CEC = 100 meq/100g) was destroyed in less than a day, attapulgite (CEC = 33 meq/100g) took 2 to 3 days, and kaolinite (CEC = 10 meq/100g) was destroyed in 4 days. It was observed that although the structure of the clays was destroyed from the alpha radiation damage, the remaining amorphous material resulting retained its sorptive characteristics for the ^{253}Es. The study of alpha radiation on clays, however, did not examine the implications the radiation damage has for the physical behavior of bentonite as a water barrier and mechanical buffer for the canister.

OBSERVATIONS

Alpha radiation damage effects have been observed the earlier[7]. Radiation damage at low loading was observed over several weeks, characteristically causing holes to appear in the sides of the clay fibers with an increase in amorphous material. The structural damage of the clays was confirmed by x-ray and electron diffraction. The total alpha doses in each clay case are given in Table 1. As expected, the time for total destruction of the structure correlates reasonably well with the total cation exchange capacity. Based upon this limited data, it would appear that an alpha dose in the range of 4×10^{18} alphas/gm of clay is required to destroy the clays completely. The dose received by montmorillonite is an upper limit since total destruction had occurred at one day.

In a high-level nuclear waste repository, the alpha-emitting radionuclides must breach the canister before they can have any effect on the backfill. At this point, one must postulate a scenario by which the radionuclides can escape from the canister and into the backfill. The scenario chosen for this paper is one in which pit corrosion has breached the canister and that radionuclides are released to the backfill at a rate of 10^{-5} of the inventory of each radionuclide. This breach is postulated to occur 1,000 years after emplacement of the waste. This scenario is consistent with the NRC regulation[2], but admittedly conserative.

The major waste forms currently under condsideration are spent fuel rods and borosilicate glass. In this paper, I will deal with spent fuel. It must be noted, however, that borosilicate glass could contain a higher waste loading than spent fuel.

The major alpha-emitting radionuclides that contribute substantially to the alpha dose at 1000 years are ^{239,240}Pu, and ^{241,243}Am. The inventory of each of these radionuclides at 1000 years can be seen in Table 2. As can be seen in the Table, the total dose per year by releasing 10^{-5} of the inventory of these radionuclides would be 1.8×10^{16} alpha/year. This is approximately 200 times less than the amount of radiation that caused total structural destruction of the clays previously studied.

TABLE 1

Alpha-Radiation Dose for Montmorillonite, Attapulgite, and Kaolinite Loaded to Their Total Cation Exchange Capacity with ^{253}Es.

Clay	C.E.C. Meq/100g	Days to Destroy Structure	Alpha Doses/gm. of Clay
Montmorillonite	100	<1	$<7\times10^{18}$
Attapulgite	30	2	4×10^{18}
Kaolinite	10	4	3×10^{18}

TABLE 2

Inventory of Major Alpha Emitting Isotopic in 1 MTHM at 1000 Years*

Radionuclide	'Ci'	alphas /sec. Produced	alphas /yr. x 10^{-5}
239 Pu	280	1.0×10^{13}	3.3×10^{15}
240 Pu	410	1.5×10^{13}	4.8×10^{15}
241 Am	830	3.1×10^{13}	9.7×10^{15}
243 Am	13	4.8×10^{11}	1.5×10^{14}
		Total Dose of /year	1.8×10^{16}

* Draft EIS. "Management of Commercially Generated Radioactive Waste" DOE/EIS-0046-D Vob 2 April 1979.

For simplicity's sake, we assumed that the migration of the radionuclides away from the breached canister takes the form of a cone, with height of 15 cm and base of 7.5 cm. This would give us a total mass of approximately 88 gm of clay assuming a bulk density of 2.0 gm per c.c. with a mixture of 80% quartz and 20% bentonite.[6]

The dose required to totally destroy the 88 gm of clay in the conical volume will be 3.5 x 10^{20} alphas. If we sum on a yearly basis the dose of 1.8 x 10^{16}, alphas coming from the waste form in the following way:

$$D = Dy\overset{n}{\underset{i\,=\,1}{E}}$$

where D = total alpha dose, and Dy = 1.8 x 10^{16}, and i = years

solving this equation for the number of years required to reach a dose of 3.5 x 10^{20} alphas indicates that the dose can be reached in approximately 197 years. This could result in a total breach of the backfill with loss of both the water barrier and structural support in small areas provided by the clay.

For ease of presentation, these calculations are obviously very simplistic and very dependent upon the assumptions. However, several factors that could exacerbate the situation have been ignored. It is well known that reaction rates increase rapidly with increase in temperature, and that bentonites are destabilized by the presence of amorphous silica and sorption of high charge ions. It may also be possible to exceed the 10^{-5} release rates assumed in this presentation. In addition, the assumption that the bentonite retains its rheological properties up until it is totally destroyed is also quite conservative. The effects of corrosion products from the canister have been ignored in this presentation. They could act as strong sorbants for the radionuclides; however, it is not clear whether this sorption would retard or promote radionuclide migration.

CONCLUSIONS

This is a very preliminary look at the possible implication of alpha-radiation damage of clay minerals proposed for high-level nuclear waste disposal. However, the general conclusions that can be drawn are:

- After breach of a canister and overpack occurs, alpha-radiation can potentially have a significant effect on clays in backfill materials.
- The possible loss or rheological properties of the backfill in localized areas may occur in periods less than 200 years after the breach of a canister. This is approximately the same time required for diffusion of radionuclides through the backfill;

however, this destruction will result in preferential water pathways through the backfill that may be much faster.

- If the backfill must be relied upon to meet the NRC 10^{-5} release rate criterion for the waste package, the prospect of alpha-radiation damage could make the demonstrations of the compliance difficult.

- If breach of a canister occurs at 300 years, the effect of alpha-radiation could be a factor of 3 greater due to higher inventories.

- The effect could be substantially greater for a borosilicate glass waste form than for spent fuel due to the higher waste loading.

It is important to recognize that these preliminary results need experimental work to better quantify them.

REFERENCES

1. Nuclear Waste Policy Act of 1982, Public Law 97-425.

2. U.S. Nuclear Regulatory Commission, Code of Federal Regulations, Title 10, Part 60, Federal Register, vol. 46, No. 130, July 8, 1981.

3. Kelshall, P. C., Case, J. B., Nelson, J. W., Rod Franzone, J. G. "Assessment of Crushed Salt Consolidation and Fracture Helaing in a Nuclear Waste Repository in Salt" Proceeding's of Waste Management 84, Tucson, AZ (1984).

4. Smith, M. J., Anttona, G. J., Barney, S. S., Coons, W. E., Hodges, F. N., Johnston, R. G., Kaser, J. D., Marabe, R. M., McCarol, S. C., Moore, E. L. Nooman, A. E., O'Rourke, J. E., Schultz, W. W., Taylor, C. L., Wood, B. J., and Wood, M. I. 1988, Engineered Barrier Development for Nuclear Waste Repository Located in Basalt: An Intergration of Current Knowledge, RHO-BWI-ST-7, Rockwell Hanford Operations, Richland, Washington.

5. Beall, G. W. and Allard, B. M. "Backfill Composition for Secondary Barriers in Nuclear Waste Repositories." U.S. Patent #4,321,158, March 23, 1982.

6. Pusch, R. 1979, "Highly Compacted Sodium Bentonite for Isolating Rock-Deposited Radioactive Waste Products", Nuclear Technology, Vol. 45, pp 153-157.

7. Haire, R. G., and Beall, G. W. "Consequences of Radiation from Sorbed Transplutonium Elements on Clays Selected for Waste Isolation" ACS Symposium Series No. 100 Ed Sherman Fried, 1979.

8. Haire, R. G., Lloyd, M. H., Milligan, W. O., and Beasley, M. L., J. Ignor, Nucl. Chem., 39, 843, 1977.

SUMMARY

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Design of a Repository for Spent Nuclear Fuel from the Aspect of Temperature

The Swedish concept for the deposition of spent nuclear fuel implies that copper canisters containing the spent nuclear fuel bundles be surrounded by highly compacted bentonite in deposition holes in about 500 m depth in hard rock somewhere in Sweden (Figure 1).

The diameter of a deposition hole may be 1.5 m, about twice the diameter of a canister. The space between canister and rock is filled with bentonite. The highly compacted bentonite surrounds the canister and the water in the rock will successively be taken up by the bentonite forming ultimately a homogeneous dense clay barrier without any gaps. It will have a very low hydraulic conductivity and a potential swelling ability to seal cracks. The 10 cm thick copper canister, alternatively lead-filled or made solid by hot isostatic pressing technique, will form a barrier between the spent fuel and the bentonite thus preventing the radionuclides to be leached. The service life of a canister may be very long, several millions of years considering the thick copper and the limited amount of oxidants which can diffuse through the bentonite from the groundwater.

The spent fuel produces heat which decays with time. One canister may contain waste corresponding to about 1kW at the deposition. The temperature will first rise and then decrease. The maximum temperature depends on the thermal properties of clay, rock and the interaction of the heat flow from other deposition holes. The site dependent geological conditions will influence the design of a repository but in principle the repository can be constructed by sinking shafts and excavating tunnels from which the deposition holes are drilled. The tunnels may be arranged in parallel arrays at one or two levels where the geological conditions are suitable.

In a repository with one level of tunnels 25 m apart and with deposition holes every 6 m, temperature will rise about 65°C from initially about 15°C in 500 m depth which means that the maximum temperature will be about 80°C (Figure 2). With two storeys and the initial temperature 20°C in the lower level, the maximum temperature will be about 80°C if the tunnels are separated by 33 m and the two storeys by 100 m (Figure 3).

These examples indicate that it is possible to moderate the temperatures in the repository design.

However, it is of profound interest for cost reasons to find out whether higher temperatures of the bentonite are acceptable.

If so, the separation between deposition holes can be smaller, or alternatively more waste can be contained in the canister. These modifications will raise the maximum temperature. For future optimization we need to know if higher temperatures in the clay are acceptable without loss of the required properties of the buffer material.

One such property is the long term chemical stability of the smectite minerals, this matter being the subject of this conference.

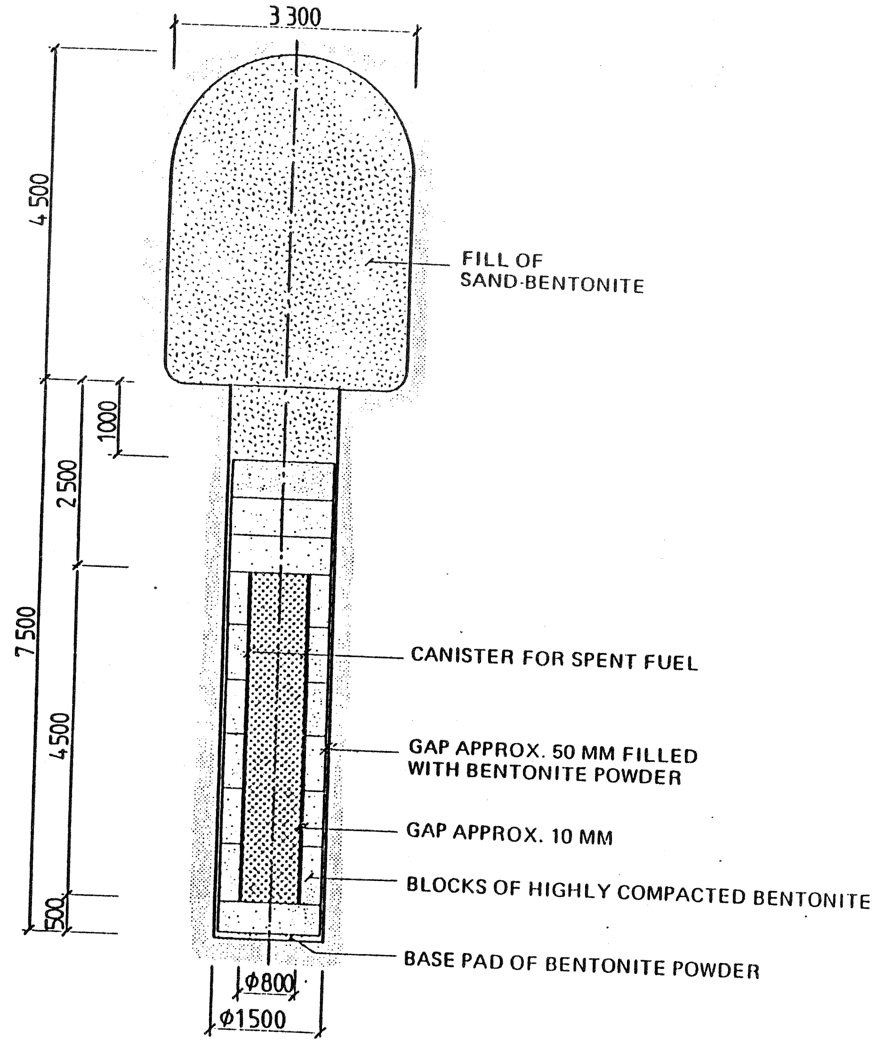

Figure 1.. Deposition hole with canister and buffer material and with backfill in storage tunnel.

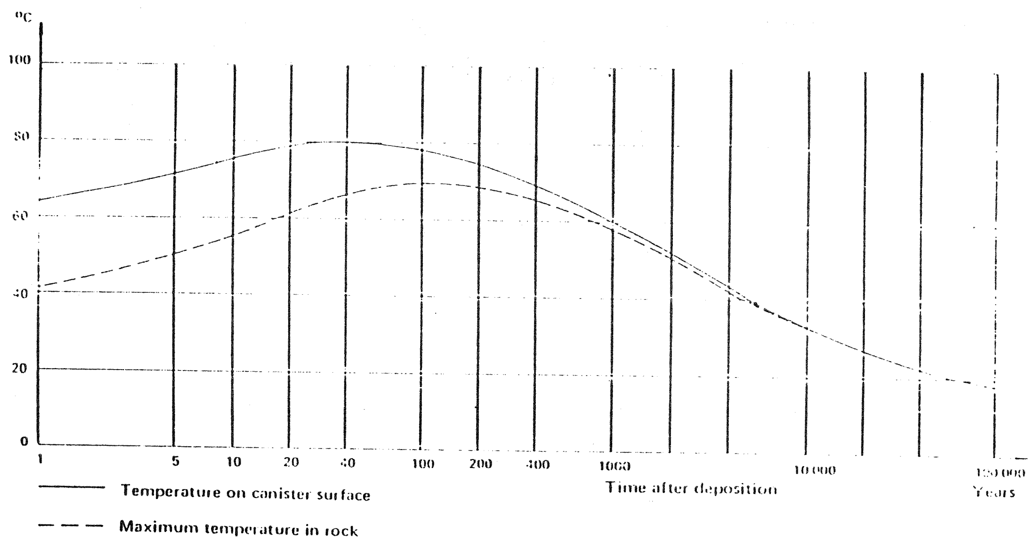

Figure 2. The temperature in the centre of a single-storey final repository.

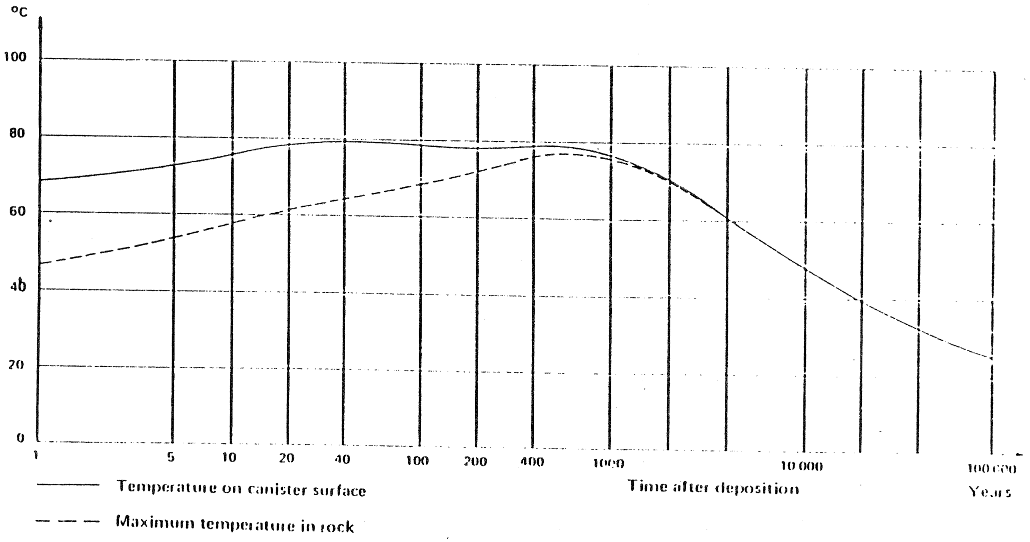

Figure 3. The temperature in the centre of a two-storey final repository.

SUMMARY

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Illite Smectite Minerals in Ordovician Bentonites in Sweden

There are several bentonite occurrences in Sweden, originating from Ordovician volcanic ashfalls. The smectite minerals initially formed from the volcanic glass, later altered to illite/smectite (I/S) minerals, with a large span of I/S proportions and of stacking order. Thus, these bentonites are very suited to the study of long term alteration.

The data presented here have been collected over many years from bentonite layers in Kinnekulle and Billingen, southwest Sweden (1,2,3). The two localities are only 30 km apart, but their geologic history has been different, manifested for instance in the degree of alteration of the smectite. The bentonites occur in flat-lying sediments, present because of intrusion of diabase, which now forms caps covering the sediments. There are several bentonite beds of varying thickness. The most interesting bed is nearly 2 m thick and is found both at Kinnekulle and at Billingen. At Kinnekulle this bed is separated from the diabase by 90 m of shales and subordinate limestone. At Billingen the corresponding distance is only 35-40 m.

The diabase intrusion occurred in Permo-Carboniferous time. At Billingen it has been dated to 290±15 Ma by the K/Ar method and by paleomagentic measurements (4). K/Ar analysis of the I/S mineral (<1 µm fraction) of the Billingen samples, all show ages 280-290 Ma, which is interpreted as a resetting of the "K/Ar clock" at the time of the diabase intrusion. Whole rock samples give a similar age.

The I/S minerals in samples at a distance of 36 m to the diabase are strongly illitic, with only 12-15% smectite layers. In another borehole, where the distance is 42 m, the smectite content is slightly higher, 15-20%. The ordering of layers is of the Kalkberg type (IIIS). The reaction temperature may have been around 300°C. Feldspar must have contributed some of the potassium, as there is no sign of the presence of this mineral, in contrast to Kinnekulle, where sanidine has been found. The supply of potassium appears to be deficient because some of the smectite has reacted to form chlorite. This "authigenic" chlorite is richer in aluminium than that derived from the biotite phenocrysts. An indication that all potassium present in the I/S mineral is that "whole rock" samples give the same age as the clay fraction.

At Kinnekulle the temperature in the strata never reached as high as at Billingen. The smectite to illite alteration stopped at a much earlier stage. Samples from the middle of the thick bed contained about 60% smectite layers with random ordering of layers. The proportion of smectite diminishes moving towards the upper boundary to about 35%, and the stacking begins to be ordered. Towards the lower contact, the smectite proportion is nearly constant at 50-55% and ordering is random. Whole rock K_2O content in the top 5 cm is 4%, decreasing to 2.5% in the middle of the bed. In contrast to Billingen, the thick bed at Kinnekulle contains sanidine phenocrysts. These are around 450 Ma.

The structure formulae of the I/S minerals might give an impression that the smectite is of beidellite type. However, a plot of tetrahedral Si versus interlayer K gives a straight line pointing to Si = 3.95, when K goes to zero, an indication that the smectite originally has been a montmorillonite.

The K/Ar ages of the thick bed at Kinnekulle range from 336 Ma at the top of the bed, gradually decreasing to 300 Ma at the middle of the bed. There is as yet no determination from the lower part. It is not quite clear how the difference of 36 Ma between the top and the middle should be interpreted. Altaner (5) from a similar study of Montana bentonites, has found the illite alteration to have a time span of only 3-4 Ma. Differences in reaction temperature, potassium activity, and in the host rock may be an explanation. Considering the Kinnekulle ages to be true ages, the illite reaction must have started at a period well before the diabase intrusion, which at Kinnekulle has not been strong enough to reset the K/Ar clock. Maximum temperatures reached in the strata probably were less than 150°C. Because the percentage of illite layers in I/S do not increase towards the lower boundary may depend on an impervious layer of silica formed during initial alteration of the volcanic glass to smectite.

From the study at this stage, it can be concluded that the temperature and potassium availability are the most important factors governing the alteration of smectite. Attaining the required temperature and if potassium is available, illite will form, if not chlorite may form.

REFERENCES

1. Byström, A. M. (1956) "Mineralogy of the Ordovician bentonite beds at Kinnekulle, Sweden" SGU, Ser. C 540, 62 pp.

2. Byström, A. M. (1957) "The clay minerals in the Ordovician beds in Billingen, southwest Sweden" Geol. Fören. Stockholm Förh. Bd 79, 52-56.

3. Vele, B., and Brusewitz, A. M. (1982) "Metasomatic and non-metasomatic low grade metamorphism of Ordovician meta-bentonites in Sweden" Geochim. et Cosmochim. Acta, 46, 447-452.

4. Priem et al. (1968) "Geochronological and paleomagentic reconnaissance survey in parts of central and southern Sweden," Phys. Earth Planet. Interiors 1, 373-380.

5. Altaner, S. P., Hower J., Whitney, G. and Aronson, J. L., 1984, Model for K-bentonite formation: Evidence from zoned K-bentonites in the disturbed belt, Montana: Geology., v. 12, p. 412-415.

Summary

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NMR-Studies on MX-80/electrolyte/water

Using nuclear magnetic resonance technique (NMR), the water mobility in water saturated MX-80 bentonite can be measured as a function of temperature, water content and electrolyte content. The water mobility in the investigated MX-80 systems can be expressed by means of the observed proton T_2-relaxation time. The results indicate, that the water mobility 1) decreases with increasing electrolyte concentration and 2) increases with increasing temperature and/or increasing water content. It is also found, that the water mobility is strongly dependent on the type of dissolved electrolyte present in the system. Thus, the presence of dissolved $CaCl_2$ or $SrCl_2$ in the investigated MX-80 systems correspond to a lower water mobility than the presence of the same amount of dissolved NaCl or KCl, other things being equal. The electrolyte effect upon the water mobility is considered to emanate mainly from the cations. Therefore, only one type of anions has been added to the systems; Cl^-. The influence of electrolyte upon the water mobility in the investigated MX-80 systems is indicated by the series

$$SrCl_2 \approx CaCl_2 < KCl < NaCl < H_2O$$

Where H_2O represents a water saturated system obtained by mixing MX-80 bentonite with distilled water.

Current studies deal with water mobility in systems consisting of water, electrolyte and MX-80 bentonite. The latter is the KBS reference bentonite which can be used as a barrier for isolation of toxic chemical wastes. Such barriers must have specified properties with respect to:

- the chemical stability
- the physical behavior in terms of the relations between stress, strain, time and temperature
- ion diffusivity and permeability.
- type of electrolyte added to the system: NaCl, KCl, $CaCl_2$ or $SrCl_2$.

MX-80 Bentonite

The bentonite used consists of the main KBS reference material: commercially available Na-bentonite, type MX-80 (trade name) from the American Colloid Company. It should be pointed out that MX-80 is not one chemical compound but a physical mixture of several compounds. The minus 2 µm fraction of the bentonite is about 85%. Approximately 75% of this fraction consists of Wyoming montmorillonite. The remaining content is mainly silt where quartz and feldspars dominate and micas, sulphides and oxides are present as minor constituents. Tables 1-3 describe the mineralogical and chemical composition of MX-80 according to Müller-Vonmoos and Kahr (1). As is shown, MX-80 contains a rather high amount of iron. This is a problem when MX-80 is studied by means of NMR technique, since the paramagnetic properties of the iron content strongly influences the result (see later section).

MX-80 is not a pure Na-clay. Besides Na^+ there are also Ca^{2+} and Mg^{2+} present as exchangeable cations in the bentonite (cf. Table 3). The chemical formula of the montmorillonite is (1)

$$(Si_{3.96}Al_{0.04})\ (Al_{1.55}Fe^{3+}_{0.20}Fe^{2+}_{0.01}Mg_{0.24})O_{10}\ (OH)_2 \quad M^+_{0.29}$$

where M^+ represents the amount of exchangeable cations[1].

Liquid Water in the System MX-80/Electrolyte/Water

The nature of liquid water near interfaces is poorly understood. However, it is well-known that liquid water in the vicinity of a solid surface is structurally modified. This has been shown in studies of various properties - viscosity, heat capacity, density etc. - of water at solid interfaces. In general, water at internal and external surfaces of montmorillonite is described as having an "ice-like" structure. This presupposes the surfaces being covered with at least two monolayers of water. In this context, "ice-like structure" is a dynamic concept which refers to time scales that are short in comparison to the time needed for motions of water molecules. Thus, in NMR-studies of e.g. montmorillonite/water systems with no paramagnetic impurities, the observed proton T_2-relaxation time associated with water influenced by the montmorillonite particle surfaces is intermediate to the T_2- values corresponding to ice and pure liquid water, respectively. This indicates 1) that the water mobility in the vicinity of montmorillonite particles is lower than in bulk water and 2) that the structure of vicinal water is intermediate to the structures of ice and water.

For a review of published papers concerning the nature of water in the vicinity of montmorillonite surfaces, the reader is referred to a comprehensive paper by Sposito and Prost (2).

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1) The original formula found in Ref. (1) contains $M^+_{0.30}$ instead of $M^+_{0.29}$. However, $M^+_{0.29}$ is necessary in order to obtain an exact balance between positive and negative charges.

Table 1. Mineralogical composition of MX-80 bentonite according to Müller-Vonmoos and Kahr (1).

Mineral	MX-80 %
Montmorillonite	75
Quartz	15.2
Glimmer	< 1
Feldspar	5-8
Carbonate	1.4
Kaolinite	< 1
Pyrite (FeS_2)	0.3
Other minerals	2
Organic carbon	0.4

Table 2. Chemical analysis of the fraction 0.2 µm and potassium content in the unfractionated MX-80 bentonite (1).

	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	FeO %	MgO %	CaO %	Na_2O %	K_2O %	MnO %	TiO_2 %
<0,2µm	59,82	19,58	3,61	0,14	2,40	1,85	0,03	0,10	0,002	Trace
	60,69	19,63	3,88	0,12	2,35	1,81	0,02	0,09	Trace	Trace
Ø	60,25	19,61	3,75	0,13	2,38	1,83	0,03	0,10	0,001	Trace
Ø								0,60		

Table 3. Cation exchange capacity (CEC) and exchangeable cations in MX-80 bentonite (1).

CEC (meq/100 g)	Exchangeable cations								
	Na		K		Mg		Ca		Sum
	meq/100g	%	meq/100g	%	meq/100g	%	meq/100g	%	meq/100 g
76.4	62,4	85,5	0,2	0,3	3,0	4,1	7,4	10,1	73,0

In this report, the interest is focused on the mobility of water in water saturated MX-80/electrolyte/water systems. The water in these systems is chemically influenced mainly by 1) internal and 2) external montmorillonite surfaces and 3) cations. The MX-80 system is characterized by a considerable interaction between the clay mineral and the cations which governs the unit layer separation and the appearance of the diffuse double layers. In the investigated MX-80 systems, the water mobility was studied as a function of temperature (t), water content (w), and electrolyte content (c). The variables were changed within the following limits:

1) w (%) : (90 , 170)

2) t (^{0}C) : (+15, +80)

3) c (moles / litre) : (0 , 0.35)

The concentration values refer to the water solution used in the sample preparation. The total amount of dissolved ions in the MX-80 systems is higher than is indicated by the value of c, since this amount is the sum of 1) the ion content in the solution added to MX-80 and 2) the amount of exchangeable cations present in the MX-80 bentonite. Thus, the concentration c_i of a dissolved ion "i" in a MX-80/electrolyte/water system is:

$$c_i = \frac{n_i}{w} \cdot 1000 + C \qquad (1)$$

Where n_i = the number of moles of ion "i" /100 g MX-80

c = the concentration of ion "i" in the electrolyte solution added to MX-80 (moles/litre)

w = water content (%) = 100 (mass of water)/(mass of MX-80)

However, except for Na^+ which is associated with a high value of n_i (cf. Table 3), it is considered that c_i = c in all cases.

Sample Preparation

Water saturated samples of MX-80/electrolyte/water were made by mixing untreated MX-80 bentonite (i.e. MX-80 of commerical quality) with distilled water or an electrolyte solution. The latter consisted of distilled water containing c moles of electrolyte/litre. Only solutions containing one of the following electrolytes were used; NaCl, KCl, $CaCl_2$ and $SrCl_2$. At water-saturated sample densities below 1.5g/cm^3 the samples were made by mixing the constituents by hand. At higher densities the samples were made by means of an hydraulic press. In this case, samples with high water contents were inserted into a steel cylinder and compressed to volumes corresponding to the desired density. The drainage of supernatant liquid was performed by means of a filter which did not let through the MX-80 bentonite.

Experimental

The determination of the water mobility in the MX-80 systems was performed by means of NMR-technique (NMR = nuclear magnetic resonance). Since it is beyond the scope of this paper to discuss the basic theories concerning the application of NMR to the study of clay minerals the reader is referred to a recent work by Fripiat (3). In a short and somewhat over-simplified way the measurement of the water mobility was carried out in the following way. A glass tube containing a small amount (< 1 cm^3) of a water saturated MX-80 sample was placed in a magnetic field within a NMR-spectrometer. As a result of the influence from the magnetic field, the hydrogen protons in the sample becomes distributed on two different energy levels. At equilibrium this distribution is given by the Boltzmann equation

$$\frac{N_\alpha}{N_\beta} = \exp(-\Delta E/kT) \qquad (2)$$

where N_α = the number of protons on the lower energy level, E_α

N_β = the number of protons on the upper energy level, E_β

ΔE = $E_\alpha - E_\beta$

k = Boltzmann's constant

T = absolute temperature

The equilibrium distribution can be disturbed by sending a short radio frequency signal with a suitable frequency against the sample. After the pulse the protons tend to obtain the original equilibrium population distribution between the two energy levels. In short, the higher the mobility of the water, the longer is the time needed in order for the system to obtain equilibrium. Since this time is directly proportional to the proton T_2-relaxation time, the value of T_2 may be used as a measure of the water mobility; thus, an increase in T_2 is associated with a corresponding increase in the water mobility. In principle, the above reasoning is correct, at least when only one type of water is present in the clay/water system.

The measurements were performed by means of a Bruker CXP-100 NMR-spectrometer operating at 90 MHz. Several measurements were carried out by means of the Hahn's spin-echo technique in order to distinguish between different water phases in the MX-80 systems (e.g. "free" and "bound" water). However, the results indicate that only one water phase is present in water saturated MX-80 systems with high densities. All proton T_2-relaxation times Presented here were measured by means of the line width at half peak height in the adsorption spectrum.

MX-80 bentonite contains a rather high amount of paramagnetic Fe^{3+} -ions (cf. the chemical formula of the montmorillonite content and Table 2). Therefore, the observed T_2-values are considerably smaller as compared to, if no paramagnetic impurities were present in the samples. No T_2-values presented in this report have been corrected for the paramagnetic effects. However, as long as only relative T_2-values in one type of system is discussed, such corrections are not needed.

Results and Discussion

The present NMR-study is carried out in order to investigate how the water mobility in water saturated MX-80/electrolyte/water systems depends on 1) temperature, 2) water content, 3) type and 4) concentration of the dissolved electrolyte present in the system. Since the negatively charged clay mineral particles mainly interact with cations and only to a negligible extent with anions, all electrolytes added to the systems contained the same type of anion. In this study, the following electrolytes were used: $NaCl$, KCl, $CaCl_2$ and $SrCl_2$. Since the NMR-study has not yet been finished, it is not possible at present to fully describe the relation between the proton T_2-relaxation time and the variables mentioned. However, a few representative results are shown in the following.

The relation between T_2 and electrolyte content was demonstrated in a series of measurements on water saturated MX-80 samples differing only in the type and amount of electrolyte added to the system. The results refer to rather dense MX-80 systems with water contents less than roughly 150 - 200%. Figure 1 shows, that T_2 decreases with increasing electrolyte content, other things being equal. The diagram in Figure 1 also shows that T_2 depends on the type of electrolyte present in the system. Thus, other things being equal, the effect of electrolyte is described by the series $SrCl_2 \approx CaCl_2 < KCl < NaCl < H_2O$ where $SrCl_2$ and H_2O correspond to the smallest and highest T_2-values, respectively. The curves A-C indicate 1) that the addition of cations to dense MX-80 systems leads to a decrease in the water mobility that is almost proportional to the cation concentration and 2) that the decrease in water mobility is described by a series similar to the one above: $Ca^{2+} \approx Sr^{2+} < K^+ < Na^+$.

In all the investigated MX-80 systems presented here, an increase in temperature, t, and/or water content, w, resulted in an increase in the T_2-value. It was found, that $T_2 = T_2(w)$ and $T_2 = T_2(t)$ both were almost linear functions within the approximately represented by the equation

$$T_2 = w \cdot \left(\frac{\partial T_2}{\partial w}\right)_t + t \cdot \left(\frac{\partial T_2}{\partial t}\right)_w + \text{constant} \qquad (3)$$

where

$(\frac{\partial T_2}{\partial w})_t$ = the partial derivative of T_2 with respect to w

$(\frac{\partial T_2}{\partial t})_w$ = the partial derivative of T_2 with respect to t.

However, it is well known that T_2 levels off at higher water contents outside the experimental limits and approaches asymptotically an upper value if the water content increases infinitely. This limit value corresponds in principle to the T_2-value associated with pure liquid water.

The relation between the proton T_2-relaxation time and 1) temperature, 2) water content and 3) electrolyte content is illustrated in Figure 2. The diagrams refer to water saturated MX-80 systems containing the same amount (moles) of electrolytes and differing only in the type of electrolyte added. The linear relationship between T_2 and the water content is clearly demonstrated. When the water content increases, flocculation takes place at different water contents as a result of differences in the electrolyte composition in the water phase. Therefore, the MX-80 systems referred to in Figure 2 containing $CaCl_2$ or $SrCl_2$ were not investigated at water contents exceeding 130%, since this value is close to where flocculation occurs. The other MX-80 systems referred to in Figure 2 did not show any tendency of flocculation within the experimental limits and consequently the corresponding graphs could be extended beyond this limit.

The relation between the observed T_2-value and the type of electrolyte present in the investigated MX-80 systems was described in an earlier section by the series $CaCl_2 \approx SrCl_2 < KCl < NaCl$. The same result is also found in Figure 2; at constant water content and sample temperature, the T_2-values in the MX-80 systems decrease in the order described by the above series. The significance of electrolyte content suggests that the water content is sufficiently high to allow the formation of double layers surrounding the clay mineral particles. A rough estimation of the interparticle spacing between the montmorillonite particles can be obtained by using the relation

$$w = S.d/100 \qquad (4)$$

where w = water content (%)

S = specific surface area (m^2/g)

d = half-distance between parallel montmorillonite unit layers (A).

Thus, using the value 600 m^2/g for the specific surface area, all MX-80 systems represented in Figure 2 have an average interparticle spacing between approximately 30 and 60 A. These spacings are considered to be sufficiently high to allow the formation of double layers. As is suggested by the T_2-measurements, the double layer formation may be highly dependent on the electrolyte composition. However, the electrolyte composition may be less important to the T_2-value at lower water

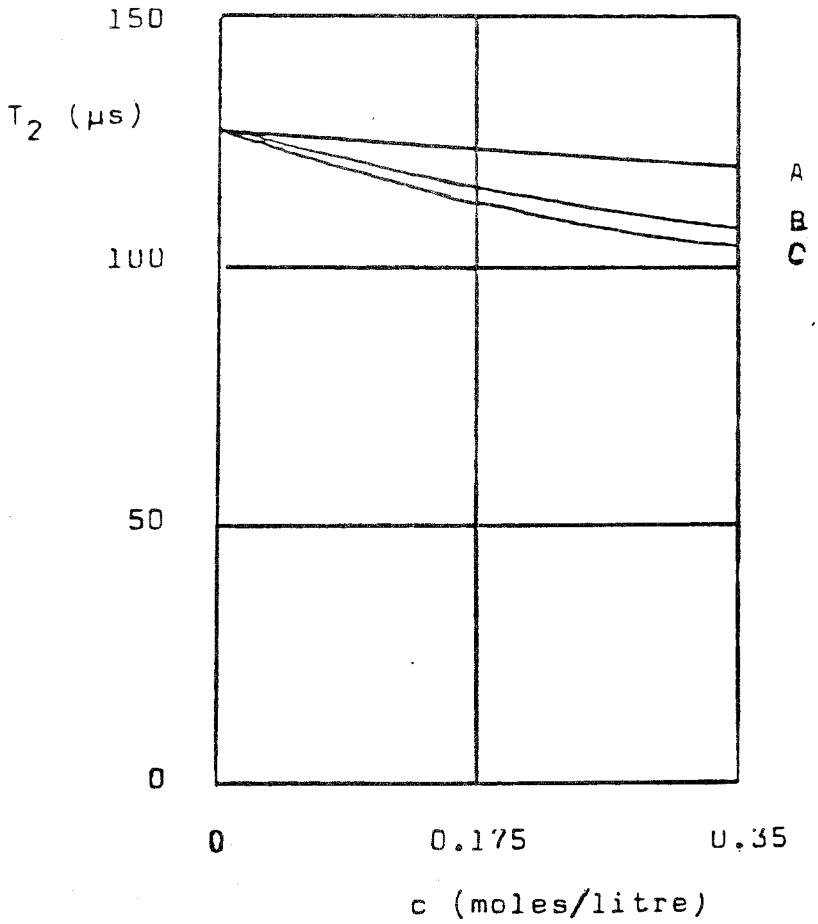

Fig. 1 Proton T_2-relaxation time vs electrolyte concentration, c in solutions used in the preparation of MX-80/electrolyte water samples. C=0 refers to the system MX-80/water. The sample temperature was in all cases +24°C and the water content 100%. Type of electrolyte added: A) NcCl, B) KCl, C) $CaCl_2$ or $SrCl_2$.

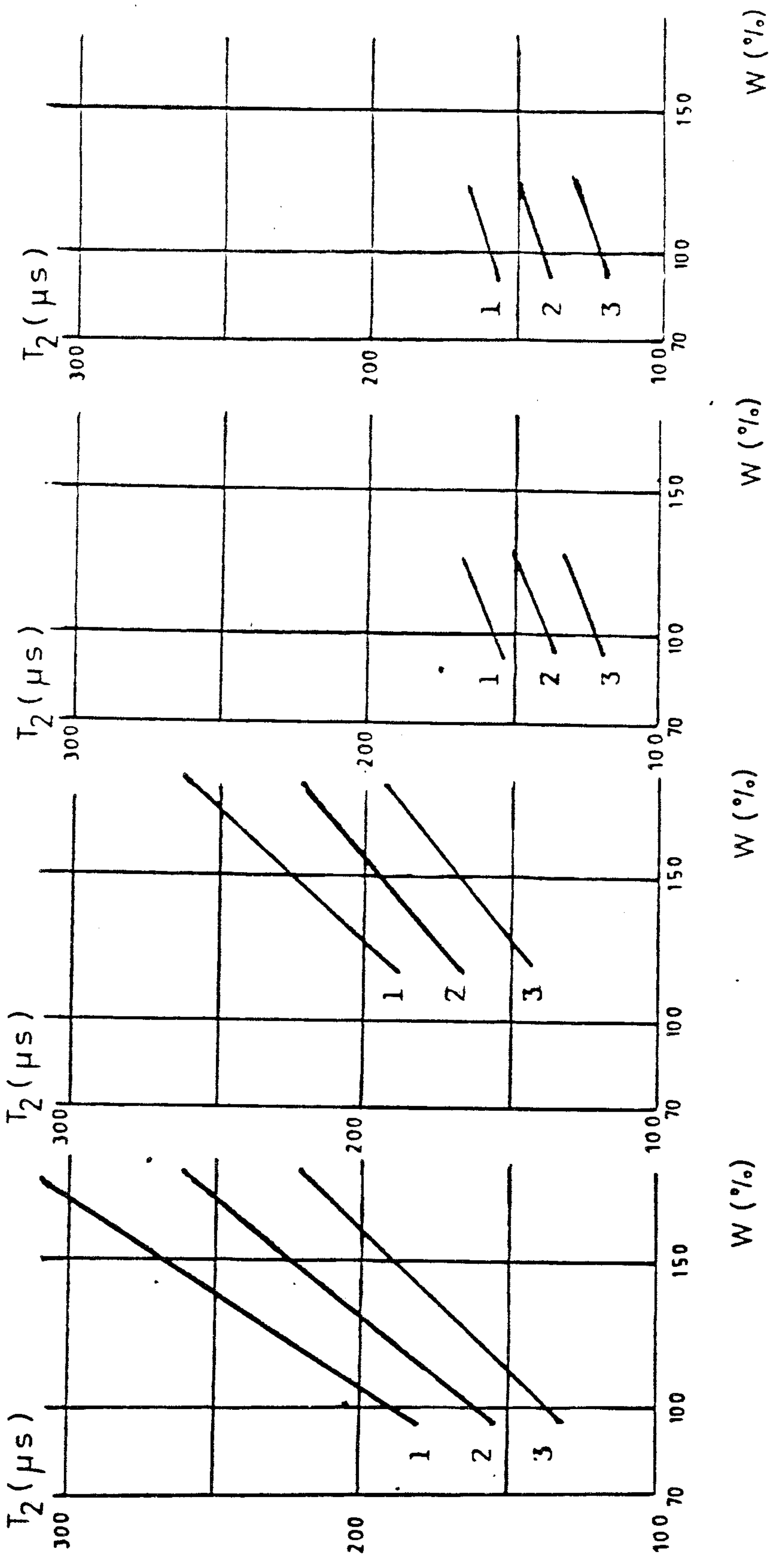

Fig. 2 Influence of different electrolytes on the proton T_2-relaxation time in some water saturated MX-80 systems. Electrolyte concentration in the solutions added to the MX-80 bentonite: 0.175 moles/litre. The solutions contained NaCl, KCl, $CaCl_2$, $SrCl_2$, respectively. Temperature: 1) +81°C, 2) +56°C, 3) +33°C.

contents - corresponding to relatively small inter-particle spacings - since the double layer formation is then more restricted. Furthermore, it is expected that below a certain water content, the value of T_2 becomes more or less independent of the electrolyte composition. This idea is then more restricted. This idea is supported by the diagrams in Figure 2. It is clearly seen that the slopes of the curves depend on the electrolyte composition in the MX-80 systems. This is also demonstrated in Figure 3, where four graphs from the diagrams in Figure 2 are shown. The graphs all correspond to the same sample temperature (+33°C). The differences found between the curves are solely due to differences in the electrolyte composition. A comparison between the curves A and B, corresponding to NaCl and KCl respectively, indicates that the T_2-value becomes less influenced by the electrolyte content when the water content decreases. The dotted extrapolations of the experimentally obtained results suggest that there is a point of intersection corresponding to a water content equal to roughly 60%. This water content is tentatively interpreted as a limit below which the electrolyte content in the MX-80 systems does not significantly influence the T_2-value. According to Equation 4 the above water content may correspond to an average interparticle spacing equal to 20 A, provided that the specific surface area is 600 m^2/g. It should be emphasized, that the above indication has not yet been experimentally verified with the NMR-technique. However, in a series of swelling pressure measurements on water saturated MX-80 systems Pusch (4) found that the electrolyte composition only influences the swelling pressure when the water content exceeds approximately 25%. This value corresponds to a bulk density of 2 t/m^3 provided that the specific gravity is 2.7 t/m^3. In principle the two methods seem to lead to the same conclusion despite the fact that their results are somewhat different: the electrolyte composition becomes decisive to the properties of the water phase only when the water content is high enough to allow the formation of double layers.

The small slopes of the curves C and D in Figure 3 are probably explained by the fact that the corresponding MX-80 systems have water contents which are only slightly below the limit where flocculation occurs. It is expected that when the water content decreases, 1) the slope-values approach the values corresponding to the graphs A and B, and 2) the differences between the curves to the graphs A-D in Figure 3 become smaller and finally vanish when the water content drops below a certain limit.

Finally, the expected relationship between the sample temperature and the proton T_2-relaxation time was confirmed; the observed T_2-value increases almost linearly with increasing temperature in the investigated MX-80 samples. However, the relation between T_2 and temperature seems to be dependent on the type of electrolyte present in the MX-80 systems. Thus, according to the results in Figure 2, the series $CaCl2 \approx SrCl<KCl<NaCl$

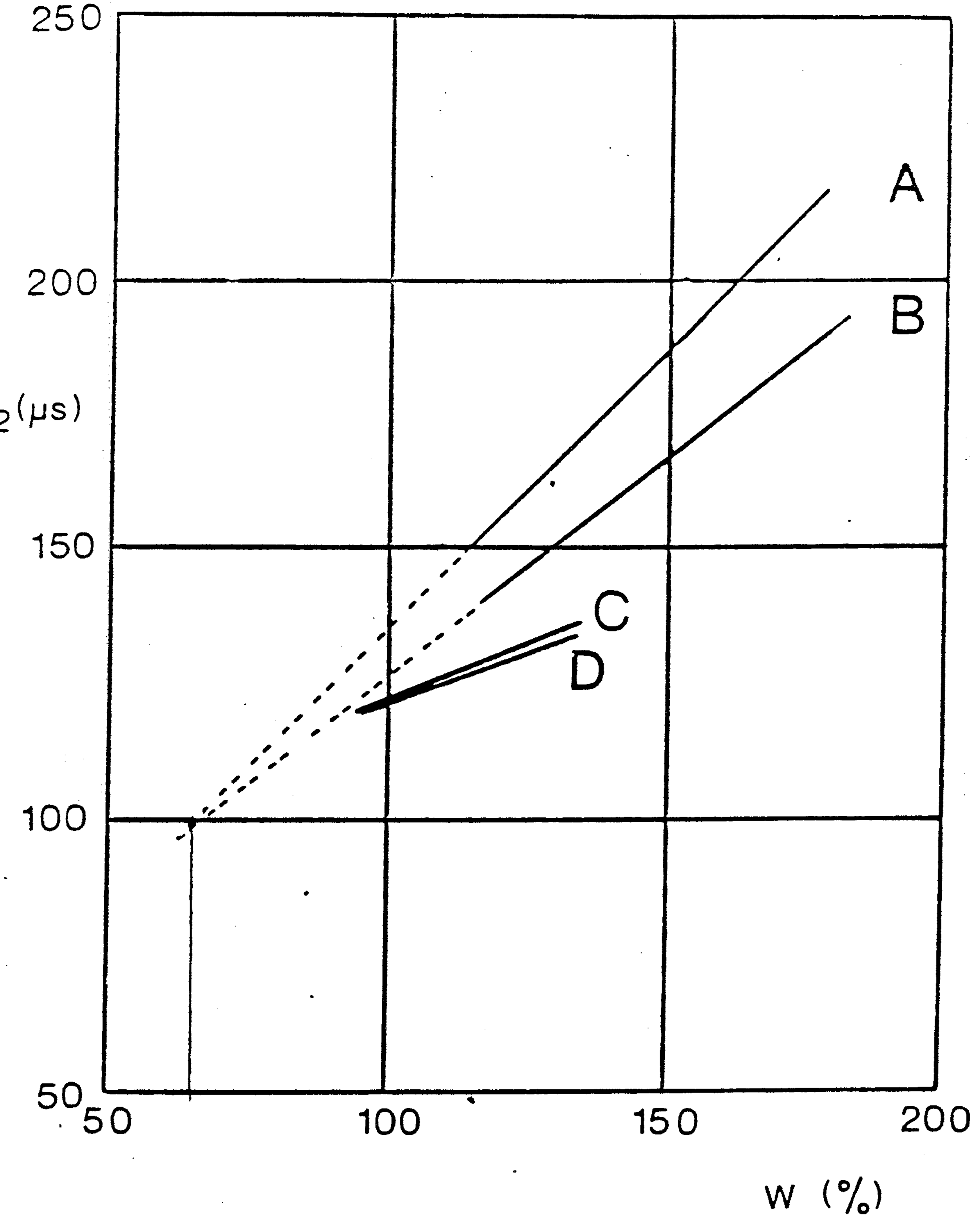

Fig. 3 The effect of electrolyte content on the proton T_2-relaxation time in four water saturated MX-80 systems. Electrolyte added to the system: A) NaCl, B) KCl, C) $CaCl_2$, D) $SrCl_2$. Electrolyte concentration in the solution added to the system: 0.175 moles/litre Temperature: +33°C.

indicates that a temperature-induced increase in T_2 is bigger in a MX-80 system containing NaCl as compared to a system containing $CaCl_2$, other things being equal.

The main object of this paper was to inform about a research project concerning NMR-studies of the water mobility in some water saturated MX-80 bentonite systems. The results presented here are only parts of a major work which has not yet been published

REFERENCES

(1) Müller-Vonmoos, M., and Kahr, G., "Mineralogische Untersuchungen von Wyoming Bentonite MX-80 und Montigel," Institut fur Grundbau und Bodenmechanik, ETH, Zürich. Technischer Bericht 83-12 (1983).

(2) Sposito, G., and Prost, R., "Structure of Water Absorbed on Smectites", Chemical Reviews, Vol. 82, No. 6 (1982).

(3) Fripiat, J. J., "The Application of NMR to the Study of Clay Minerals" in "Advanced Chemical Methods for Soil and Clay Minerals Research" edited by Stucki, J. W. and Banwart, W. L., Reidel Publ. Co., pp 245-315 (1980). NATO Advanced Study Institute Series, Series C: Mathematical and Physical Series.

(4) Pusch, R., "Swelling Pressure of Highly Compacted Bentonite", SKBF/KBS Technical Report 80-13 (1980).

SUMMARY

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1. GENERAL ISSUES (WORK IN ITALY)

It is important to consider the role of smectites (and other clay minerals) not only as buffer and backfill materials in hard rock repositories (granite, basalt, etc.) but also in disposal facilities in argillaceous rocks.

Clay minerals containing substantial proportions of smectites (20 - 40%) are currently being considered as host rocks for high-level, heat emitting wastes in Italy and Belgium. These clay minerals are relatively young (Pliocene and Oligocene) and consequently not strongly indurated or with a dominating illite content. They vary from medium/high plasticity to quite stiff units. Present concepts in both countries envisage the use of the excavated clay as the main component of the backfill, possibly with the addition of bentonite among other binders.

In addition to repository disposal of HLW, present Italian studies are also considering the use of deep boreholes from the surface. Again the concept would require the use of local clay minerals and bentonite as borehole sealants.

In slight contrast to the pure bentonite buffer concept for crystalline rocks, the buffer unit in a clay repository would aim to have very similar bulk properties to the host rock, and ideally it would be the objective to restore the geotechnical properties of the formation around the waste packages and in the galleries and shafts. This is not completely possible, but the concept can be seen to raise a number of questions on clay behaviour in addition to those being considered for bentonite-granite systems. Thus, apart from an interest in the thermal stability of smectites (and other clays) and the longevity of their performance as hydraulic barriers, the Italian programme is also specifically interested in the following issues:

1) Geotechnical properties of stiff clays with swelling potential, in the context of tunnel stability and design.

2) Behaviour of pore fluid (and pore pressure development) in partially distressed clays and the effect on tunnel lining design and containment properties of the clay in the near-field.

3) Convergence rates (time dependent creep) of different clays, and the practicality of withdrawing tunnel liners (completely

or partially) in a repository as backfilling proceeds (to ensure a better seal).

4) Mineralogical interactions between reconstituted clay backfills and host clays, in particular the nature of the bond.

5) Geotechnical properties of a mixed host clay/bentonite backfill, especially the time dependent development of strength, and the behaviour on transfer of load from the host rock to backfill, or the interaction of swelling pressure with overburden pressure in a plastic medium.

6) Geochemical interactions of carbonate-rich clay minerals with various smectites, including Na-montmorillonite. Role of cation exchange on longevity of physical and chemical properties of smectite.

In order to answer some of the questions, a series of laboratory tests is underway on the hydraulic and strength properties of clay-clay and clay-cement bonds, both at ambient pressures and at loads simulating disposal depths of 300-400 m.

In addition, an underground research laboratory is to be constructed (beginning early in 1984) in marly clays at a depth of 180 m. The measurement of stresses in the tunnel walls and their convergence rate will be one of the prime features of the work, which also includes in-situ heating experiments to study the thermal and thermo-hydraulic response of the clay.

Owing to variability of the Pliocene clays in Italy, both in terms of mineralogy and geotechnical properties, the solution to repository and borehole sealing problems will be very site-specific. It should be borne in mind that although the buffer/backfill in a low-competence clay host rock has different primary functions than that in a granite (e.g. restoring continuity of hydraulic properties rather than acting as a separate diffusion barrier) the data requirements are similar in each case.

2. CHAIRMAN'S SUMMARY AT THE CLOSING SESSION

The Problem

The use of smectites (and for that matter any clay-based mixture) as seals, buffers and backfills can potentially make use of several of their more useful properties:

- mechanical buffering
- hydraulic "shielding" (allowing only diffusive transport)
- sorptive capacity for radionuclides

The mechanical buffering role is well accepted and presents no conceptual difficulties. Also sensitivity analyses of total disposal systems invariably show that the limited ability of a clay buffer to sorb the significant nuclides (compared with the capacity of the host rock) makes the latter property unimportant.

At the present stage of research it is widely accepted that the only property of significance in terms of long-term performance of a disposal system is the flow barrier provided by the clay. This means that transport of corrodants to the waste package and nuclides away from it is by diffusion only in the near-field. In the far field clay seals act to prevent hydraulic short-circuiting of otherwise established groundwater flow paths.

Given that the hydraulic function is paramount, the central questions which must be answered are:

- How long do we require integrity of hydraulic properties?
- How hot (and for how long) can the buffer be allowed to get before we can no longer guarantee these properties?
- What geochemical environments adversely affect these properties?

The answer to the first question is somewhere between 100,000 and one million years, depending on the concept.

To solve the second and third questions we have recourse to:

1) Thermodynamic models - although the general opinion is that they are of little use without some adequate field control since kinetic data are so poor.

2) Natural analogues - small scale analogues of the heating of smectite clay minerals by igneous bodies for example.

3) Extensive field data - depth and time of burial of sediments, compaction history and development of pore fluid chemistry.

The last two must make use of the first in their analysis.

The Answer

With this background in mind, the following pertinent questions were raised, and the appended responses elicited from the workshop.

1) Will cation exchange (Na for Ca, Cu, etc.) significantly affect long-term smectite properties, and in this respect are Ca smectites better than or as good as (or worse than) Na smectites?

This seems to be site specific, and the possibility of using mixed smectite/other clays is well worth considering. Essentially ion-exchange may be a problem, but something which can relatively easily be accounted for in design. For loosely packed HCB fills (<1.6 t/m3 dry density) then the problem may be acute. Generally clay properties should be optimized to the site and use made of local material wherever possible. Other smectites could be very useful in this respect.

2) Is soda-activated calcium bentonite better or worse than natural sodium bentonites?

Probably it is equivalent to or better than natural Na-bentonite since it may have enhanced thermal stability and plasticity.

3) In the laboratory smectites can show short-term stability at elevated temperatures (100° - 600°C), but what is the effect of time (i.e. 10^5 - 10^6 years)?

This problem still needs more study, and the best way forward seems to be by the study of natural analogues to get at the kinetics of the illitisation reaction.

4) Is there a reasonable limiting temperature for various disposal concepts, and how conservative should we be?

The consensus was to be "reasonably conservative". For clay/granite host rocks the round figure of 100°C is still favoured, but in basalt temperatures up to 300-320°C are suggested. There are various chemical advantages to higher temperatures among which are minimisation of corrosion by the silicate layer, fixation of certain nuclides in stable mineral forms, and general economics.

5) What are the most conservative alteration products of smectites, should the seal properties be lost?

At high temperatures we are considering framework silicates, but these may in any case be self-cementing. At low (and more realistic) temperatures the end product would be fully converted illite. This would probably have hydraulic conductivity increased by about two orders of magnitude. Radiation damage may lead to alteration to generally amorphous material, but this may not be a problem in many concepts (particularly if the canister has a long life).

6) Long-term stability is site specific, but can we predict even generically the nature of the illitisation reaction as a function of time?

The general conclusion was, that provided temperatures were never to exceed 100°C, then a guaranteed longevity of more than one million years was possible for the hydraulic properties of a smectite buffer/seal.

Summary Points

The following points summarize the more important issues addressed during the workshop.

1) The techniques for emplacing and predicting the initial behaviour of both seals and buffers seem well proven in crystalline rocks, but need further study in clay hosts.

2) The main feature of interest in a clay buffer is the chemical transport of corrodants through it; in a clay seal it is the hydraulic properties of the bond (not of the seal itself).

3) Smectite is expected to collapse partially on a 10^5 - 10^6 year timescale (maybe less) but overall performance should not be radically affected.

4) Tri-octahedral smectites are more appropriate seals than dioctahedral smectites.

5) Experimental and thermodynamic studies of clay mineral stability are ambiguous and should be validated by field data from natural analogues.

6) Eventually, smectites will be used in a range of filling and sealing activities in a range of geochemical environments. Consequently, we must optimize the design of seal mixtures and not concentrate work wholly on pure systems or on conservative concepts.

7) Several topics were indentified which would merit more study, or discussion at future workshops. These included:

   - geotechnical properties of mixed clay backfills,
   - geotechnical properties of plastic/stiff clay host rocks at depths of 300 - 500 m,
   - swelling, bonding and pore pressure behaviour of clay seals in clay host rocks,
   - chemically tailored buffers; are they necessary and do they have different physical properties,
   - role of micro-organism in buffers (especially in sulphate reduction and corrosion),
   - development of economic backfills using more realistic mixes of smectite with other minerals,
   - definition of numerical requirements of seal properties, for borehole plugs especially (what is required of them and for how long).

SUMMARY

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The Corrosive Nature of Sodium Bentonite and Factors that Affect the Hydrothermal Transformation of Smectite into Illite

Dr. Karlsson made the point that if smectite is to be useful in protecting canisters, it should not contain or develop corrodants. We have found in our experiments that bentonite itself is a corrodant. Bentonite can dissolve substances through ion exchange. We have been using bentonite to dissolve sparingly soluble substances such as celestite, barite, K-feldspar, and apatite. It also works well on copper: in our experiments, run with distilled water, metallic copper and Na-Wyoming bentonite, approximately 1 g of clay dissolved 6 mg of copper. Of course, this reaction is highly dependent on pH and Eh conditions, and needs to be investigated further. At the near-neutral pH of this experiment, assuming a density for the bentonite of 2000 kg/cubic meter and a density for copper of 9.0 g/cubic centimeter, a meter thickness of bentonite will dissolve a canister by a thickness of 0.13 cm. Thus, there is little danger of breaching a 10-cm thick canister by this effect, although much more copper would be dissolved at lower pH. These are rough calculations from rough experiments, and they need repeating. The problem comes, however, in the alteration of smectite's properties due to absorption of copper. Interlayer copper may change the swelling properties of clay by:

1) replacing monovalent Na^+ by divalent Cu^{2+};

2) oxidation of octahedral ferrous iron by interlayer Cu^{2+};

3) collapse of the interlayer due to the penetration of copper into the octahedral sheet by the Hoffman-Kleman effect, as discussed at the meeting by Dr. Banin.

When the canisters fail, smectite can dissolve insoluble radioactive substances by the same ion exchange effect, and thereby enhance its own destruction by alpha radiation, as discussed at the meeting. Bentonite also will attack the wall rock, thereby supplying potassium to the clay by dissolution of K-feldspar. The ion exchange effect would be minimized by using a Ca- rather than a Na-bentonite.

Another topic brought up at the meeting was the hydrothermal alteration of smectite into illite. This reaction would cause the clay to lose its swelling, cation exchange, and plastic properties. The reaction is influenced by:

1) interlayer chemistry-interlayer potassium is most reactive;

2) temperature--the reaction begins in nature at about 60°C, but may not occur until greater temperatures are attained if potassium is not present;

3) 2:1 layer chemistry--trioctahedral smectites are less reactive than are dioctahedral smectites;

4) pressure--increasing pressure decreases the reaction.

These effects are discussed in some detail in reprints of papers distributed at the meeting.

It is difficult to predict what will happen to clay by hydrothermal experimentation, however, because clays frequently react according to Ostwald's step rule. Equilibrium often is not attained in the necessary short-term laboratory experiments, and the final product is difficult to predict. It would be good to look at dikes that penetrate bentonites and shales at shallow depths to see what alteration has occurred. Such studies are being conducted by Dr. Robert C. Reynolds at Dartmouth College.

In short, for the highest smectite stability, it would be best to use a Ca-saponite or stevensite, rather than Na-montmorillonite as proposed. Of course, these systems may also have some problems.

SUMMARY

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Radiation effects can have a profound effect on the chemical and physical properties of any material. Although there has been only limited work on radiation effects on sheet silicate structures such as smectite, one can anticipate possible effects. In this presentation, I briefly summarize some of those effects.

As summarized by others (Weber et al., 1982, Radioactive Waste Management) the principal sources of radiation in high level waste are alpha-decay events of actinide elements (long-lived) and the beta-decay of fission products (short-lived). For most solids the principal radiation effects result from the displacement of atoms from their periodic structure by direct knock-on collisions of alpha particles and the recoil nucleus. The alpha particle has a range of less than 10 microns and displaces several hundred atoms, while the recoil nucleus has a range of fractions of a micron and may displace thousands of atoms. Ionization-induced excitations can also lead to displacements in some materials, most notably ionic solids. In addition, alpha and beta radiolysis can cause significant changes in colution chemistry (McVay et al., 1981, Nuclear and Chemical Waste Management; Burns et al., 1982, Science).

The scenarios by which a smectite backfill might be exposed to either alpha or beta radiation fields depends critically on the properties of the canister (shielding effects and lifetime). With proper shielding and a minimal lifetime (100 years) the beta radiation field experienced by the backfill will be minor. The alpha field will not extend beyond a few microns, and thus the backfill will not experience any alpha-event damage until the canister is breached. Unfortunately, the actinides are long-lived and will be present beyond the normally expected lifetime of most canisters. Direct sorption of actinides as they are released from a canister will be the source of any potential deleterious effect.

Potential effects from the beta field can be rather easily evaluated by conducting experiments in a gamma field using a Co-60 source. Preliminary experiments (doses of 3×10^{10} rads, approximately equal to 10^{20} beta decays per cm^3) conducted by James Krumhansl (personal communication, Sandia National Laboratories) suggest the following effects:

1. No structural effects (detectable by x-ray diffraction) on the bentonite for dry irradiations.

2. Production of significant amounts of carbon dioxide and hydrogen (probably due to the presence of sorbed water and organic material). To the extent that this may lead to the reduction of ferric iron, it could cause the formation of mixed-layer clays.

Additional effects would most likely be due to radiolysis of pore solutions or interlayer water. Significant effects have been demonstrated on the leach rates of waste forms and my also occur for backfill materials. (McVay and Pederson, 1981, Journal of the American Ceramic Society).

Potential effects due to alpha-decay events have been summarized by Ewing and Haaker (1981, Nuclear and Chemical Waste Management) and Matzke (1982, Radiation Effects). These effects may include:

1. Significant changes in volume (and hence swelling capacity; see Bradley et al., 1983, PNL-4452).

2. Changes in cation exchange capacity (Spitsyn et al., 1981, Scientific Basis for Waste Management IV; have seen this effect for gamma irradiations).

3. Loss of crystalline periodic structure which can change chemical stability (e.g. increase leach rate). Refer to the presentation by G. Beall (this meeting and Haire and Beal, 1979, ACS Sysposium Series, No. 100).

Thus, any concern for the chemical and physical stability of smectite as a backfill material must be placed into the context of potential radiation effects which will vary as a function of time, the type of radiation and the lifetime of the canister.

SUMMARY

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Clay-Water Interaction

In a clay gel the molecules of water are distributed between two populations. These two populations represent either two distinct phases or two distinct domains of a heterogeneous system. These two phases are separated by a narrow boundary where the gradient of the molecular dynamic properties is very steep, in spite of the fact that the molar transfer free energy is very small, e.g. of the order of 10^{-2} kT (T = absolute temperature; k: Boltzmann constant).

Phase A contains water molecules which are located in pores of various diameters and geometries between aggregated clay microcrystals, called hereafter clay tactoids. The rotational-diffusional correlation time of water molecules in phase A, is about 3×10^{-12}s at 295 K. It is thus identical with that of the pure liquid. Moreover, the nuclear magnetic resonance (NMR) pulsed field gradient (pfg) technique applied to the proton shows that the self-diffusion coefficient (D_a) in phase A is the same as in pure liquid water (D_o). Also, the non-Arrhenius behavior of D_a vs 1/T is very similar to that of D_o.

These observations support the idea that the microdynamic behavior in phase A is not different from that of pure liquid, and in particular that the diffusibilities are identical. Therefore, the permeability in the clay gel is entirely controlled by the tortuosity and it should obey the physical laws described by percolation theory.

Phase (or domain) B contains water molecules which are submitted to surface force fields. Their rotational correlation time (at 295 K) is about 10^{-10}s and the activation energy of the fast reorientation motion is lower than that in the pure liquid. Thus, the hydrogen bond network of liquid water is influenced by surface effects. The perturbation length, perpendicular to the surface is 10 Å or less. There is no long range effect generated by the surface on the structure or dynamic properties of the bulk liquid. It is possible to define the volume of phase B as the product of 10 Å time the tactoid external surface. In that limited volume, the selfdiffusion coefficient of the water molecule is about two orders of magnitude smaller than in phase A.

The volume of phase B is not sensitive to the presence of electrolytes (for instance up to a 1 M KCl concentration) nor to the external pressure (up to 5 kbar) but it changes below the normal freezing point of water (~273 K).

As a clay gel becomes more enriched in solid, the discrete volumes associated with each tactoid overlap each other. Above the freezing point of water, molecular exchange between phases A and B is very fast. At 295 K, the lifetime of a molecule in phase B is of the order of 10^{-8} - 10^{-9}s.

Because this fast molecular exchange between phase B and the fraction of phase A already frozen is progressively suppressed below freezing point, the phase B volume is modified.

To summarize, the permeability will contain both a tortuosity and a diffusibility factor only when the molar fraction of phase B, called x_b, is of the order of the molar fraction in phase A, or $x_a = 1 - x_b$.

An important factor in the choice of clay minerals to be used in a repository is the exposure of its specific surface area to water, namely that part of the total specific surface area to which the volume of phase B are associated.

REFERENCES

1. J. J. Fripiat, J. Cases, M. Francois and M. Letellier (1982). J. Colloid. Interface Sc. 83, 378-400.
2. J. Jonas, D. Brown and J. J. Fripiat (1982). J. Colloid Interface Sc. 89, 374-377.
3. J. J. Fripiat (1980). Bull. Soc. Franc. Mineralogie, 103, 440-443.
4. J. J. Fripiat, M. Letellier and P. Levitz: "Interaction of water with clay minerals." Proceedings of the British Royal Society. "Symposium on the structure, the properties and use of clay minerals" (1984).
5. J. J. Fripiat and M. Letellier: "Microdynamic behavior of water in clay gels below the freezing point," J. Magn, Reason.

SUMMARY

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Simulation of Clay Minerals-Solutions Interactions by Using Solid Solution Models

The Modeling Approach: was developed for 15 years in water-rock interaction studies (e.g. of R. M. Garrels, F. T. Mackenzie, then H. C. Helgeson etc...) and applied in different fields of research in geochemistry such as:

- weathering processes (low T, P), alteration, evaporation, cation exchange.
- modern geothermal alteration, diagenetic evolutions, ore hydrothermal deposits (at higher T, P).

The basic idea: Many natural systems (rock+solution+gases) are thermodynamically UNSTABLE systems. Their change is therefore spontaneous, due to potential energy under a kinetic control. The modeling approach will try to DETECT the UNSTABILITIES first, and then to CALCULATE the way systems go back to STABILITY:

- the first step (detection) is no more than a thermodynamic reading of chemical analyses (activity concept) and calculation of saturation states of minerals in solutions. Numerous computer models have been developed to do this: SOLSAT, EQUIL, EQ3, SOLMNEQ, WATEQ...

- the second step (simulation) starts from the detection diagnostic and tries to follow the system along the chemical possible reactions. Models like PATH CALC, DISSOL, EVAPOR, THERMAL allow these simulations.

Water-Rock Interaction and complex mineral phases: How can we take into account the variable composition clay minerals?

- As a first approximation, minerals were, and are sometimes still considered as pure end members ($CaCO_3$, NaCl, a clay of given compositon). The equilibrium condition (mass-action Law) between these phases and the aqueous solutions is then a simple relation between aqueous species activities only. The calculation will determine the quality of each mineral produced or dissolved in a given simulated process.

- In order to fit the compositions of real minerals it is often necessary to introduce high order solid solutions. The equilibrium condition is then split into (n) relations, one per end-member of the solid solution. These (n) relations, concern some aqueous species activities <u>and</u> the activities of the (n) end-members of the solid solution.

By this extension, the Mass-Action Law concerns both solid and liquid phases and this has been found very important in mass tranfer calculations even if, today, the solid solution models are still rough approximations.

<u>Clays and solid solution models</u>: With clay minerals we reach the maximum complexity of solid solution fitting.

- The variability of chemical composition is due to the existence of three different non-independent sites of mixing for the cations in the clay structure (tetrahedral, octahedral, interlayer).

- The number of possible end-members for the solid solution is therefore very high and the solid solution appears generally as undefined.

Two types of models have been proposed in the literature:

- site-mixing models (Kerrik and Darken, Stoessell, Helgeson, Aagaard). In these models, the cation mixing in different sites is considered as ideal or regular thermodynamically, which corresponds to a non-ideal, non-regular mixing of the classical molecular end-members (like pyrophyllite, muscovite etc...).

- molecular mixing models (Tardy and Garrels for Free-Energy estimations, Tardy and Fritz, for the clay modelling). In the model <u>all possible</u> end-members are allowed to participate in a unique solid solution phase. The stability constants are estimated at low temperature and calculated at higher temperatures using Cp (T) functions. The importance of a given end-member in the solid solution (mole fraction) is proportional to its saturation index in aqueous solution. This leads to an ideal solid solution model in terms of molecular mixing, but allows to introduce later activity coefficients for the end-members.

First applications of this model have shown that it gives a reasonable fit of the clay role in water-rock interactions in very different geochemical environments and physico-chemical conditions:

- cation exchange in soils and sediments,
- low temperature weathering processes (dilute solutions),
- evaporation of solutions in closed basins (in saline brines),
- hydrothermal alterations of granites in nature.

At the very least, the modeling approach will help geochemists to combine mass balance conditions, and stability limits of minerals.

In the case of hydrothermal alteration induced by the condition of waste storages, we try to use it in order to estimate the maximum of risk in a minimum of time.

REFERENCES

1. Aagaard P. and Helgeson H. C., 1982, Amer. J. of Sci., 282, pp. 237-285.
2. Duplay J., 1982, Thesis, Universite Louis Pasteur, Strasbourg, pp. 1-110.
3. Fritz B., 1981, Sci. Geol., Mem., Strasbourg, 65, pp. 1-197.
4. Helgeson H. C., Brown T. H., Nigrini A. and Jones T. A., 1970, Geochim. Cosmochim., Acta, 34, pp. 569-592.
5. Helgeson H. C., Delany J. M., Nesbitt H. W. and Bird D. K., 1978, Amer. J. of Sci., 278-A, pp. 1-229.
6. Kerrick D. M. and Darken L. S., 1975, Geochim. Cosmochim. Acta, 39, pp. 1431-1442.
7. Stoessell R. K., 1979, Geochim. Cosmochim. Acta, 43, pp. 1151-1159.
8. Tardy Y. and Garrels R. M., 1974, Geochim. Cosmochim. Acta, 38, pp. 1101-1116.
9. Tardy Y. and Fritz B., 1981, Clay Minerals, 16, pp. 361-373.
10. Tardy Y., Duplay J. and Fritz B., 1981, In Developments in Sedimentology, 35, Van Olphen and Veniale, Ed., pp. 441-450.

SUMMARY

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Mineral Transformation Scenarios

For an approach to the question of smectite-stability one suitable way seems to be with start from feldspar decomposition and their transformation to phyllosilicates.

The comparatively little difference in size between Si and Al in covalent bonding is a fact. Both are able to coordinate in tetrahedrons but at ordinary temperature and pressures Al prefers the octahedral form. Both of them are sharing oxygens. As long as AL < Si they form indefinite tetrahedral networks. 3-dim. are mainly feldspars and 2-dim. phyllosilicates. In this paper we do not discuss the other types.

The feldspars orthoclase, albite and anorthite as well as mixed forms of them are not stable at temps and pressures different from those at the moment of their creation. Influence of air and water at ordinary earth surface conditions gets the following reactions of anion transformation run:

$$\left[AlSi_3O_8\right]^{-}+2(OH)^{-}+2O^{2-} \longrightarrow \left[(OH)_2\middle|AlSi_3O_{10}\right]^{7-}; \qquad \text{mu}$$

$$\left[Al_2Si_2O_8\right]^{-2}+2(OH)^{-}+2O^{-2} \longrightarrow \left[(OH)_2\middle|Al_2Si_2O_{10}\right]^{-8}; \qquad \text{ma}$$

$$4\left[AlSi_3O_8\right]^{-}+3H_2O+O^{-2} \longrightarrow 3\left[(OH)_2\middle|Si_4O_{10}\right]^{-6}+4Al^{3+}; \qquad \text{py}$$

$$2\left[Al_2Si_2O_8\right]^{-2}+3H_2O+O^{-2} \longrightarrow \left[(OH)_2\middle|Si_4O_{10}\right]^{-6}+4AlOOH; \qquad \text{py}$$

We give here those ions the names mu, ma and py respectively and hold in mind that py exists in two different modifications with respect to source and that these modes probably are different in properties. Further, they are not equally fit to receive and join cations and other mineral species.

Now it is time to remind that

$O_2 + 4e^- \rightarrow 2O^{2-}$ and

$H_2O + O_2 + 4e^- \rightarrow 4\ (OH)^-$

These are of certain interest with respect to electron flows and movements that may take place in and around a nuclear repository. The tendency of phyllo-, ino- and sorosilicates to share oxygens can be understood as a result of oxygen deficit. At ultimo oxidation $Al^{[4]}$ tranfers to $Al^{[6]}$ to become AlOOH boehmit, the most stable form of alumina. At low pH we can regard Al^{3+} as the end member. Si forms H_4SiO_4 and possibly crystalline SiO_2.

In the solubility diagram we find how alumina is constant at pH 5 - 8 and how it drastically increases at all extreme pH as well low as high. The stability of quartz is continuously increasing with as well pH as temperature. The latter comparatively faster than alumina. We will now make a first simplified approach to the question of stability in smectites especially montmorillonites. Pure feldspars, clean water and air are thought to be present. As earlier described, oxidation of feldspars produced the anions mu, ma and py, and an origin in plagioclase is suggested by ma. In reality, materials occur in the form of debris, aggregates, molecules and ions that behave in a way of balanced collaboration depending on z-potential shape, distribution of charge, dispersion PZC, pH, Eh a.s.o.

If alkalies and Ca are permitted to drain away, margarite, Ca-illite, paragonite, muscovite and corresponding hydrominerals are formed. If the ubiquitous alumina is not drained sudoit can be formed.

If it is possible for draining water from weathering mafic rocks upstreams or laterally in a banded inclined ground with for instance hyperite in granite, Fe and Mg ions have a chance to form chamosite with mu and amesite, thuringite, berthierine and daphnite with ma. Now let us have a look at what can happen if and when the weathering continues. It is then time for the Al-tetrahedrons in micas to change coordination state for 4 to 6.

$$4\left[{}^{-}(OH)_2\middle|AlSi_3O_{10}\right]^{-7}+10H_2O+4O^{-2} - 3\ \left[(OH)_8\middle|Si_4O_{10}\right]^{-12}+4AlOOH;$$

$$2\left[(OH)_2\middle|Al_2Si_2O_{10}\right]^{-8}+2H_2O+4H^{+} - \left[(OH)_8\middle|Si_4O_{10}\right]^{-12}+4AlOOH$$

So the anion Ka0 was formed. Even that one is in two different shapes with respect to the origin (comp. kaolinite and halloysite).

Now we are a little more familiar with the fundamental construction units in the world of phyllosilicates.

For growth they have two seperate dispositions. The first one is in the plane with tetrahedral connections and the other in plane-parallel layers attracted by charges and others. The construction units can be jointed to more complicated combinations and build anions like for instance that of glauconite

which anion corresponds to

ma + 33 py. So is nontronite ma + 5 py.

Some of the chlorites are very indistinct especially in the cation member. It is often depends on the quality of Fe to change the valency very easily.

From debris point of view it is tempting to regard the aniones of

daphnite	as	mu + ma
thuringite		2py + 3ma
pennine		py + mu
saponite		2py + ma
beidellite		py + mu
a.s.o		

On beidellite it is fascinating to calculate on the decomposition of Labradorite An 67. The anion transformation is

$$\left\{\begin{array}{lll} 1 \times \left[AlSi_3O_8\right]^{-} + 2(OH)^{-} + 2O^{2-} & \longrightarrow & \left[(OH)_2 \middle| AlSi_3O_{10}\right]^{7-} \\ 2 \times \left[Al_2Si_2O_8\right]^{2-} + O^{2-} + 3H_2O & \longrightarrow & \left[(OH)_2 \middle| Si_4O_{10}\right]^{6-} + 4AlOOH; \end{array}\right\}$$

$$-\left[(OH)_4 \middle| AlSi_7O_{20}\right]^{13-}$$

that is the beidellit -anion.

As a second step in this simplified approach to the task we will have a look at cation too. The are dedicated to occupy the positions offered by the anion charges.

For example mu can appear and build as follows:

with KAl_2 + mu = muscovite
$NaAl_2$ + mu = paragonite
$K\ Mg_3$ + mu = phlogopite
$K(Fe^{II}, Mg, M)_3$ = biotite

The alkali ion takes seat to compensate the charge deficit caused by Al-tetrahedra and Al as well as Mg enter di- and tri-oktahedral layers respectively.

What has been mentioned above can serve, maybe as an introduction to the phenomenon of regular and irregular interlayering of clay minerals and stacking of those with limited symmetry. With this background in mind we are prepared to imagine the destiny of a montmorillonite under a few comparatively uncomplicated conditions.

We write it as follows:

$$\frac{Al_5Mg\ \left[(OH)_6 \middle| (Si_4O_{10})_3\right]}{Na\ \ (H_2O)_{12}}$$

and get the picture of a three-layer-lattice mineral without Al-tetrahedron and with a distinct composition

First calculation:

Percolating fresh water and good draining for Na, Mg and H_4SiO_4;

$$2\left[\frac{Al_{10}Mg_2\ \left[(OH)_{12} \middle| (Si_4O_{10})_6\right]}{Na_2\ \ (H_2O)_{24}}\right] + 16H_2O \longrightarrow$$

$$\longrightarrow 5Al_4\ (OH)_8\ Si_4O_{10} + 4MgO + 2Na_2O + 28H_4SiO_4$$

The result is kaolinite and to prevent a collapse of the smectite it may be reasonable to study the reaction thermodynamically and plan for mineralogical buffering.

Second Calculation:

Freedrain for H_4SiO_4 and Na_2O, deposition of AlOOH and MgO inflow.

$$\frac{Al_{10}Mg_2\left[(OH)_{12}\middle|(Si_4O_{10})_6\right]}{Na_2\ (H_2O)_{24}} + 4MgO+19H_2O \longrightarrow$$

$$\longrightarrow Mg_6\left[(OH)_8\middle|Si_4O_{10}\right] +20H_4SiO_4+10AlOOH+Na_2O$$

The result is antigorite!

Third calculation:

Observations are reported that montmorillonite has participated in clay alterations to illite. A total formula could be:

$$\frac{Al_5Mg\left[(OH)_6\middle|(Si_4O_{10})_3\right]}{Na\ (H_2O)_{12}} + \tfrac{1}{2}K_2O \longrightarrow$$

$$\longrightarrow KAl_4\left[(OH)_4\middle|AlSi_7O_{20}\right] + \tfrac{1}{2}Na_2 +MgO+5H_4SiO_4+3H_2O$$

The anion transformation:

$$\left[(OH)_2\middle|Si_4O_{10}\right]^{6-}+AlOOH+3H_4SiO_4 \longrightarrow$$
$$\left[(OH)_4\middle|AlSi_7O_{20}\right]^{13-}+2H_2O+7H^+$$

A high pH will obviously speed up the reaction. But the proper question is if any reaction of this type has any chance at all to run.

Earlier we let feldspars with ignous rock origin and consequently solidified and crystallized at fixed rational composition at eutectics, loose Si and Al successively and that is OK but the task to go the opposite direction with K+Al substituting Si in solid tetrahedron pattern seems to be a real bit of a problem and must under these conditions be considered advanced.

The actual environmental conditions for such on substitution are quite different than others, for instance, at precipitation from a liquid. Surely the real fact is another one. Observations seem to be relevant but hardly complete. Maybe the montmorillonite cation py is connecting mu ions laterally to its network and forms what is judged an illite. The conception illite is not distinct and can probably, with some right, be said to be a continuous series of mixed clays.

Earlier we made beidellite from labradorite. The actual rock does not change in texture other than porosity increases as the aluminium is removed. Often one talks about residual kaolin or primary kaolin consisting of original quartz, mica and kaolinite. When then the weathering goes, then the primary kaolin looses its structure as the mica gives up its solid shape. Secondary kaolin is then sedimented, which is different from precipitated kaolinite. These secondary kaolins can be deposited in as well lacustrine as marine environment. A third alternative was the cretaceous sea. The chemical content in various recipients can contribute to forming of special minerals.

Another mode of formation is represented by the plutonic ash deposits. Their chemical composition corresponds closely to the feldspars added with some mafic components of Fe and Mg. Such ashes are reactive and by setting on for example a shallow beachwater where the breakers provide a lot of oxygen high Eh can be obtained.

SUMMARY

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Effect of pH on Smectite Stability

Experimental studies at Whiteshell Nuclear Research Establishment on the hydrothermal stability of montmorillonite indicate that solution pH influences both the extent and type of reaction.

After hydrothermal treatment at temperatures between 150° and 300°C for up to 30 days, the pH of montmorillonite suspensions (measured at 25°C) decreases from 9.5 to between 3 and 6 for Na-smectite suspensions and from 8.5 to between 5 and 6 for Ca-smectite suspensions. The magnitude of the pH reduction at lower temperatures is uncertain, but our results suggest that, at temperatures above 150°C, Na- and Ca-smectites rapidly lose the capacity to buffer pH in the mildly alkaline range.

A series of hydrothermal tests on montmorillonite stability revealed two reaction trends. If the acidity of the montmorillonite solution system is controlled by the clay, final pH values in the range 3 - 5 are observed, and sheet silicates are preserved in the montmorillonite. Reaction products are smectite and mixed-layer illite-smectite. However, if the pH is controlled by the fluid, using bicarbonate or hydroxide in solution to give a final pH between 6 and 12, destruction of the sheet silicates is observed. Reaction products are a complex mixture of sheet and framework silicates, quartz, and Fe- and Al-oxyhydroxides. At intermediate final pH values (6-8), feldspars are common reaction products. In the alkaline region ($pH > 8$), a zeolite (analcime/wairakite) is also produced.

Similar alteration trends are observed in natural systems, e.g., the clay-carbonate and zeolite assemblages in burial metamorphism [1]. The alteration of smectite to other sheet silicates, particularly illite, is well documented. Abundant evidence also exists for the formation of framework silicates (feldspar, zeolites) in low-temperature metamorphic and hydrothermal systems of pelitic composition. Alkali feldspar is a common authigenic mineral produced during diagenesis. The persistence of K-feldspar in the weathering profile, and its occurrence as a detrital phase, indicate its stability at low temperatures. Feldspar formation is favoured (relative to clay minerals) by high activity of alkalis and high pH. Zeolites are abundant in low-temperature alteration series of volcanic sequences and their sedimentary derivatives (including bentonites), but are also found in marine and saline lake sediments, and in burial metamorphism of pelites. Complex zeolite assemblages develop in hydrothermal areas at temperatures below 100°C [2]. Zeolite formation is favoured (compared with clay-carbonate assemblages) by:

(i) low partial pressure of Co_2 [3]

(ii) high silica activity

(iii) high activity of Na, K, and Ca

(iv) high pH

(v) low total pressure

(vi) closed systems (restricted groundwater flow [4])

Granitic groundwaters are typically Na-Cl dominated, with low total dissolved solids and low alkali activity. The data of Helgeson et al. [5] indicate that such groundwaters are in theoretical thermodynamic equilibrium with clay minerals at temperatures between 25°C and 150°C. However, groundwaters found at depth in granitic terrains in the Canadian Shield are Ca-Na-Cl brines, with total dissolved solids in the range 50 - 100 g/L and correspondingly high alkali activity. These brines lie much closer to the theoretical stability field of the framework silicates at 25°C and, at higher temperature or silica activity, are in equilibrium with feldspar rather than clays. Increasing the pH of these brines moves them well out of the sheet silicate stability field.

Experimental data, theoretical predictions and observation of the behaviour of natural systems all indicate that, while smectites commonly alter to form illite (or other clay minerals such as kaolinite), transformation to framework silicates (such as feldspars and zeolites) and quartz is not unusual even at low temperatures, particularly in alkaline systems.

These results have important consequences for the stability of smectite in the context of its use as a buffer component in the Canadian Nuclear Fuel Waste Management Program. The high alkali activity of the Canadian Shield brines raises the possibility that smectite may transform to framework silicates (feldspars and zeolites), or quartz, rather than other clay minerals during the period of the thermal transient. This is even more likely if the pH of the groundwater is high, as could occur, for example, if large amounts of concrete were used in vault construction or grouting. Cementation of the clay buffer by brittle framework silicates or quartz would result in the loss of plasticity and swelling capacity, as well as possible volume changes. Decreased porosity and permeability due to cementation could be advantageous. However, embrittlement of the buffer could result in fracturing and the development of flow paths for groundwater, thus compromising the role of the buffer as a barrier in which mass transport is diffusion controlled.

REFERENCES

1. Zen, E-An., (1974), "Burial Metamorphism," Can. Mineral. 12, 445-455.

2. Kristmansdottir, H., and Tomasson, J. (1978) in "Natural Zeolites. Occurrance, Properties, Use," (Ed. L. B. Sand and F. A. Mumpton), Pergamon Press, Oxford, pp. 277-284.

3. Thompson, A. B., (1971), "P_{CO_2} in Low-grade Metamorphism: Zeolite, Carbonate, Clay Mineral, Prehnite Relation in the System $CaO-Al_2O_3-SiO_2-CO_2-H2O$," Contribs. Mineral. Petrol. 33, 145-161.

4. Barrer, R. M., (1982), "Hydrothermal Chemistry of Zeolites," Academic Press, London, 360 pp.

5. Helgeson, H. C., Brown, T. H., and Leeper, R. H., (1969), "Handbook of Theoretical Activity Diagrams Depicting Chemical Equilibria in Geologic Systems Involving an Aqueous Phase at One Atm. and 0° to 300°C," Freeman, Cooper and Co., San Francisco, 253 pp.

SUMMARY

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Important Chemical Properties of the Bentonite Clay Buffer

In the recently published Swedish study on the direct disposal of spent nuclear fuel (KBS-3), Part I-IV, SKBF/KBS, Stockholm, (1983) highly compacted bentonite clay has been suggested as a buffer between waste-canisters and the walls of the deposition hole. Copper is suggested as the canister material and the repository is placed at a depth of about 500 m in granitic rock. The waste load in one canister and the relative spacing of the canisters were chosen so that the bentonite will be kept at a temperature well below 100°C. Of course, other waste disposal concepts using bentonite but being otherwise different may have other demands on the buffer material. Still, I think, it could be instructive to highlight some points concerning the relative importance of the bentonite buffer properties in the safety evaluation of the disposal system according to KBS-3.

1. Transport from the Canister

The dense bentonite has a very low hydraulic conductivity, restricting the water flow in the near-field to the narrow fissures of the surrounding rock. If the canister fails, released radionuclides will have to penetrate the bentonite buffer by diffusion in order to reach the flowing groundwater. The very slow transfer of dissolved radionuclides from the bentonite to the flowing water in surrounding rock is in addition to the diffusion through the bentonite a very important mechanism for transport resistance. An extrusion of bentonite into the fissures causing stagnant conditions there would be especially effective in this sense.

The relative importance of the bentonite buffer for the retention of radionuclides in the KBS-3 concept is small. Simply stated; short lived radionuclides will decay anyhow and long lived will only be delayed. However, this is again very much dependent on the waste disposal concept chosen and the relevant release scenarios. Other concepts with less expectations on canister lives will presumably show a different picture.

One very important buffer property is the filtering of radionuclides in the form of particles. The further transport of these species in the geosphere is difficult to assess and it is therefore a relief to be able to show that colloides or larger aggregates do not move or at most diffuses extremely slowly in the bentonite buffer.

2. Transport to the Canister

The only groundwater constituent found at 500 m depth in granitic rock in Sweden likely to attack copper is sulphide. Therefore, the transport of sulphide to the copper canister is the most probable rate determining step in the corrosion process. Again, the transfer from the flowing water to the buffer is an important part of the resistance, probably even more important than the diffusion through the buffer.

3. Chemical Buffering

The stability of copper and solubility of radionuclides are dependent on pH. For the safety assessment it is therefore important that pH is kept within a reasonable and predictable interval. The bentonite with its intimate mineral-water contact will act as a solid pH-buffer preventing pH-changes due to radiolytical or other chemical reactions which may be difficult to foresee. Redox controlling agents and other additives giving the bentonite favourable chemical qualities have been discussed. However, new additives often give new possibilities for unwanted interactions with the bentonite. This can be difficult to foresee and assess in the safety analyses. The pure system has the advantange of simplicity and it is easier to find and study analogies in nature.

4. Quality and Durability

The full-scale tests in the Stripa mine and numerous related experiments have shown the very good qualifications of the bentonite buffer. It is, of course, also important to show that the basic protective qualities are not lost in the far future of a closed repository and much investigation work has been concentrated on what bentonite shouldn't do then.

- It shall not contain or develop corrodants. Since bentonite is a natural product, limits have been set to what it may contain of sulphide, sulphate, organics, etc. which may have an adverse effect on the canister.

- It shall not leave the repository. The penetration of bentonite into narrow fissures and the effect of water quality on bentonite dispersion have been carefully studied.

- It shall not transform away from the plastic clay state. Whatever happens to bentonite, it is of great importance that it remains plastic, fills the deposition hole and does not develop cracks or channels. An eventual transformation of bentonite into some other clay material like illite must, therefore, not necessarily be a drawback in this sense; provided that the basic protective qualities are not lost.

This workshop certainly has the potential to make a valuable contribution in addressing this last point.

SUMMARY

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Alterations Mechanisms, Rates and Effects on the Physical Properties of the Clay Overpack

The prepared presentations and associated discussions of Session II were directed at questions of possible and probable alterations and their potential effects on the physical properties of smectite clay overpacks during the 10,000 to 100,000 year lifetime of a nuclear waste repository. These presentations and discussions extended over two half-day sessions of the Workshop. The purpose of this summary is to present a brief overview of both the scientific and technical issues discussed and the conclusions or remaining questions that emerged that are of special importance in reaching final decisions about the utilization of smectites in repositories.

Professor Armin Weiss began his discussion of the long term stability of smectites with two questions: How do we define stability and how do we define long term? In the context of this workshop it is clear that long term must mean 10,000 to 100,000 years; i.e., the life of the repository, and that stability must mean the continued ability of the clay to effectively isolate the surrounding environment from contamination by radionuclides. The needs for both accelerated testing methods and for extrapolation methods that can be used with confidence, a common thread that extended throughout the Workshop, were pointed out.

From review of old foundry literature and from the results of his own research Dr. Weiss has been able to assemble data on the effect of heat treatments to 180-350°C on cation exchange capacity, dry strength, and plasticity of smectites. He distinguished three alteration processes with different half-times and different mechanisms:

1. Several hours--heating to 120-150°C can lead to fixation of interlayer cations in high charge regions.
2. Days to weeks - reorientation of structural (OH) groups involving the proton close to the center of the empty octahedral sites.
3. Several months - a high activation energy process that has a threshold temperature of 250°C and involves dioctahedral smectities only, wherein a more uniform charge distribution is developed.

An important conclusion is that trioctahedral smectites are more thermodynamically stable than dioctahedral. Furthermore, large, well-ordered crystals are more stable than small, less-ordered crystals. It has been found that the presence of iron may accelerate reaction rates.

Dr. Amos Banin addressed thermal effects and the influences of adsorbed ions on free swelling of smectites. Data were shown to indicate the decrease in specific surface area with temperature of heating for smectites with different adsorbed cations. The free swelling decreases in relation to the decrease in specific surface. Both are a consequence of the penetration of cations into the crystal structure leading to a reduced particle charge.

The temperatures for initial collapse of smectites were indicated in relation to the adsorbed cation type as follows:

Cation(s)	Temperature
Li, Cu	100°C
Ni, Zn, Mn, H-Al	200°-300°C
Fe^{+++}	400°C

An important unanswered question is whether very long heating periods would cause significant reduction in these reaction temperatures.

Dr. Banin pointed out that a pure smectite may not be required to achieve the required swelling and sealing properties. Mixtures with other clays; e.g., kaolinite may be suitable. He also noted that groundwater composition may influence the proportions of different exchangeable ions in the clay and that predictions on the basis of the sodium adsorption ratio could be useful. Finally, we should consider the possibilities for ion exclusion owing to the membrane action of thick clay barriers.

Dr. Ann-Marie Brusewitz has approached the problem of smectite-illite transformation rates and mechanisms through the detailed study of potassium bentonites at several sites in Sweden. Relative illite-smectite proportions are being evaluated in relation to age (by K/Ar dating), temperature and chemical/mineralogical environment. Interpretive studies of this type, in which transformations to the present condition are related to probable time, temperature, pressure, and chemical histories, provide a legitimate basis for the predictive studies needed to address the present problem of smectite stability in nuclear waste repositories.

Dr. Stephen Altaner concluded from a field case that the transformation rate of smectite to illite seems to be controlled by the rate of diffusion of K^+ into the smectite. The reaction is:

X^+-smectite + K^+ + Al^{3+} $\rightarrow$ Illite + Si^{4+} + X^+ + H_2O

Time and temperature both favor the transformation.

If diffusion is the rate controlling transformation mechanism, then concentration gradients and a kinetic equation containing the activation energy can be used for analysis. Using assumed parameters, a potassium diffusion coefficient of 10^{-7} to 10^{-8} cm^2/sec was calculated by Dr. Altaner. It is now necessary to extrapolate these findings to the repository situation. To do so will require consideration of tortuosity differences between the case analyzed and the smectite clay pack.

Dr. Bertrand Fritz explored the possibility that clay mineral-solution interactions can be simulated using solid solution models. Some possibilities for doing this were discussed. Among the possible approaches are through detection using aqueous speciation considerations or mass actions laws and evolution calculations for pure and "real" minerals. The problem is difficult, however, because of interdependent stabilities and the need for choices in modeling clay solid and liquid solution. Dr. Fritz presented examples of predicted clay compositions for different solution compositions. He suggests that an iteration between field observations and laboratory and theoretical results is needed, because the modeling approach by itself will not work.

Dr. Arne Gustafsson approaches the analysis and prediction of smectite alteration from both stochiometrics and geological points of view. A first approach to smectite stability may be through analysis of continuous transformations of margarite to pyrophyllite. Can there be a parallel genesis of clay minerals, with progression down the list leading to greater stability?

Dr. Gustafsson's ideas can lead to an understanding of regular and irregular interlayering and the stacking of clay minerals. Additionally, he indicated difficulty with the concept of K^+ and Al^{+++} entering a smectite lattice to cause tranformation to illite.

Robyn Johnston presented test data to illustrate that system pH may have a big effect on the end products. The presence of concrete will raise the groundwater pH, and a possible consequence could be cementation and embrittlement of a clay buffer due to the formation of zeolites, silica and/or feldspars. She emphasized also that fluid-solids concentrations and flow rates must be considered as well.

Dr. Dennis Eberl addressed the question of smectite to illite transformation. He has equations for three possible reactions. Because the reactions proceed in steps, it is difficult to predict long-term field behavior from short-term laboratory tests. He stated that transformations develop in nature at temperatures greater than 50 to 60°C. This is a considerably lower temperature than was suggested as critical by other Workshop discussors. The influence of pressure on transformations was also addressed by

Dr. Eberl. Increasing pressure is thought to favor formation of a more expandable phase. He concurred with the earlier conclusion by Dr. Weiss that trioctahedral clays are more stable than dioctahedral.

Dr. James K. Mitchell reviewed some physical, chemical, and rheological properties of smectites in seeking an answer to the basic question of the Workshop; i.e., can we rely on smectites for sealing of nuclear repositories? He identified four important behavior considerations:

1. Volume change properties
2. Stress-strain-time and strength properties
3. Conductivity characteristics
4. Durability and possible changes with time.

Of these 1, 3, and 4 are of greatest importance in the present problem. The need to consider both compositional and environmental factors in assessing properties was emphasized. Thus the placement conditions will have a major influence on properties of a clay in a repository. When considering the long-term stability of smectites for the nuclear waste containment application, the key question really is, does transformation matter? That is, will alterations lead to changes in those physical and chemical properties that are being relied upon for waste isolation?

Dr. Roland Pusch, the final scheduled speaker for Session II described the conduct of and presented some results from full-scale field experiments in the Stripa Mine in Sweden. In these experiments compacted blocks of Wyoming bentonite are used, and measurements are made of temperatures, water contents, and swell pressures as a function of time and location. Very useful data are being accumulated to help assess the practical consequences of prolonged heating and exposure to groundwater.

SUMMARY

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Swelling Pressure of Metabentonite and Cementation

The swelling pressure of a metabentonite sample from Kinnekulle has been determined investigating the material crushed smaller than 2mm, and the material after complete particle disintegration by ultrasonic treatment (M. Müller-Vonmoos, and F. Jenny, 1970). By ultrasonic treatment, the swelling pressure increased from 1.8 to 7.2 N/mm^2 at a dry density of 1.74 Mg/m^3, and from 17.7 to 42.3 N/mm^2 at a dry density of 2.02 Mg/m^3 respectively. Forces of particle disintegration by ultrasonic treatment are much smaller than swelling forces. Therefore, bonding forces of cementing material like free silica broken up by the ultrasonic treatment will not reduce swelling pressure of the metabentonite sample drastically. But the cementing material may reduce the water uptake by lowering the permeability.

Müller-Vonmoos, Max, und Jenny, Felix, 1970:

"Einfluss der Beschallung auf Körnung, rheologische Eigenschaften, Sedimentationsverhalten und Injizierbarkeit wässriger Opalit-Suspensionen".

(Schweiz. Mineralog. Petrogr. Mitt. Band 50, Heft 2)

SUMMARY

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Use of Dense Na-Smectite as Canister Overpack

Introduction

The Swedish KBS-3 multibarrier concept for the disposition of highly radioactive, unreprocessed reactor wastes implies that copper canister containing radioactive material be surrounded by dense Na bentonite clay (Figure 1).

The dense bentonite is applied in the form of blocks of highly compacted, granulated bentonite powder. The blocks, which are manufactured and trimmed so as to fit well into the deposition holes, are not water-saturated to start with. They take up water from the surrounding rock and this makes them swell and form a tight contact with the rock and the canisters. When they ultimately become saturated with water a considerable swelling pressure will be exerted by them due to their confinement. In this state, i.e. when the bentonite is in equilibrium with the surroundings with respect to the effective stresses as well as to the pore pressure, it forms a medium with a very low hydraulic conductivity and a low ion diffusivity. In addition to these valuable properties the dense bentonite is also self-healing in the sense that voids or local passages in the clay, caused by slight rock or canister displacements, will be sealed by the

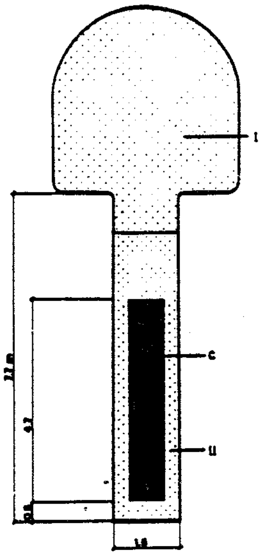

FIG. 1. Cross section of tunnel with deposition hole. Canister (C) containing highly radioactive wastes is embedded in highly compacted bentonite (II). The tunnel backfill consists of sand and bentonite (I). All dimensions are in metres.

swelling of the clay. Finally, the high ion exchange capacity means that the migration of radionuclides through the clay barrier after corrosion of the canisters will be retarded or largely hindered.

The swelling properties, the hydraulic conductivity, and the ion migration properties are largely determined by the physical state of the pore water in the dense bentonite.

Clay Material and Pore Water

Granulometry and Mineralogy

A commercially available granulated bentonite, the American Colloid Company type MX-80 (Na-Wyoming bentonite), was used to produce samples and blocks of highly compacted clay for the KBS-related research in Sweden. This clay powder is therefore the main KBS reference material. It is characterized by a clay content (<2 µm) of approximately 85%, and a montmorillonite content of about 80-90% of this fraction. Silt is the dominant remaining fraction, which mainly consists of quartz and feldspars as well as some micas, sulphides, and oxides. Wyoming bentonite is not a purely sodium-saturated clay; spectrometric analyses show that it has a content of about 30 ppm Ca, 15 ppm Mg, and 70 ppm Na in the pore water. Clay-adsorbed Na equals about 60 meg per 100 g, while the corresponding amounts of Ca and Mg are about 5 and 3 meg per 100 g, respectively.

The air-dry bentonite powder, which consists of silt and sandsized aggregates, has a natural water content ranging between about 8 and 14% depending on the air moisture. BET-analyses yield a specific surface area of about 700 m^2/g of MX-80 powder.

Water

In most tests the pore water used for water saturation of the highly compacted clay powder was a synthetic groundwater (called Allard's solution) with 65 ppm Na, 18 ppm Ca, 4 ppm Mg, 4 ppm K, 123 ppm HCO_3, 70 ppm Cl, 12 ppm H_2SiO_4, and 10 ppm SO_4 (pH~8). This is considered to be representative of the groundwater at 500 m depth in Swedish crystalline rock. In certain tests, distilled water and NaCl (0.6 M) and $CaCl_2$ (0.3 M) solutions were used for the water saturation.

Microstructure

The microstructure of granulated bentonite powder of the MX-80 type, as revealed by electron micrographs (SEM), is illustrated by Figure 2. The aggregates are strongly anisotropic and characterized by a very small interparticle spacing in the air-dry condition. By compaction under moderate pressures the overall particle orientation is largely random although,he detailed arrangement of adjacent particles is face-to-face, whereas at very high pressures the aggregates are forced together, resulting in large contact surfaces and deformation of the aggregates. In practice, the production of blocks will be run at 50-100 MPa pressure, yielding a bulk density of approximately 2.1 t/m^3 at a water content of 10%, which corresponds to approximately 50% water saturation. This compaction pressure does not cause any marked tendency of the individual particles to be oriented perpendicularly to the applied pressure.

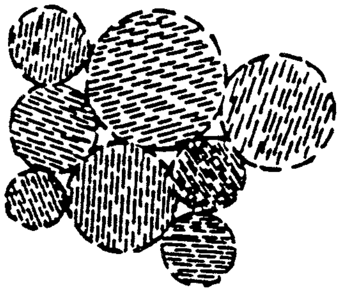

FIG. 2. Schematic microstructure of air-dry MX-80 bentonite powder.

When the bentonite blocks are exposed to water, as will be the case in the deposition holes in a repository, they take up water. In the course of water saturation the particle aggregates expand and most of the interaggregate voids will be filled by a clay gel formed by the expanding aggregates. Eventually, a condition of considerable isotropy and homogeneity with respect to the orientation and spacing of the montmorillonite particles will be reached at moderate and high densities. If no swelling of the blocks is permitted in the course of the water saturation, the final bulk density will be 2.2-2.3 t/m^3. In practice it will not be higher than about 2-2.1 t/m^3 since a certain amount of swelling, to fill joints, slots, etc. and to displace the tunnel backfill, will take place.

Mineral-Water Interactions

Physical State of the Pore Water

A large amount of energy is released on adsorption of the first 1-3 water molecule layers onto dry clay particle surfaces. This is partly due to the hydration of exchangeable cations but also, in the case of smectites, to the hydration of internal and external mineral surfaces. Substantial evidence has accumulated pointing to strong fixation of the first molecule layers. Thus, recent studies support the view that one or a few water molecule layers are firmly adsorbed at most silica surfaces. Studies of water in illite as well as montmorillonite have disclosed short spin-spin coherence times, which suggests high proton mobility and thus some degree of structural order.

As shown by Forslind, the fit between a montmorillonite lattice (preferably the Edelman-Favejee model, cf Figure 3) with hexagonal patterns of hydroxyl groups and a water lattice, should create ordered water-molecule layers over considerable distances. Forslind's theory logically explains the strong swelling potential and the development of high swelling pressures at high bulk densities.

There is no doubt that the mineral/water interaction is of profound importance as to the physical properties of clays, and since this interaction is largely different for various clay minerals, any change in mineral composition in the canister overpack needs to be taken into account.

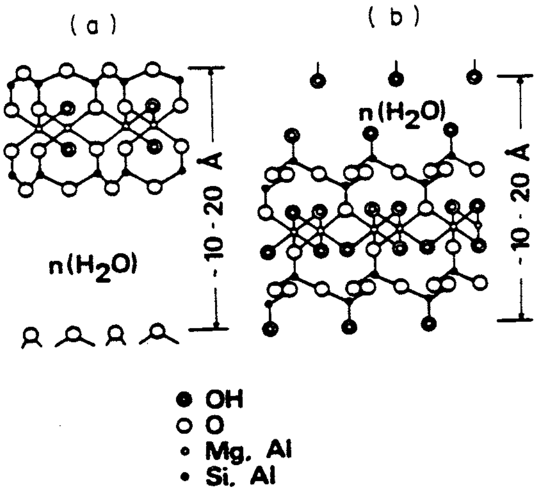

Fig. 3. Possible models of the montmorillonite crystal lattice: (*a*) according to Hofman, Endell, and Wilm; (*b*) according to Edelman and Favejee.

Stress Concepts

The conventional soil mechanical stress concepts hold for dense water-saturated Na bentonite although, the interparticle contacts in this type of clay are largely established through water films. Thus, the swelling pressure, which is developed through water-ion-mineral interactions, can be interpreted as a grain or effective pressure. The pore-water pressure, or rather the pressure of the liquid-water phase, can only be defined for larger voids that are more or less interconnected throughout the clay.

If highly compacted, water-saturated bentonite is allowed to expand, water will be taken up from the surroundings and there will be an underpressure in the water in larger water passages for as long as the expansion proceeds. If it is stopped, the water pressure in such passages will be entirely determined by external groundwater conditions.

Physical and Mechanical Behavior of Dense Na Bentonite

Water Uptake in Confined, Unsaturated Na Bentonite Blocks

If the boundaries of a confined block of highly compacted bentonite are wetted, water is absorbed and transported towards its center because of the suction potential, which is very high when the water content is low, i.e., for small interparticle distances.

In principle, the rate of water migration is therefore, governed by the potential gradient produced by the different average interparticle distance at the water front and in shallow, water-saturated parts of the block. This can be interpreted as a diffusion process where the concentration gradient is equivalent to a water-content gradient. A large number of tests, which will be briefly described in the subsequent text, have confirmed that this simple model can be accepted for practical purposes. The actual transient water uptake and migration, which is associated with a simultaneous microstructural reorganization is very complex.

Swelling Pressure

More than 90 experiments were performed in which the development of the swelling pressure produced by water uptake was determined (Figure 4).

A new swelling pressure oedometer was designed for these tests, the main principle being that its own deformations, and thus also the volume change of the sample were negligible (<0.1%) throughout the water uptake process and the measuring operations. The samples were prepared by uniaxial compaction of air-dry bentonite powder to various densities, and subsequent water uptake under confined conditions then started with simultaneous, intermittent determination of the swelling pressure. The diameter of all samples was 50 mm and their height was 0.5-50 mm, depending on the type of test. Wetting took place through one or both of the finely porous filters of stainless steel that confined the sample. Both ways turned out to yield practically complete water saturation.

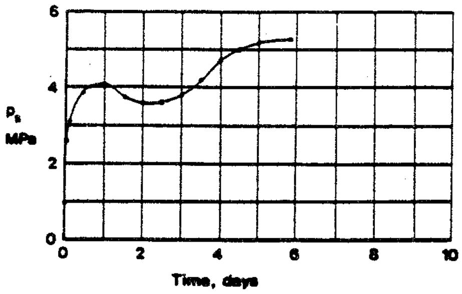

FIG. 4. Development of swelling pressure of a 20 mm thick MX-80 sample with an initial bulk density of 1.75 t/m^3 at 10% water content (ρ_{sat} = 2.00 t/m^3; distilled water; 20°C).

The rate of water uptake, or rather the time required to obtain complete, or practically complete water saturation was interpreted from the swelling pressure measurements. This was soon after the onset of the water uptake whereas the second was developed after a longer period of time, i.e., the time required to produce water saturation. The fairly high initial degree of saturation suggests that the phenomenon is not related to the hydration of different types of surface. The first peak is probably related to the energy of the elastic network of aggregates that is built in by the compaction, and to some extent to the pressure produced when the aggregates start to take up water while they are still strong structural units. The water uptake produces an increased interparticle distance that reduces the shear strength in the contact regions of adjacent aggregates. These are then easily displaced and deformed by the local stress fields, causing a relaxation after the first peak and thus a drop in the recorded swelling pressure. Further water uptake is associated with a redistribution of particles, by which the clay is transformed from an aggregated to a more homogeneous, dispersed state. A successively increased number of active interparticle bridges, acting as springs, is then formed; this increases the swelling pressure and eventually leads to a second maximum.

The successive redistribution of particles during and after the water uptake, leading to complete water saturation, is a time-consuming process at room temperature. The major part of this redistribution, causing internal self-healing, takes place within a few days or weeks after saturation. Complete equilibrium, however, may require several days or weeks and even at very high bulk densities there will always be certain parts of a clay element where the interparticle spacing is larger than average, and where the pore water is only insignificantly affected by the mineral lattices.

Figure 5 shows the swelling pressure of water saturated MX-80 bentonite plotted versus bulk density. Tests run with distilled water and Allard's solution gave values ("fresh") that are considerably higher than those obtained from tests with saline solutions ("salt"). Qualitatively, this is in agreement with electrical double-layer theories as well as with Forslind's water-structure model but, quantitatively, there is a large discrepancy between the experimental data and theoretically derived curves using double-layer theories, except for a narrow density interval. The essential fact is, however, the very obvious, unique relationship that exists between swelling pressure and bulk density when the latter quantity exceeds about 2 t/m^3, i.e., the lower boundary of the density range that is of primary interest to KBS.

Thus, neither the salinity of the pore water nor its composition seem to affect, substantially, the swelling pressure at such high densities. Considering the fact that 2 t/m^3 corresponds to the thickness of an average water film between parallel montmorillonite basal planes of 2-3 water molecules, depending on their coordination, the probable explanation of this phenomenon is that electrical double layers are not, or only partly, developed. According to the Derjaquin-Landau, Verwey-Overbeek (DLVO) theory the net repulsion force, and thus the swelling pressure, between Na montmorillonite particles is expected to drop when their distance is reduced from some 15-25 Å (1.5-2.5 nm) to about 10 Å (1 nm). The experiments instead give evidence of a greatly increased swelling pressure which suggests that the interparticle water complexes largely determine the swelling pressure. In this context it is worth noting that a 10 Å (1 nm) interparticle spacing corresponds to the decay width of steric stabilizing water structures on mica surfaces according to Derjaquin and Churaev and many others. The present swelling pressure study thus supports Low's conclusion that surface-water interaction is the primary cause of swelling pressures in Na montmorillonites.

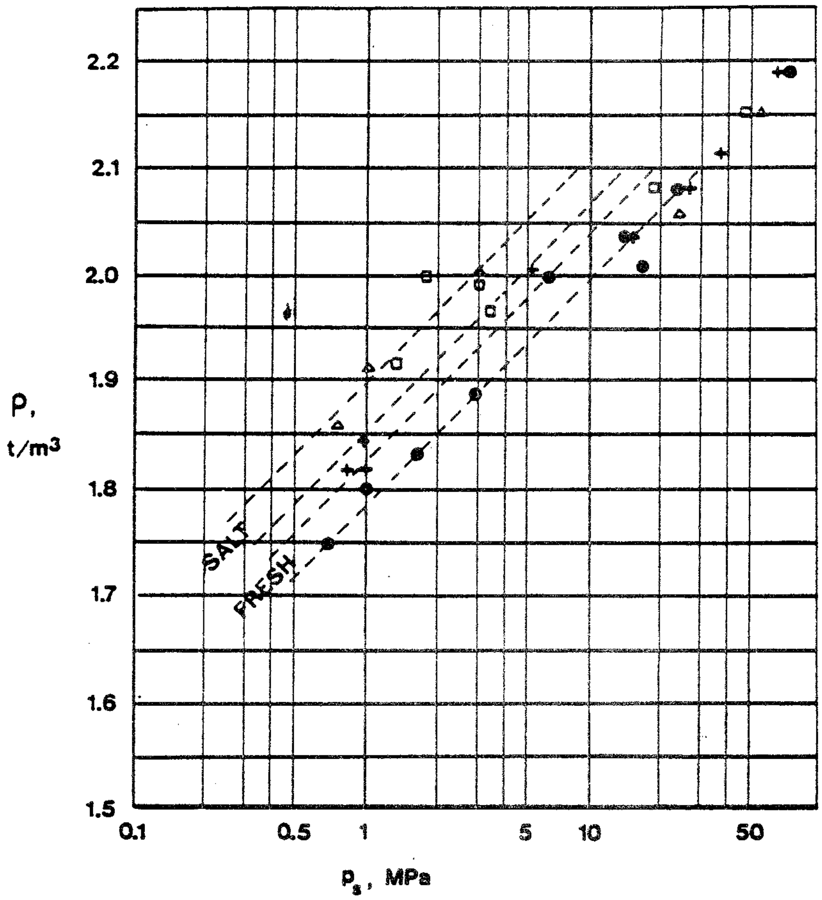

FIG. 5. Recorded swelling pressure of MX-80 bentonite at 20°C. NOTES: + artificial groundwater; ● distilled water; △ 0.6 *M* NaCl solution; □ 0.3 *M* $CaCl_2$ solution.

Hydraulic Conductivity

The swelling pressure oedometer, in which the sample is confined between two fixed filter stones, was used for the determination of the hydraulic conductivity of water-saturated clay samples, which were approximately 5 mm thick. The lower filter stone was connected to a cylindrical vessel containing pressurized, de-aired Allard's solution. In most tests the pressure was varied systematically so as to yield a successively reduced hydraulic gradient on the order of 10^4, 5×10^3, 2×10^3, and 10^3. Each pressure was held constant until stationary flow conditions were approached. The percolated water quantities were extremely small and the flow rate was therefore determined by observing the rate of displacement of a water meniscus in a calibrated capillary tube, the accuracy of the hydraulic conductivity being on the order of 5×10^{-15} m/s. The relationship between bulk density and hydraulic conductivity is illustrated by Figure 6.

The evaluated hydraulic conductivity was also found to be a function of the hydraulic gradient illustrated by the example in Figure 7. It confirms the observation of Hansbo and others that the rate of water flow through fine-grained clays often deviates from Darcy's law.

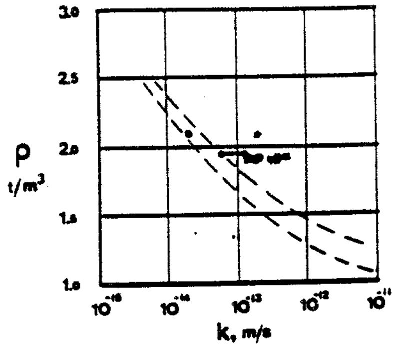

FIG. 6. Permeability versus bulk density of saturated MX-80. Dots represent 25°C, stars 75°C. Where two values are given for one and the same density, the lower represents the hydraulic gradient 10^3, and the higher the gradient 10^4. Broken curves are upper and lower boundaries of values derived from the literature.

Particle rearrangement through swelling cannot have been of great importance since the pore water chemistry was unaltered in the saturation and percolation stages. Erosion effects leading to particle migration are known to be important but probably only when the hydraulic gradient is successively increased, which produces clogging by the freed particles. Although such factors may have contributed to the observed gradient-dependence of the flow rate, it was probably caused by water viscosity anomalies in the author's opinion. While water flow through clays of low

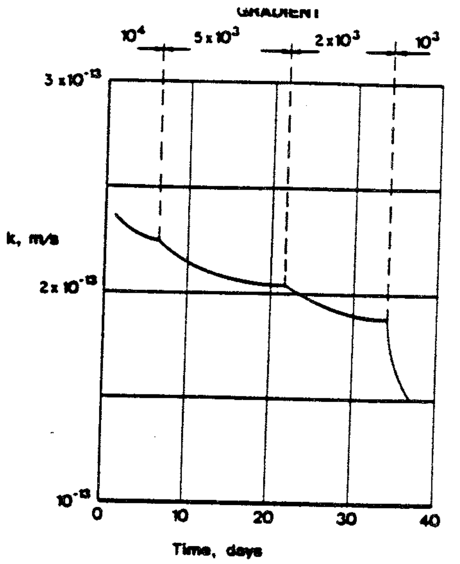

FIG. 7. Example of permeability test with smoothed curve for the coefficient of permeability *k* versus time after start of the test.

density can be considered as the motion of a fluid with a definite and constant viscosity, it should rather be regarded, in the case of dense bentonites, as a shear- induced displacement of a structured medium. This would be compatible with the idea of ordered or at least highly viscous vicinal water, with a drop in structural stability at increasing distances from the smectite mineral surfaces.

Diffusion of Radionuclides

The diffusivity of Sr^{2+}, Cs^+, and I^- was determined by using the swelling pressure oedometer with the bentonite sample being confined between filter stones, and kept in contact, at one boundary, with solutions containing the tracers ^{85}Sr, ^{134}Cs, and ^{131}I. The results from the experiments are still being evaluated but it is clear so far that the traditional pore diffusion model is not valid for Na bentonite with bulk densities higher than approximately 2 t/m^3. According to this model the radionuclide diffusion should be slowed down by a factor corresponding to K_d, which is a function of the ion-adsorbing power of the mineral phase. A higher diffusivity of I^- than of Sr^{2+} and Cs^+ would thus be expected but this is contradictory to the observations which have yielded diffusion coefficients of the order of 2×10^{-11} and 8×10^{-12} m^2/s for $Sr^{2+}$and Cs^+, respectively, and 2×10^{13}-4×10^{-12} m^2/s for I^-. The data seem to be better accommodated by a diffusion model where the positive ions can move within the interlamellar space, whereas anions migrate only in the larger continuous water passages. The diffusion coefficients arrived at are only a few percent, or less, of the corresponding coefficients for diffusion in free water.

Swelling and Self-healing of Na Bentonite

If a confined, homogeneous, water-saturated bentonite block is exposed to water and free to swell, it will do so. The swelling is caused by a water uptake that is governed by the same basic mechanisms as described previously for the transformation of unsaturated into saturated clay.

There are a number of practical applications for which the swelling ability is of great importance, such as:

1. The dense bentonite core of the KBS-3 concept is required to swell and fill up the space between the canister and the surrounding rock, so that homogeneous conditions and a perfect contact with the confinement is developed.

2. Boreholes in rock can be sealed by filling them with highly compacted blocks of bentonite in perforated metal pipes inserted in the holes. The bentonite takes up water, swells through the holes, and eventually forms a homogeneous mass that fills the hole completely and in which the pipes will be embedded.

The swelling capacity of dense bentonite is considerable, as can be concluded from test series using swelling pressure oedometers. A number of samples with a density of approximately 2.1-2-2 t/m^3 after saturation were allowed to swell to a predetermined volume and bulk density. At that stage they were confined and after 3-7 weeks the samples were extruded and investigated with respect to the distribution of the water content. This turned out to be remarkably uniform even for a sample that was allowed to swell an additional 35% of its original volume in one direction. Thus, this sample was divided into five equal parts that were found to have water contents of 41, 35, 35, 34, and 35 percent, respectively, after 7 weeks.

Conclusions

It is clear that the main physical properties of the dense smectite-rich canister overpack discussed here, i.e. the high swelling capacity and the very low hydraulic conductivity, make this material very suitable. However, if mineral alterations can take place in repository lifetime (10^6 years) under the ambient thermodynamical conditions, to what extent will the physical properties be changed? This workshop has provided reassuring answers in some cases but not in all cases: The question requires further investigation in these instances.

SUMMARY

Dr. R. Pusch and Dr. A. Jacobsson
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Aspects of Smectite - Illite Transformation

The present investigation of the transformation of smectite to illite conducted with advice from Professor D. M. Anderson, SUNY, does not imply any particular ion replacement process, except for K^+ -uptake in interlayer positions. This leaves open other reactions than those postulated by Howard & White ("Clay metamorphism: A natural analog for argillaceous backfill behavior") who state:

"The mechanism of illitization for smectite clays involves the substitution of Al^{3+} for Si^{4+} in the tetrahedral sheets and the creation of a negative layer charge deficiency along with the concomitant fixation of K^+ in the interlayer which balances the charge and collapses the interlayer space, expelling water."

There are several reasons for the assumption that significant Al replacement of Si might not be required. One is that there is no a priori difference between the crystal lattice structures; Grim (1953) has stated that only one-sixth of the Si are replaced by Al in the tetrahedral sheets. Another reason is illustrated by Velde's[1] proposed phase relation diagram (see "Figure 10 and 24"), which shows no significant difference in R^3 content ($R^3 = Fe^{3+}, Al^{3+}, Ti^{4+}$) while M is different ($M = Na^+$, K^+ and $2 \times Ca^{2+}$).

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1) Developments in sedimentology, Elsevier

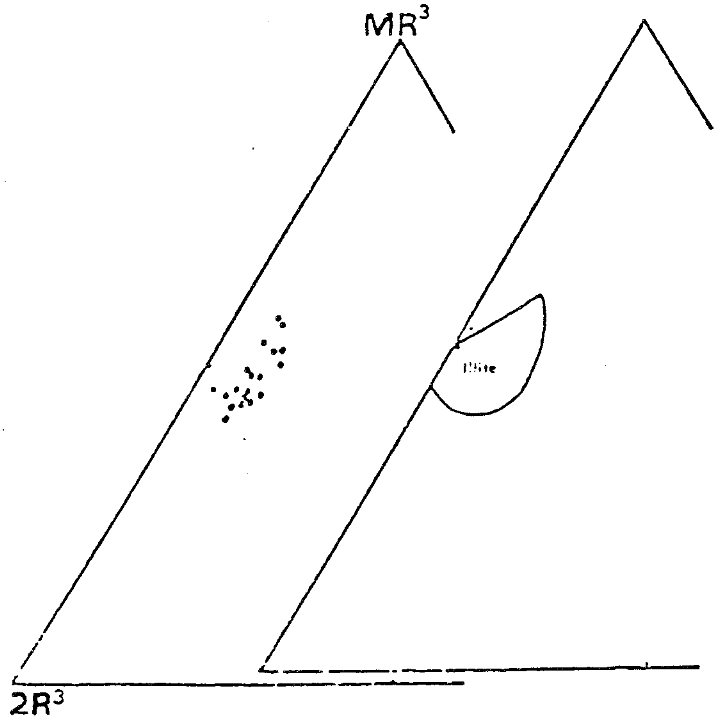

Fig. 10. Natural illite compositions plotted in $3R^2 - 2R^3 - MR^3$ coordinates.

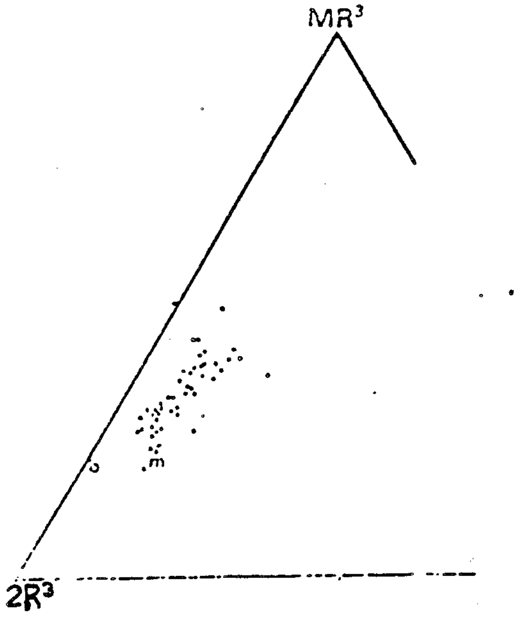

Fig. 24. Chemical compositions of natural fully expandable dioctahedral montmorillonite in the MR^3-$2R^3$-$3R^2$ coordinates. b = beidellite. m = montmorillonite.

Further indications of insignificant differences in Si/Al ratios between smectite and illite is offered by Krauskopf[2], who stated:

> "One of the ions most firmly held by montmorillonite is potassium, K^+, a big ion whose size enables it to fit snugly between layers of the clay structure. Clays which have a deficiency of positive charge due largely to substitution in the tetrahedral layers (hence close to the surface of the layers) hold the K^+ especially tightly, so that only part of it is replaceable by other ions. These clays, with successive layers held together by K^+ ions, have properties different from montmorillonite and are given the name illite. (The term hydromica, often used in European literature, is practically a synonym). The illite structure is transitional to that of muscovite, in which the amount of K^+ is greater and bears a constant relation to the amounts of Si and Al. The difference in structure between montmorillonite, illite, and muscovite may be symbolized by the ideal formulas.
>
> $AL_4Si_8O_{20}(OH)_4$ Montmorillonite
>
> $K_{0-2}Al_4(Si_{8-6}Al_{0-2})O_{20}(OH)_4$ Illite
>
> $K_2Al_4(Si_6Al_2)O_{20}(OH)_4$ Muscovite
>
> The term "illite", therefore, is less a name for a definite mineral than a name for a group of substances with composition intermediate between montmorillonite and muscovite. Recent work, in fact, suggests that much so-called illite is a mechanical mixture of fine-grained montmorillonite and muscovite, or a clay containing alternate layers having a montmorillonite and a muscovite structure. The name is convenient, however, as a general term to designate clay materials with less potassium than that corresponding to the mica formula."

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2) Introduction to Geochemistry

SUMMARY

(Outline of Informal Remarks)

Dr. Marc Wood
The Basalt Waste Isolation Project
Rockwell Hanford Operation
Richland, Washington 99352

- DEFINE FUNCTIONS OF BACKFILL MATERIALS
    - Regulatory Criteria
    - Characteristics of Site Geology
    - Engineered Barrier Design Concept
- DEFINE PROPERTIES OF MATERIAL EXPECTED TO PERFORM FUNCTIONS
    - Recommend Composition and Physical Properties (Density, Particle Size Distribution) Which are Required to Satisfy Functional Needs
- ENGINEERED BARRIER REQUIREMENTS
    - "Complete" Containment of Waste for 300-1000 Years
    - Controlled Release of Radionuclides (1 part in 10^5)
- BACKFILL (WASTE PACKAGE) FUNCTIONS IN A REPOSITORY LOCATION IN BASALT
    - Chemical Reactivity to Promote Moderate pH and Low Eh
    - Diffusive Control of Mass Transport
    - Sufficient Strength to Support Canister
- EXPECTED RESULTS
    - Minimization of Canister Corrosion
    - Minimization of Radionuclide Oxidation State and Solubility
    - Candidate Backfill Material

75% Basalt
25% Sodium Bentonite

- SUMMARY OF EXPERIMENTAL WORK
  - Substantial Reaction at 300°C in Hydrothermal System:
    - Reaction Products

      Bentonite → Albite & Qtz

      Basalt → Zeolite (Mordenite)+
      Fe-Smectite+
      Cristobalite ±
      (Illite & Fe-Hydroxide)

      Bentonite + Basalt → Zeolite
      Fe-Smectite
      Cristobalite
      Mixed Layer Clay?
      (Fe Enriched Bentonite)

    - Expected Dominant Reaction is

      Basalt Glass → Smectite + Zeolite + Qtz

  - Hypothesis:

    Illitization is not a Favored Reaction in the Basalt System

  - Irreversible Loss of Structural Water Between Dehydration Temperatures of 370 and 440°C
  - Hydraulic Conductivity Values of <1 x 10^{-8} cm/sec for Dry Densities of >1.7 g/cm^3
- PRELIMINARY CONCLUSIONS
  - Primary role of smectite is to provide and maintain low permeability environment around canister and waste form. Chemical properties are not particularly important (e.g., buffering capacity, ion exchange)
  - Geochemical environment in basalt (e.g., low K^t, Fe, low flowrate) is unlikely to degrade the favorable smectite properties through hydrothermal alteration.
  - Peak backfill temperatures can be engineered to eliminate irreversible dehydration of smectite, thereby avoiding the loss of swelling capacity.

PARTIAL TRANSCRIPT OF THE PROCEEDINGS

This partial transcript of the presentations and discussions was made from a magnetic tape recording of approximately 90% of the program. All participants have had an opportunity to correct or revise a draft transcript. This version includes all corrections and revisions that have been requested or suggested.

This material is included in addition to the summary statements provided after the conference adjourned in order not to loose the many insightful remarks and valuable observations and conclusions that resulted from this exceptionally stimulating and pleasant meeting. The reader is requested to be understanding of the informality and spontaneity that characterized this workshop.

SESSION I

Introduction: D. M. Anderson

Let me review the plan and the rules that we have thought you could agree to as we conduct this two day session. But first, by way of background, let me explain how we have all come to be here together. Some years ago, Roland Pusch and I met in Sweden when I was visiting at the Royal Institute of Technology. We became acquainted over discussions of mutual interest: smectite minerals. Over the years we have maintained contact over fields of mutual interest. As the Swedish government became interested in the safe disposal of nuclear waste, the Swedish Nuclear Fuel Company (KBS), the organization that took responsibility for this part of the program, established contact with some of the clay minerals experts and scientists in Sweden and in Europe.

This subject eventually began to be a topic of conversation between Roland and myself. We knew that there was going to be a time when we in the United States would also be talking about the same subject. We decided that we would try to bring some of the U.S. scientists into the picture. Initiatives were made by the Swedish Nuclear Fuel Company to accomplish this through meetings, various scientific organizations, and so forth. One of these initiatives was to sponsor a workshop at the State University of New York at Buffalo that would bring together half a dozen people rather quietly to consider some of the aspects that were of particular interest in the Swedish design for waste disposal. The proceedings of this workshop were circulated and finally published as a technical report by the KBS organization.

We have attempted to put this report in your hands as background material for this meeting. I am not sure, however, that all of you have received it. If I may I would like to ask by show of hands how many have seen this report. I see approximately half of us; probably the rest of you have it in the mail at your home or will receive it shortly. We have several copies here for those of you that would like to leaf through it as the workshop progresses and if for any reason you do not eventually get a copy when you get back home, please contact me and I will make sure that you do get a copy of this report.

Let me summarize the main purpose of that early workshop and the results. The central question was: Are smectite minerals stable enough to exhibit their favorable properties as a sealent and also as a plastic buffer material over a very long period of time in the environmental surroundings to which this material might be subjected to in the Swedish design for waste disposal? Now the Swedish design is a very conservative design, as most of you know. The basic design had already been reviewed by the National Academy of Sciences in the United States and by comparable bodies in other places. It was generally agreed that it is a conservative and quite safe design. Nevertheless, there was concern about the possible behavior of smectite minerals if the boundary conditions established in that design for temperature and pressure were to be exceeded, or if chemical species were to be inadvertently released or introduced into the smectite buffer material. So we chose as our original topic, the chemical stability of smectite minerals over long periods of time in varying temperature and pressure fields.

The discussions were narrowly focused on this and everyone in the workshop, held at Buffalo, agreed to restrict attention to this very simple and central question. After about two days of discussion and some computations, it was concluded that if the surrounding environmental temperatures did not exceed 100 to about 120 or 150 degrees, the transformation of smectite to illite would not occur in the interval of time envisioned as necessary for the performance of this buffer material. The diffusion of iron in and out of the buffer material from groundwater that might be circulating at rates that were considered to be possible in the granitic environment of the Swedish repository were also considered and found to be essentially negligible. We would like to hear today, of course, any second thoughts that may have arisen as to those conclusions and to carry this discussion a little further.

We would like to inquire during this two day workshop, in a more intimate and detailed manner, into the alteration processes that might be possible or expected under slightly different circumstances or more widely varying circumstances, and we would like also to pay particular attention to the question of process rates. I know, however, that because the fields of interest surrounding the occurrence and properties of smectites are large and interesting, we are going to have to discipline ourselves very strictly in order to stay on this topic and to the central question which is: Are smectite minerals suitable and reliable buffer materials for such an important and critical application?

To facilitate the discussion of this question and to bring us after two days, to a conclusion that all of you will feel comfortable with, we have decided to conduct our discussions in a semiformal format. It is not possible with our number to be totally informal. Neither are we going to be conducting ourselves in the formal fashion of a professional society meeting. We will not, in general, expect polished professional presentations. Instead, we are going to encourage everyone to speak in an informal manner, but trying to focus on the main point or the main conclusion of the observation or remark that you wish to introduce into the proceedings. Let us all try to speak directly and plainly to the central issues. Such direct statements, very likely, will evoke objections and possibly some argument from some of us around the table. But in the interest of making rapid progress and in narrowing differences of opinion in order to shape agreement and a consensus on fact, we would like you to adopt this style for today and tomorrow. The program is arranged so that in the beginning we will have general remarks on the smectite minerals and their characteristic behavior to set the stage. We will then turn, as quickly as possible, to more detailed discussions of possible alteration mechanisms, rates of alteration, and the resulting effects on physical behavior and properties. We hope by the end of tomorrow to produce summary conclusions. We also should identify the problems that we cannot agree upon, problems that are important to this inquiry but which at the present time do not have answers based on factual experience or data. These are questions and issues that require further consideration or further investigation and study.

You will notice from the program that most of you have been identified as taking a leading part in one or more of these sessions. The titles that have been chosen for you are not necessarily the titles that you would have chosen. Please feel free to deviate from this to the extent that you must to feel comfortable. We will have the chairmen for each session to intercede and limit a too lengthy discussion or to put discussions that wander too far afield back on track. We hope that this all can be done in a way that will be satisfactory to all of you.

Now, before I ask for the presentations to begin, I would like to introduce everyone. In alphabetical order, we have with us: Dr. Stephen Altaner, University of Illinois; Dr. Amos Banin, NASA-Ames Research Center; Dr. Anders Bergström, SKBF/KBS, Sweden; Dr. Ann-Marie Brusewitz, Swedish Geological Survey; Dr. Torbjorn Carlsson, Royal Institute of Technology, Sweden; Dr. Neil A. Chapman, ISMES, Italy; Dr. Dennis Eberl, U.S. Geological Survey, Denver; Dr. Rod Ewing, University of New Mexico; Prof. J. J. Fripiat, C.R.S.O.C.I., France; B. Fritz, Université Louis Pasteur, Strasbourg, France, Dr. Arne Gustafsson, Hoganas AB, Sweden; Ms. Robyn M. Johnston, Whiteshall Nuclear Research Establishment, Canada; Dr. Gunter Kahr, ETH Zürich, Switzerland; Dr. Fred Karlsson, SKBF/KBS, Sweden; Prof. James Mitchell, University of California, Berkeley; Dr. Max Müller-Vonmoss, ETH Zürich, Switzerland; Dr. Roland Pusch, The Swedish State Power Board, Sweden; Prof. Armin Weiss, Universität München, West Germany; Dr. Marc Wood, Rockwell Hanford Operation, Washington.

I am going to turn to Andres Bergström to begin our morning's introductory discussions. He will tell us a little bit about the significance of this workshop as he sees it, and some of the problems that he would like us to address. Next, we will begin our agenda and hear from each of you.

The beginning presentations were not recorded. The transcript begins with the remarks of Dr. J. Fripiat soon after he began speaking about the sensitivity of certain techinques of measurement: ...because they change with cation.

Dr. Fripiat:

You can get higher if you go from the sodium to the calcuim form, it does not matter. What matters is that with this technique which is more sensitive as I was telling you, after let us say, three statistical layers of water, you reach here a value which is exactly the surface energy of water. That means that it is a water-interface. That means, at the scale of the heat of immersion measurement, after three layers there is no more effect of the surface on water. So, one concludes that we are dealing with short-range forces, from the thermodynamic point of view.

So much for the unsensitive technique. Now, let's look what a sensitive technique would reveal. I pick up as an example here, that the deuterium relaxation rate (the inverse of the relaxation time) obtained for a suspension of Hectorite in D_2O. Here (Fig. 1) you have the mass ratio of clay over water. Very often people take the reverse ratio, so that means that you have almost 10 percent of ectorate in water, here 15 percent, there 5 percent, and you can see that we have been as low as .05 percent. First, as you can see you get a straight line, and this straight line extrapolates exactly at the value of D_2O. That means that in Phase A, what I have called pore water the dynamic properties of water are exactly the same as you would have in pure D_2O. In addition, the slope of this curve, and we could go through mathematical treatment but I don't think that's necessary here, is proportional to the volume of Phase B, the volume of the water on the surface, whatever the surface is. And now if we take the surface available to water obtained by the Harkins and Jura technique, which is the heat of immersion, and if we divide the volume of phase B by this surface area, we obtain the thickness of the water layers affected by surface forces. In that case, we are at exactly the same conclusion as that obtained from heat of immersion of measurements: it is between three and four layers. So that at two different scales of the energy domain, separated by seven orders of magnitude (I insist on that), you obtain the same answer. That means, that there is no more than, let's say three layers of water, i.e., 10 A thickness; and no more.

You will note that in spite of the apparent disagreement between this conclusion and the conclusion that Duwayne was stressing, the disagreement is just on one point. When you take any of the various properties, such as Philip Low is doing and you divide the weight of water by the total surface area, you get the wrong answer because the total surface area has nothing to do with the area which is available to water. I speak of the water which is in fast exchange with the surrounding water. By fast exchange I mean, the water which is exchanging very rapidly between the two phases.

I would like to give a number. I will give it in terms of the correlation time. The correlation time, which corresponds to the rotation and diffusional motion of liquid water at room temperature, is about 3 x 10^{-2} seconds. In phase B the correlation time is of the order of 10^{-10} seconds; in phase B it is somewhere between 10^{-9} or 10^{-8} seconds. I would like for you to keep in mind these numbers. You see that there are two orders of magnitude of difference between what I call free water, depending more or less on the diameter of the pore, as long as they are larger than about six layers of water. If they are smaller than 20 Angstroms, then you have an overlap of the B phases. If they are larger than, let's say 20 Angstroms, you get back to this value.

Now I would like to elaborate on these two points. First of all, I would like to talk about diffusivity of water in phase A, and again I say that we have performed these measurements on a very, very stiff gel. That means, for those working with clay suspensions, I am talking in terms of about 15% by weight of Hectorite in water. That's a stiff paste. You can hardly stir it with a spoon, you know, it's really very difficult. We have also worked with sepiolite which gives a very strong gel, some millions of centipoise. In this case we reached a concentration of 10% of sepiolite by weight. I would like to show some of our measurements, using the pulsed magnetic field gradient. Here is the calibration curve that we used. It is for pure water and shows the curvature which is so characteristic of water. It's a non-Arheneous behavior. You have super-cooling here and you can measure with the pulse field gradient technique, values from room temperature or higher down to about -30°C. Now, here we have the ratio of the diffusion-coefficient obtained in clay suspensions at different temperatures. These are the ratios of the observed diffusion-coefficient in this clay suspension to the different phase, to the diffusion-coeffient of water, pure water, at the same temperature. And you can see that we have used Gellinite, 65% Kaolinite, 12% Hectorite, 7% Lapponite and sepiolite, the average value here, considering the accuracy of the pulsed field gradient technique, is about 10 percent.

I would like now to show the effect of pressure and the effect of temperature. We have studied clay suspensions up to 5 K-bar. We have measured the relaxation time of both D_2O and H_2O. Here are the activation energies that we got for the rotational diffusion motion in Phase A. As you can see, within the experimental uncertainty, you are quite close to the 4.55 K-cal/mole, which are well known, even under high pressure. Phase B, however, gives a completely different picture. In phase B, as an average, you have an activation energy which is much less. This means, the strong hydrogen network bonding which is associated with liquid water is broken in phase B. There is no effect of hydrogen bombing on this correlation time. In that case, Duwayne and I are in agreement. In this limited space, about 10 Angstroms, the hydrogen network is completly destroyed with respect to what it is in water. But surprisingly enough, instead of increasing the rate of rotation of the water molecule, the rate of rotation of the water is much less, it is two orders of magnitude smaller. And you see, also, that the effect of pressure going from one bar to 5 K-bar has no significant effect on this surface, B, phase.

Now I would like, because this is the favorite subject of our chairman,and I say that on purpose because I think that you may be pleased to learn this, that we went to D_2O measurements below room temperature. There is a very surprising effect. When you go below freezing temperature, the only D_2O relaxation that you see is the D_2O associated with phase B. The D_2O in phase A doesn't show up. You can't pick up the signal, it's much too broad. But you can pick up the signal of water in phase B. Here you have the variation for 10 percent hectorite gel below room temperature. Notice the drop of the relaxation time going from just about freezing to the freezing point. You see that one gets a well defined minimun. Here is the relaxation rate obtained for D_2O in polycrystalline ice. This is pure D_2O. You see that the value for D_2O in phase B is completely different. This has nothing to do with the behavior of water in ice, since you are looking at D_2O belonging to phase B. An interesting point here is the following: you see the straight line here, this straight line was obtained in the one layer hydrate of Halloysite by Maribel Cruze, a few years ago. This is quite similar in behavior to the microdynamic behavior that you get when you have a large excess of D_2O in phase B. This means, the microdynamic behavior of D_2O in phase B of D_2O in the one area layer hydrate of Halloysite is quite similar except for one thing; the activation energy is very different from the activation energy that you get for the one layer hydrate of Halloysite. Here, the activation is of the order of 11 K-cal/mole. This is very interesting because in Phase B we are seeing that below the freezing point the activation energy was significantly lower than the activation energy in phase A. Why is the activation and energy of water in Phase B, below the freezing point, much higher? There are probably several explanations, but there is one explanation that we can suggest. It is that this liquid water phase which remaims on the surface doesn't make strong hydrogen bonds with the surface but it makes strong hydrogen bonds with the ice crystals.

Now I would like to come to the problem of smectite. Consider the tactoids, and here again, I will be very controversial. We have measured the surface area of smectite from very dilute to very concentrated suspensions. What we do, actually, is to measure the size of the tactoid. Surprisingly enough there is no change in size of the tactoid, if you keep the exchangeable cation constant. But I have to define exactly the experimental conditions. We did not take the fine fraction. We took the fraction below 5 microns; we didn't go to fractions smaller than .2 microns. In this case, the size of the tactoid doesn't change. But if you go from sodium to calcium, you change the size of the tactoid; with Hectorite you double the size of the tactoid when you go from sodium to calcium. Now, I know what will be your objection. What about x-ray data which shows expansion? Then my next question is what about the absolute measurement?

TABLE 2 - Comparison between the slope of the empirical equation (3) observed for 1 M KCl sepiolite D_2O suspensions and sepiolite suspensions in pure D_2O.

TEMPERATURE (K)	($KCl + D_2O$) (s^{-1})	(D^2O) (s^{-1})
299	16	15.7
279	19	18.7

TABLE 3 - Activation energy of the rotational correlation times in the temperature range 10-60°C for phase a and phase b in a kaolinite suspension (C = 1.65).

SOLVENT	PRESSURE	PHASE a (kcal mole^{-1})	PHASE b (kcal mole^{-1})
D_2O	1 bar	5.2	1.8
	5k bar	4.6	1.8
H_2O	1 bar	4.1	1.1
	5k bar	4.0	0.7

RATIO OF THE DIFFUSION COEFFICENTS OF WATER IN THE SUSPENSION (Ds) TO THE DIFFUSION COEFFICENT OF THE PURE LIQUID (D0) BETWEEN 328 AND 277.5 (±1) k°

SUSPENSION	TEMPERATURE	Ds/Do
KAOLINITE C = 0.65	328	0.74
	316	0.90
	304	0.96
	293	1.04
	283	1.10
	277.5	1.12
		$M = 0.98$ $\sigma = 0.14$
HECTORITE C = 0.12	328	1.09
	316	1.04
	304	1.15
	293	1.13
	283	1.33
	277.5	0.92
		$M = 1.11$ $\sigma = 0.13$
C = 0.07	316	1.13
	304	1.25
	293	1.36
	283	0.98
	277.5	0.87
		$M = 1.12$ $\sigma = 0.19$

SUSPENSION	TEMPERATURE	Ds/Do
LAPONITE C = 0.1	316	0.85
	293	1.05
	283	1.13
	277.5	1.31
		$M = 1.08$ $\sigma = 0.19$
C = 0.05	316	0.94
	304	1.04
	293	1.0
	283	1.08
		$M = 1.02$ $\sigma = 0.06$
SEPIOLITE C = 0.1	328	1.27
	316	1.20
	304	1.26
	293	1.
	277.5	1.04
		$M = 1.15$ $\sigma = 0.125$
C = 0.06	328	0.66
	316	0.64
	303	0.82
	293	1.0
	283	0.98
	277.5	0.86
		$M = 0.828$ $\sigma = 0.15$

What is the number of layers that are coherently separated by x-layers of water? You remember the work of Norrish showing that you can get a fraction of, let's say, 150 to 200 Angstroms. The problem is how much of the clay contributes to the 001 reflection. If the answer is 10% then I don't disagree. If the answer is 90% then I strongly disagree. And there is additional proof of what I say here. There have been neutron scattering studies of this and there is only one case to my knowledge where they report to have seen complete separation of the layers and that's in a Li-Hectorite, the very fine faction, smaller than 0.2 microns. In this case you get complete separation. In all other cases, one gets tactoids. I think that we have to consider a tactoid as a textural unit which is present in the suspension. When I say that it doesn't change, I mean that it doesn't change within a factor of two. You don't get unlimited swelling and you don't have dispersed clay in water, as you would expect.

Now, the problem is this: if there is no change in the water structure beyond 10 Angstroms and if the tactoids are there, why do gels form? What is the reason one can form gel, a strong gel? This is more relevant perhaps, to the purpose of this meeting. I think, but I have no proof, that the spontaneous hydrolysis of clay, and I emphasize that there always is hydrolysis of clay, produce enough of polymers of silica, alumina and so on, working as a glue, gluing particles together. This, of course, is very difficult to prove because we are talking in terms of very small amounts. But I would like to show that it's probably not directly related to charge. I am going to show here the extension numbers. Here are extension numbers of phase B, depending upon electrolyte content. This is for Sepiolite. Sepiolite is one of our favorite clays because it has no iron and it has a very high surface area available to water. It doesn't form tactoids. It is a tactoid by itself, of more than 500 m/g. Here you have a number which is proportional to the volume of phase B. It's the slope, actually, of one of the straight lines that I have shown. One molar Kcl more, no KCl, same slope. So there is no effect in the case of sepiolite, at least of the double layer extension on the aggregation. That is very good! I think that I have been extremely aggressive but I think that's the way to make some progress.

Dr. Anderson: I think we can see the possibility of sharpening our focus on one important point: the degree to which hydrogen bonding is an important factor. Professor Fripiat has presented some quite concrete evidence that we can discuss between sessions so that before the day is finished tomorrow, we may have something more definite to say about hydrogen bonding. Meanwhile, we have at least one or two more people who also should speak in this session; the session in which we shape the questions and lay the basis for a more detailed discussion of mechanisms, rates, and so forth this afternoon and tomorrow. I should like now to call on Dr. Eberl to give a brief presentation on a view that he has to present to us.

Dr. Dennis Eberl

This one (Figure 1-5) has to do with the interaction between smectite and canister and smectite in the wall run. We have heard this morning that it is very important not to have corrosive materials in the smectites, such as sulphide, etc., which can corrode the canister. I would like to make the point this morning, (I want to make sure my path is clear to run to the door if I have to), that smectite itself is a corrosive material. Here are some experiments we have done to prove this. Barite, of course, is a highly insoluble minerals but it does dissociate a little into barium ions and sulfate ions. This is a dissolution reaction that can be described by a solubility product.

If we put a smectite clay into this system, say a sodium clay, then barium being a divalent ion is preferred in the clay over sodium. So a barium ion will go in and replace two sodiums which come out associated with the sulfate and are quite soluable. So in addition to dissolution here, we also have an ion exchange reaction going on which can be described by the selectivity coefficient. Using this method of putting an ion exchanger such as bentonite into the system you can dissolve orders of magnitude more of an insoluble substance than you can if you just put the substance in the water alone.

We didn't discover this effect, of course, this has been known for a long time but we just had to look into it a bit more. Here's our perimental method. Into a centrifuge tube, we put a dialysis bag containing about 0.15 and 0.2 grams of clay. We put our barite powder on the bottom here, then added the water. We then shook it for anywhere between one and 54 days. We wanted to study this effect kinetically.

There are several ways of measuring how much barite has dissolved. One way is to simply measure the sulfate content of solution. That will give you a measure. Or you can take the clay out of the dialysis bag, dry it down, dissolve it and analyze it for barium. You can also study the amount of sodium that has come into the solution and get a handle on things that way. We did all three methods; they all gave the same answer for how much barite is dissolved. Here we see the milligrams dissolved in our system. This was something like 20 milliliters of water containing 150 milligrams of clay. In barite alone, 0.2 milligrams dissolved; in the case of barite plus sodium-Wyoming bentonite, 2.6. This is an order of magnitude greater. Then we tried several other types of Na-bentonite and observed the same sort of thing. But if you have a calcium bentonite, then the effect was very small. This is because for calcium, being a divalent cation, there is no preference really for barium over calcium in the clay interlayer. There is a little exchange but not like that observed in the case of a going in for a monovalent.

We then did it also for strontium sulfate, and you can see the effect here is fairly large. Now for this effect, as I said we studied it between one and 54 days, we found no difference between one day and 54 days. This suggests that equilibrium had been reached in one day or less. We then did a conductivity study where we have the log of time versus the conductivity of the suspension. As you can see the reaction was over in about 10 minutes, so it is a very fast effect. Now we calculated and measured the equivalent fraction of barium on the bentonite after the experiment. From thermodynamic calculations we could calculate what it should be based on the selectivity coefficient of the clay and the solubility product. This is a very simple calculation. The effect can be described by equalibrium thermodynamics pretty well, as you can see. The agreement is very close, considering we were using literature data for the selectivity coefficient to measure our own, except for the first value. So this is how you do the calculation: solubility product, selectivity coefficient, equivalent fraction, and you combine these equations and solve the resulting quadratic equation for the equivalent fraction of barium on the clay.

Now we also tried this experiment using copper, which bears directly on the point of this discussion. It turns out that Wyoming bentonite can dissolve copper quite readily. Now we did a preliminary experiment that probably should be repeated before we talk about it in public, but I'll tell you about the results of it. One gram of Wyoming bentonite in our experiments dissolved six milligrams of copper. Now to get a rough calculation based on that density of copper, the density of benonite and so on, it turns out that about a meter of bentonite can dissolve about a millimeter of copper. In our experiments we used distilled water. Of course, in changing the pH one changes things around a bit. Now since the container walls are going to be about 10 centimeters thick, this isn't very important with regard to breaching the canisters but about 20% of the exchange sites became saturated with copper. In other words, there is the possibility of changing a monovalent clay into a partly divalent clay, thus affecting its swelling properties.

Another thing that happens is that the copper tends to change the oxidation state of the octahedral iron in the clay according to some experiments by McBride. Here are a few more data on barite. I don't want to take too much time but if you plot the log of the ionic strength of the solution, assuming that all of the ionic strength is due to the sodium and sulphate or calcium and sulphate in the solution, versus the log of the milligrams of the barium sulphate dissolved, this is a theoretical calculation, you have one kilogram of clay and one kilogram of solution. This is how much can be dissolved just by the solution alone. This is how much can be dissolved if you put a kilogram of calcium clay in the solution. You can see that at some point it is several orders of magnitude more than the solution and the sodium clay, several orders of magitude more than just the calcium clay. You can change things by changing the ionic strength of the solution. You can alternately dissolve and precipitate barite. Probably the same thing would be true with copper. The log of the solubility product is plotted against the equivalent fraction of the cation on the exchanger. An equivalent fraction of zero means that the clay, you start with the calcium clay, the exchanger, an equivalent fraction of one would mean in the case of lead sulphate in the system that all of the exchange sites would be filled with lead. You can see that a sodium exchanger is more effective than a calcium exchanger. Let's take Anglosite, for example. This is plotted at 5 x 10^{-3} molar or something like that. You can see a calcium exchanger in this system would be quite ineffective in dissolving Anglosite, having only two percent or something of its exchange site full of lead. But with a sodium exchanger 80 to 90 percent of its exchange site would be filled with lead in this system. You can see that with siderite, the effect would be very minor. Siderite is so insoluble that you wouldn't get much iron moving into the interlayer.

We also did these calculations for feldspars. In this case we consider the clay acting on the canister. We also consider the clay acting on the wall run. We think that perhaps only the solutions are important for supplying potassium to the bentonite. Actually the clay can dissolve feldspar in the wall rock and change the potassium content of the clay. We show the equivalent fraction of potassium on the exchanger on the left here and the log of the sodium hydrogen ratio of the solution. Here K-spar is in equilibrium with quartz and these K-spar bars are in equilibrium with amorphous silica. Let's take a ratio of sodium to hydrogen of 4, for instance. You can see that if you have a amorphous silica in the system, a highly silicious system, you wouldn't get much of an effect. But if you have an equilibrium with quartz, then roughly 70 percent of the exchange sites on the clay would be covered with potassium. And muscovite is intermediate. The way these reactions were written the muscovite dissolution does not depend on the activity of the silica.

Here are curves for aluminum hydroxide. This could be gibbsite or it could be the octahedral sheet of clay minerals or it could be other aluminum compounds. These plots are for interlayer aluminum hydroxide or interlayer trivalent aluminum. Again, how much aluminum goes into the interlayer depends on the sodium hydrogen ratio of the system. If you get a high enough hydrogen-ion concentration or a low enough sodium concentration, depending on which curve you use, you can fill all of the sites and clay with aluminum and drastically influence the swelling property in the clay. The weathering reaction, the exchange reaction, using either trivalent aluminum which goes into the interlayer as trivalent aluminum or trivalent aluminum going into the interlayer as divalent aluminum hydroxide. Interlayer AL3+ involves solving equation and this is for interlayer ALOH. This is how the calculations were done. The shape of these curves has been shown to be right experimentally by Drs. Bach and McCauley who did some of these experiments about ten years ago. Clay can also dissolve radium out of mill tailings. That's all I have to say, for now.

FIGURES

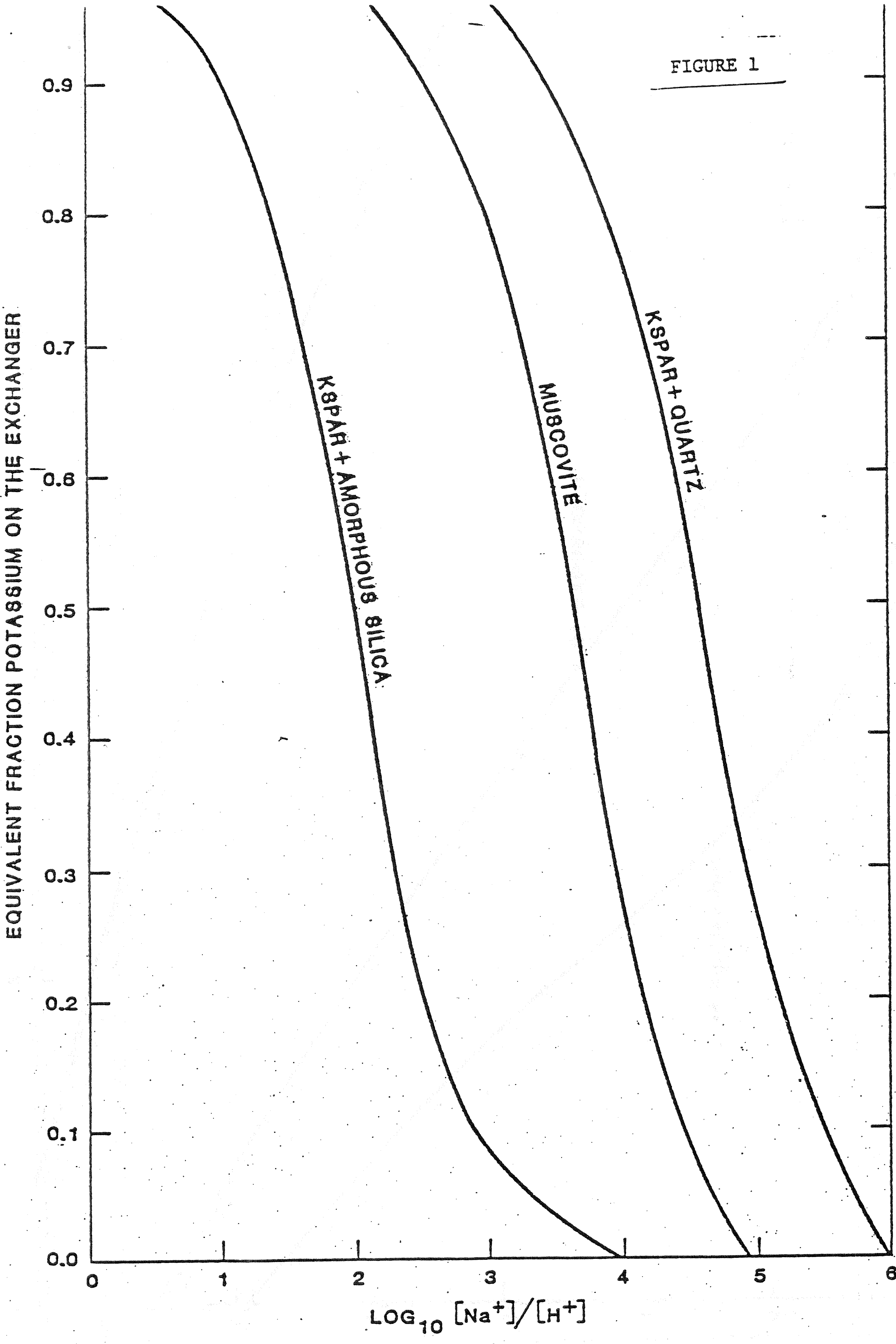
Figure 1. Equivalent fraction of potassium at equilibrium in an initially sodium-saturated montmorillonite as a function of the log of the solution composition for the dissolution of muscovite and potassium feldspar (KSPAR).

Figure 2. Log of the milligrams (mg) of barite dissolved by one kilogram of a sodium exchanger (eq. (16) and eq. (17)), a calcium-exchanger (eq. (13) and eq. (17)), and by one liter of solution only as a function of the negative log of solution ionic strength. See text for system composition. It is assumed that ionic strength is a function only of Na^+ or Ca^{2+} and SO_4 in solution.

Figure 3. Equivalent fraction of the cation from a divalent sulfate or carbonate on an exchanger at equilibrium for an initially calcium (eq. (13)) or sodium eq. (16)) - saturated exchanger as a function of the negative log of the solubility product of the salt. See text for system composition. Examples of sparingly soluble divalent salts are depicted at their solubility products. Solubility products are from Benson and Teague (1980).

Figure 4. Grams of barite dissolved at equilibrium as a function of cation exchange capacity and exchanger selectivity (K_C) for an initially sodium-saturated exchanger (eq. (16) and eq. (17)). See text for system composition.

FIGURE 1


EQUIVALENT FRACTION POTASSIUM ON THE EXCHANGER
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
KSPAR + AMORPHOUS SILICA
MUSCOVITE
KSPAR + QUARTZ
0
1
2
3
4
5
6
LOG10 [Na+]/[H+]

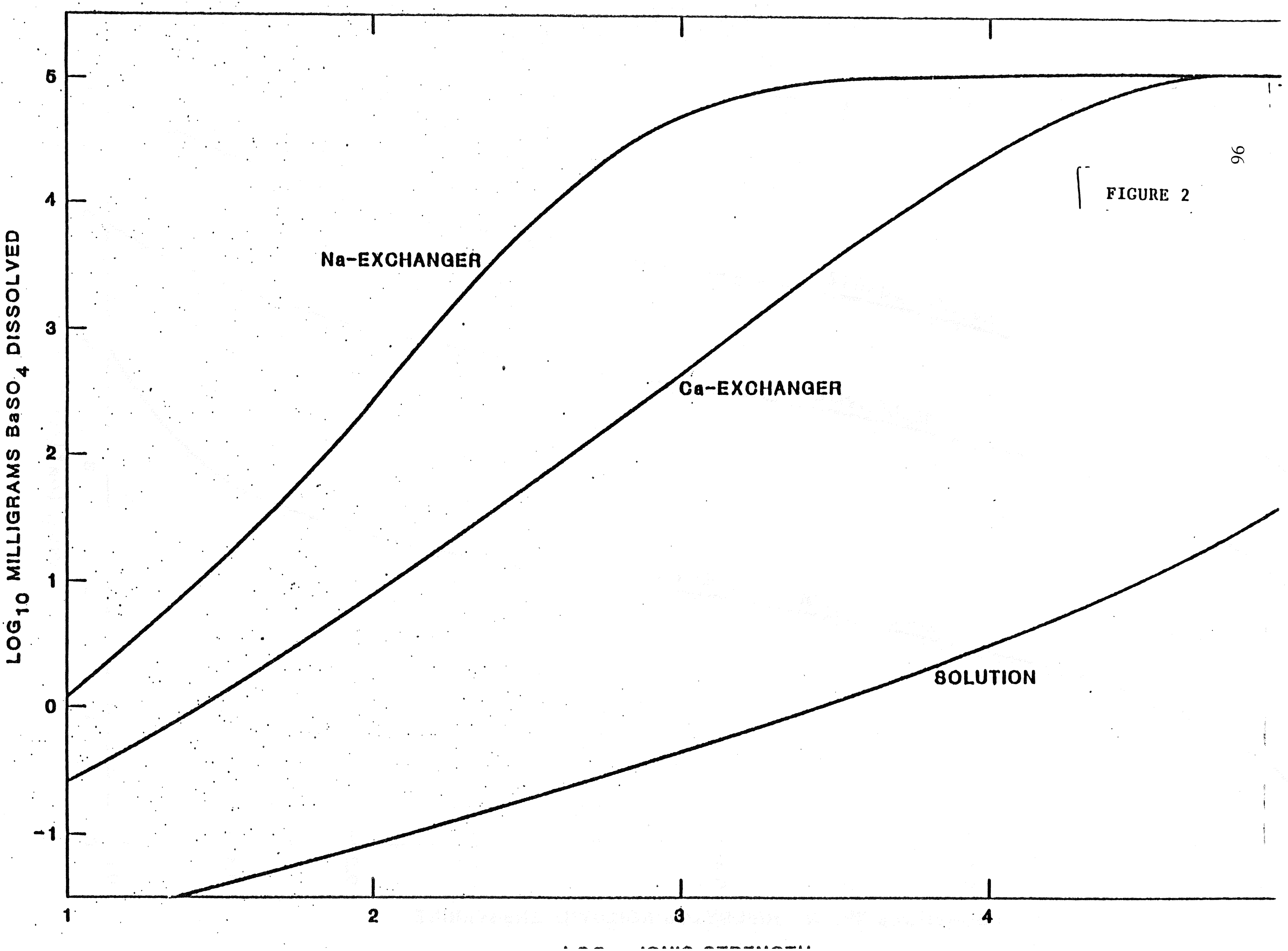


FIGURE 2

LOG$_{10}$ MILLIGRAMS BaSO$_4$ DISSOLVED
5
4
3
2
1
0
-1
1
2
3
4
Na-EXCHANGER
Ca-EXCHANGER
SOLUTION

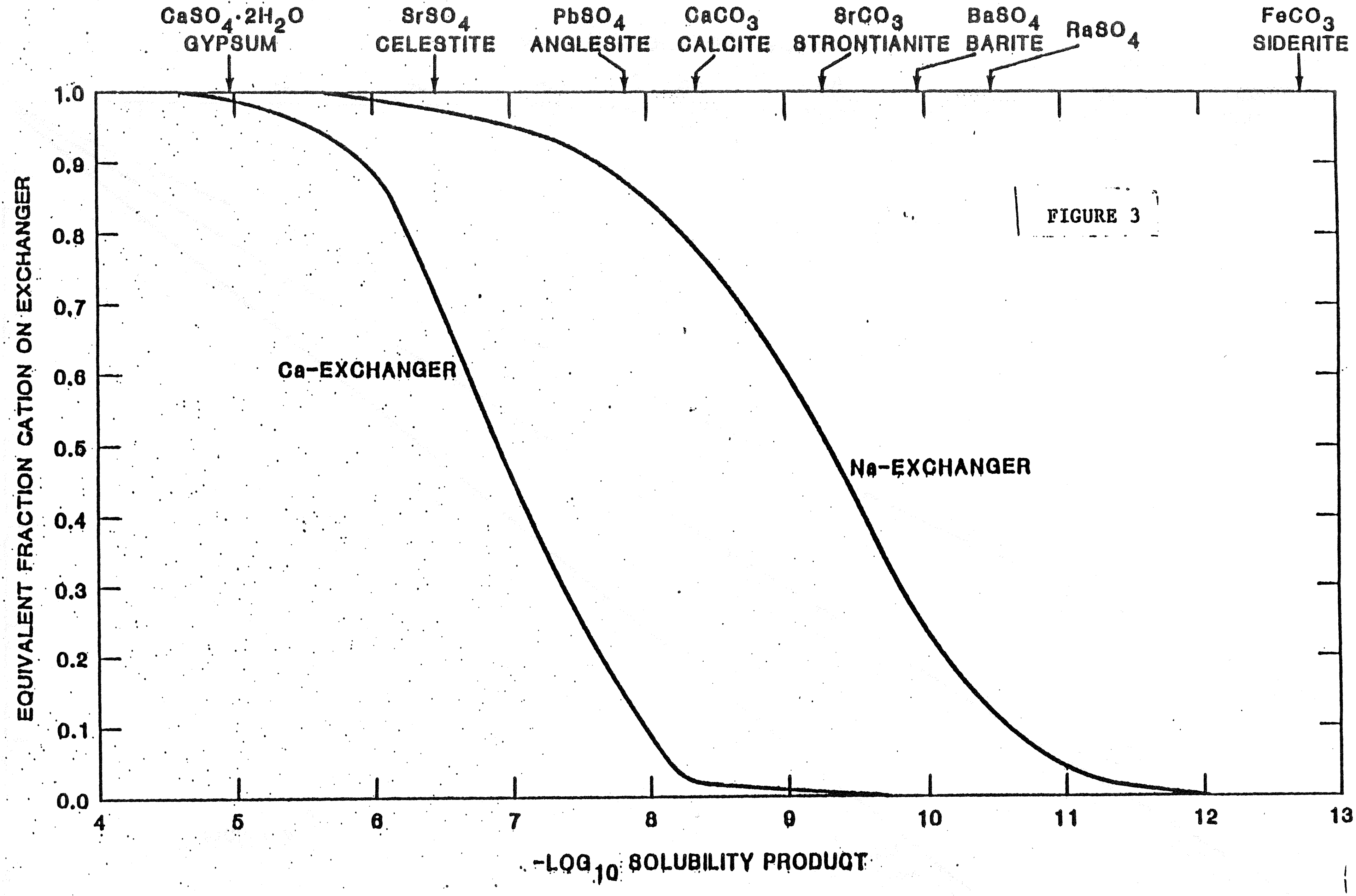

$CaSO_4 \cdot 2H_2O$ GYPSUM
$SrSO_4$ CELESTITE
$PbSO_4$ ANGLESITE
$CaCO_3$ CALCITE
$SrCO_3$ STRONTIANITE
$BaSO_4$ BARITE
$RaSO_4$
$FeCO_3$ SIDERITE
EQUIVALENT FRACTION CATION ON EXCHANGER
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Ca-EXCHANGER
Na-EXCHANGER
4
5
6
7
8
9
10
11
12
13
$-LOG_{10}$ SOLUBILITY PRODUCT

FIGURE 3

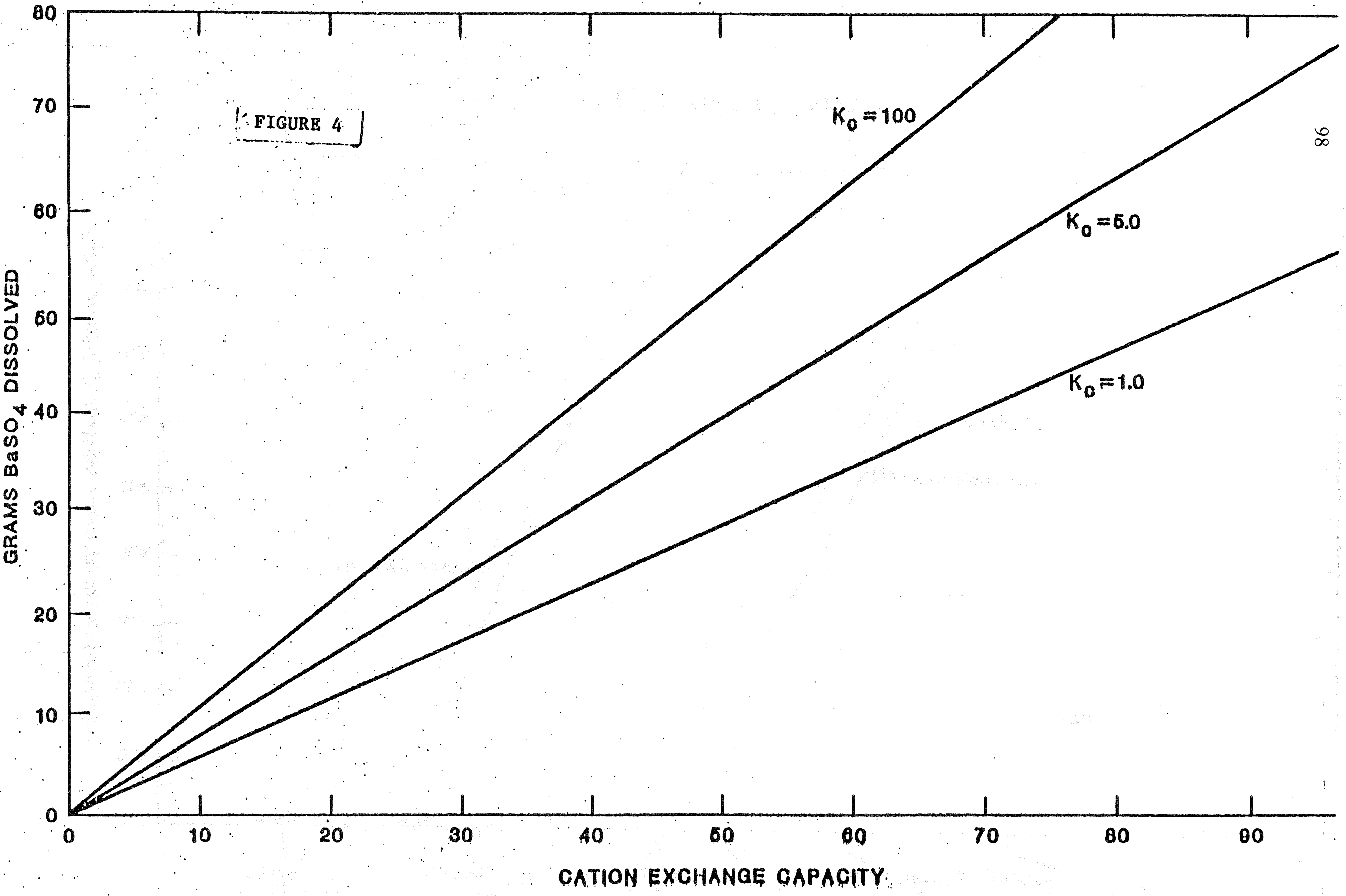
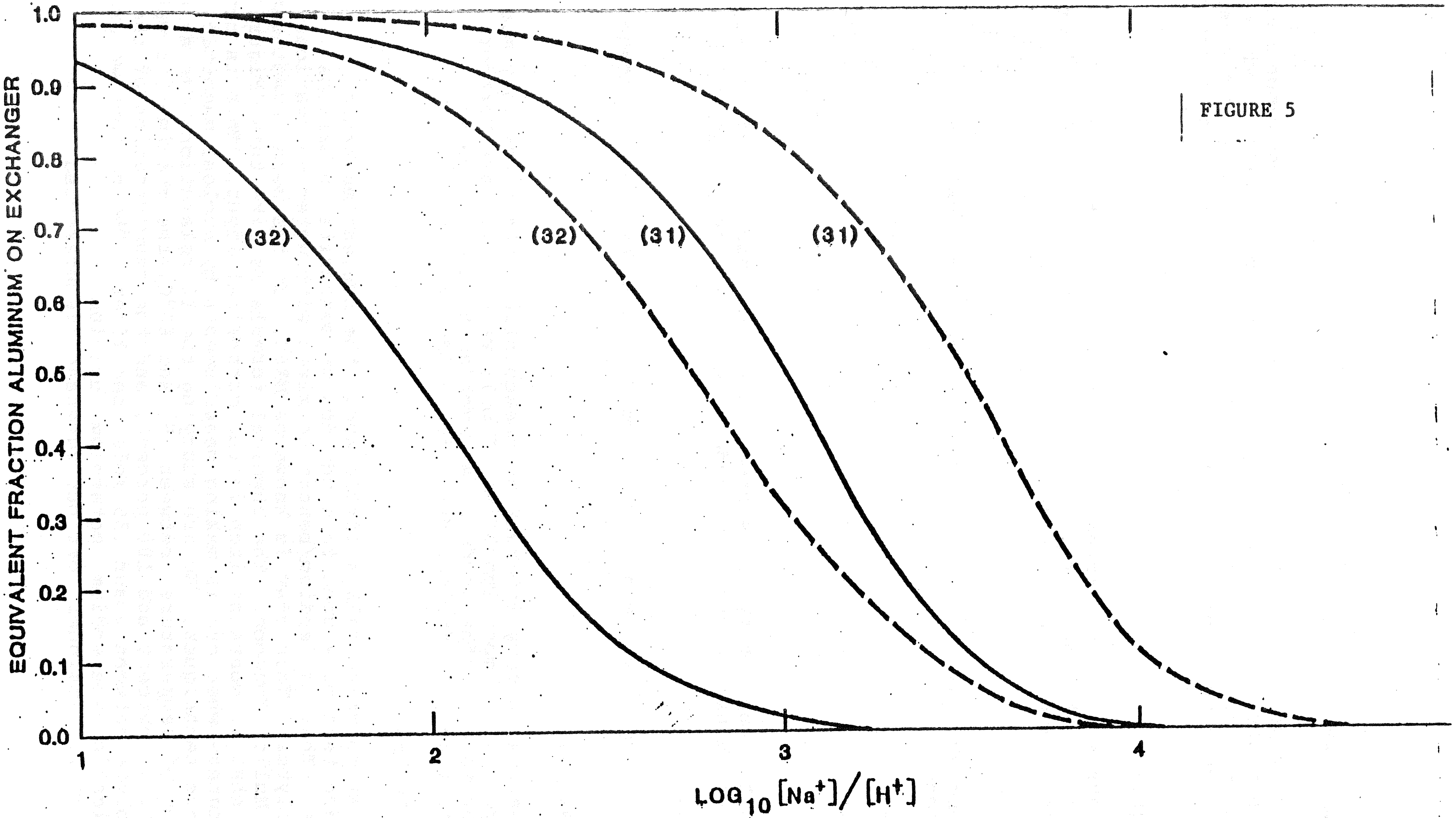

GRAMS $BaSO_4$ DISSOLVED
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
60
70
80
90
CATION EXCHANGE CAPACITY
$K_0 = 100$
$K_0 = 5.0$
$K_0 = 1.0$

FIGURE 4

FIGURE 5


EQUIVALENT FRACTION ALUMINUM ON EXCHANGER
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
(32)
(32)
(31)
(31)
1
2
3
4
$LOG_{10}[Na^+]/[H^+]$

Question: (Barely audible)

Your experiments with copper were done around room temperature. Do you have any feeling as to say in a repository situation where temperatures can be 100 or more degrees centigrade, do you have any idea if there would be more solubility of copper and exchange on the clay?

Dr. Eberl:

I guess it would depend on how temperature affects the oxidation of the copper and how temperature affects the dissolution of copper oxide. I don't know how that would be.

Dr. Weiss:

Were your experiments with copper done under reducing conditions?

Dr. Eberl:

No.

Dr. Weiss:

In the repository it is expected to have anoxic conditions then copper would have a very low tendency to react; do you agree?

Dr. Eberl:

If it is in the monovalent form, it would have less tendency to react.

Dr. Anderson:

That was a very interesting presentation; thank you very much. Although it is almost lunchtime, I believe we could ask Torbjorn Carlsson to say a few words in as much as he has also been experimenting with Nuclear Magnetic Residence techniques.

Dr. Carlsson:

I am going to talk a little about the nuclear magnetic resonence techinque used to study dosium-bentonite in various systems. That is, sodium/bentonite mixed with water and various electrolytes. This clay is known as MX80. It has been investigated by Dr. Muller-Vonmoos. The chemical formula is like this (Figure). We see that it contains iron in the octahedral layer. This is not so fortunate when one is making measurements by nuclear magnetic resonance techniques. We are studying the T2 relaxation time as a function of temperature, between 15° and 80°C, the gravimetric water content, 15 percent and 100 percent, and the concentration of the electrolyte between 0 and .35 moles per liter. The cations we are investigating are sodium, potassium, calcium or strontium...(remainder lost but substance is presented in the summary).

Dr. Banin:

"... exchange sites of the clay. This includes many ions not only those that are divalent or trivalent; it is the size that matters, not the charge. There are two exceptions: copper and lithium that are operating at a lower temperature. In this particular reaction the forces that we see resulting in the reswelling of the clay after heating, relates to the penetration of the organic molecules between the platelets. If the interaction of the platelets is strong enough, penetration will not occur. The interaction between the platelets is a result of van der Waals forces. But if they are negatively charged, there is repulsion. If a cation penetrates into the crystal structure as was described a short while ago by Dr. Weiss, it reduces the excess negative charge, thus reducing the repulsion, and collapse can take place. What we see here, and I leave lithium and copper out for the moment, is that for ions that tend to take a six-fold coordination, a temperature of about 300-400 degrees is sufficient to enable them to penetrate. First of all, their water of hydration is lost at a relatively low temperature between let us say 100 degrees and 200 degrees, then at temperatures above that to have acquired enough energy to penetrate into the existing structure of the clay, then they occupy the internal sites and collapse takes place.

For the larger ions, Sodium, Potassium, etc., or Calcium, Rubidium, etc., penetration will take place only after some dehydroxyation and rearrangement of the internal structure of the clay, about about 500 to 600 degrees. So it seems that using a graph like this, and this is the first conclusion I want to reach, one can extrapolate to the situation that may exist at elevated temperatures when other ions are present on the surface of the clay. For example, ions that might be released from a canister, such as cesium or strontium, on the one hand, or some of the lanthanides or actinides and so on, judging from their size they will mostly fall some place here. They usually have radii which is larger than one Angstrom unit. So they fall into this group and may collapse the clay at lower temperatures.

Now, I want to say something about the copper ion with regard to the situation that might develop in a repository. I plotted also the temperature of the beginning of the collapse. For lithium and copper the change starts at about 100°C. For the intermediate size ions the temperature has to reach higher values, say bout 200°C to around 300°C for collapse to start. For the larger ions collapse starts about where the temperature where the lattice actually changes. It seems, therefore, that there may be a situation near the wall of the canister because, as was said before, copper may be dissolved through ion exchange interaction that there will be some penetration of copper into the clay even at lower temperatures. This may be a factor that may affect performance in the long run. I noticed in a recent publication that there is a proposition to have a copper block in the holes. But that is a small point. So this is one point which I wanted to make.

Dr. Wood:

When you speak of collapse, does that mean you have irreversible collapse?

Dr. Banin:

This is a good question. I should say exactly what we measured. We measured the least swelling in ethylene glycol menoethyl ether. This is a polar molecule and may or may not be similar to water. However, from other experiments that we did, there were large similarities between EGME and water. In most cases EGME has more penetrability than water.

Dr. Wood:

The reason I am interested, is that we just completed a series of experiments in which we dehydrated the clays at various temperatures for periods of up to a year. We observed that when we dehydrated the clays from 250°C to 550°C, (sodium bentonite) we have complete loss of swelling and apparently complete loss of structural hydroxyl groups between 370°C and at 440°C. After a year of heating at 370°C we do see some reswelling. We also ran it with a differential scanning calorimeter, looking at the endothermic peak, and found that at 440°C there is no structural water loss; at 370°C there is still remaining structural water.

Dr. Banin:

I expect that if your diagnostic problem belongs here, but with some smaller ion, the whole process would start at a lower temperature because, as I said, here we actually applied a shock of several hours of heating and reheating. You are talking about a situation where you heat or reheat for a year. That may be a different situation. I would speculate that the relative behavior would be the same.

Dr. Anderson:

You have suggested that copper from the canister might become a problem by a reaction of this sort. Could you suggest a way of estimating whether or not this is a serious problem? For example, could you estimate how rapidly the alteration front would move outward from the source of the copper in terms of the exchange capacity or the charge in imbalance perhaps?

Dr. Banin:

Well, this is really tied up to another problem that I wanted to discuss later on, namely the interaction between sodium and calcium in terms of exchange. I would say leaving other chemical considerations aside, which may be an oversimplification but just let's do it for the time being, we can took at copper as a divalent ion that in solution behaves similarly to calcium when it competes with sodium. So we actually look at an advancement of an exchange front of a divalent ion in this case copper, with sodium clay, assuming that sodium clay is the clay being used. So there it is limited really by the amount of copper that is released not by the advancement, not by any diffusion process because I would think that the rate limiting step would be the dissolution of copper from the canister. So the question really is how weak is the dissolution of copper from the canister. Once it is dissolved, it shouldn't take a long time at all for it to propagate through.

The second point that I want to make relates to the swelling of mixtures of smectite with kaolinite. Let me clarify the thinking here. We were faced with a similar problem in trying to develop materials which would be economically useful for the sealing of ponds. There are some resemblances between that problem and the problem that has been presented here. The main factor there is economical considerations which may be stronger than here, but the problem is here. Still, the mechanical, physical and chemical properties that we are looking for were about the same because we wanted to develop an impermeable layer which would not have a large shrinkage during cycles of swelling and reworking. For that purpose we used three different smectites mixed with kaolinite. I will show, if I can get the first slide, the result. What is shown here is just a simplified map of the mixtures containing various proportins of kaolinite. This is 1 percent, 5 percent, 10 percent of kaolinite, excuse me and this is 100 percent kaolinite. We see the changes in swelling, freeswelling, of montmorillonite when it is mixed with kaolinite. We wish to see if there is any interaction between the two components. You see results from a swollen clay after it was dried and shrunken. There is a large change in volume simply because swollen clay was Wyoming bentonite containing 5.5 grams of water per gram of clay. When this water was lost, there was a large reduction in volume. And then as we change the content of kaolinite, there are swelling and shrinking changes. As we go through the three grades of smectite, the bentonite being a sodium bentonite, highly swelling, two Corsica bentonites which are rather similar to Wyoming bentonite but which swell less and, finally two local clays from Israel, which are very low in swelling compared with these other two. When we put together the data on these experiments, we see that there is really very little interaction. If you look at this, the percent of kaolinite, try to read this, because it's really not readable, against the swelling; this is for Wyoming bentonite, Corsica, and Roman bentonite. Kaolinite alone swells to about 1 gram per gram, and it is mostly inbibition and not swelling. The main point I want to make is that when you mix these clays you get very little interaction. This is shown by the fact that there is a straight line which connects the 100 percent smectite with the 100 percent kaolinite showing that there is no interaction when the two are mixed. My point, in relation to what we are discussing here, is that maybe in some cases one does not need the high swelling of pure sodium montmorillonite. Maybe by using mixtures of low quality montmorillonite the operation might become much simpler. And, the main point is that when you mix these clays, their swelling abilities are simple composites which depend on the mixing ratio and the singular swelling ability of each component.

This is different from what is observed when you mix sand and clay. I think the difference is mainly to do with the different particle size distribution where you mix sand and clay. Usually, you have a very large difference in particle size distribution between the sand and the clay. Using kaolinite you can have a low swelling component with a size distribution which is much more similar to that of the swelling component. This might be an interesting point to pursue.

Now the last point I want to make relates to a question raised during the presentation this morning. I believe somebody mentioned that they have to make a selection between a sodium clay and a calcium-magnesium clay. I think the problem in Canada had to do with the ground water containing high concentrations of calcium. I just want to point out from experience it's relatively easy to predict what will be the percent of absorbed sodium after equilibration with a certain solution using the SAR (Sodium Absorption Ratio). Usually there is a relationship of about 1-to-1 between SAR and the same absorbed sodium after equilibration. Judging from the data that was shown this morning, the SAR of the water and the groundwater there is about ten. This means that it will take a long time for 34 of those layers of clay that directly interact with the water (and there is here a question of diffusion and mass flow through the plug). It may take a relatively short time for the material to come to a equilibrium with high salinity water. Then the sodium clay would actually become a sodium-calicum clay. So it really is a question how one should go about using a sodium clay, with all the difficulties that may arise economically, in a situation where it is quite likely that it wouldn't take long before it would be exchanging and becoming a calcium clay. Now this may be a very slow process when the type of compound clay that has been describe is used. In this case, the flux of water through the plug may be slowed down considerably. Probably a more careful calculation has to be done to see what time scale is involved before such a change would occur. This would have to involve the total concentration of the ground water. If it is a brine it is one situation; if it's a much more dilute concentrated situation its a different situation.

Dr. Mitchell:

Now we are going to consider smectite-illite, transformation rates and mechanisms should be most illuminating. We will now hear from Dr. Brusewitz.

Dr. Brusewitz:

The title given is somewhat misleading. "A preliminary report on Swedish potassium bentonites" is more relevant. Many may have heard of the name Kinnekulle in connection with illite/smectite minerals, of which some of the very first were collected at this place in an Ordovician bentonite bed. Thanks to the interest in these minerals by, for instance, D. M. C. MacEwan, and John Hower and coworkers, the name Kinnekulle appears quite often in the literature. It originates from a hill, rising prominently in the landscape some 250 m above the surroundings. The hill is built up of Palaeozoic sediments covered by a diabase cap shielding the underlying sediments from erosion. There is a similar area 30 km to northeast, but larger, namely Billingen. The first figure shows a map of Scandinavia, where some Palaeozoic sediments have been marked - Kinnekulle (K), Billingen (B), Skåne (Sk), and Gotland (G) - which are interesting in this connection because they all have bentonites of Ordovician age. Silurian bentonites are also present in all of the localities except that of Billingen. The chief minerals of these bentonites are now illite/smectities of various compositions.

Figure 2 shows a part of the Billingen area. Two bore holes have been marked, 4.5 km apart, from which samples were collected. In the upper left corner a schematic profile shows the bentonite zone as a horizontal black streak in the surrounding calcareous shale.

The ash fall giving rise to the bentonites occurred about 450 My ago. The diabase was intruded around 300 My in Permo--Carboniferous time. The intrusion made contact at different levels at Kinnekulle and at Billingen as will be seen from Figure 3. The major part of the Silurian is preserved at Kinnekulle, whereas at Billingen the minor part remaining of the Silurian has been strongly affected by the intrusion and shows signs of metamorphosis. The thick bentonite bed (about 2 m) occuring at both localities in the middle Ordovician strata is considered to belong to the same ashfall. At Kinnekulle there are 90 m between this bed and the diabase. At Billingen the corresponding distance is half this value or smaller, depending on where the bore holes have been placed, e.g. 42 m in hole 15/73, and 36 m in hole 16/74. The distance of the bentonites to the diabase seems to have been very important for the geothermal conditions, and thus for the extent to which smectite alteration to illite has proceeded.

In the next figures (Figures 4, 5, and 6), I have compiled some of the chemistry. At Kinnekulle the Silurian layers, 30-40 m below the diabase contact, have a high potassium content and the clay mineral is nearly illite, with less than 10% smectite units.

The bentonites are very thin. Looking at the thick bed, referred to as the B-bed, some 60 m further down in the strata, we have an interesting, successively diminishing potassium content from the top of the bed (4%K_2O) towards the middle part with 2.4%K_2O, corresponding to an increase in smectite proportion of the interstratified minerals. In the lower part of the bed the smectite proportion does not seem to change in a similar way towards the lower boundary, but remains quite constant as judged from XRD.

Just above the B-bed there are two thinner beds, A-beds with K_2O around 5%, having a nearly ordered structure. They have not been included in this study. Below the B-bed there are a number of bentonite beds, varying in thickness from a few centimeters up to one meter, the so-called C-beds. Samples from these beds were collected from the Kullatorp core, drilled in 1946. The A-beds and the upper part of the B-bed were sampled at the Stora Mossen excavation in 1955, and the lower part of the B-bed from the KBS core, drilled at Stora Mossen in 1982. The C-beds have a potassium content between 4% and nearly 6%, and a correspondingly higher illite proportion. The stacking is more ordered the higher the potassium content. It is obvious from these C-layers that the thickness of a bed strongly influences the degree of alteration.

Figures 5 and 6 show results from the Billingen cores. The temperature, as mentioned earlier, definitely has been higher than was the case at Kinnekulle. The smectite proportion is around 18-20% at the thick bed of core 15/73. There seems to be a tendency to somewhat lower proportion at the two boundaries. The other Billingen core nearer to the diabase contact shows only 12-15% smectite units and good ISII stacking order. In addition to chlorite from biotite alteration, there seems to be a chlorite of authigenic type present, richer in aluminium. Kaolinite is present in nearly all samples at both localities.

The results of the chemical analyses of Kinnekulle have been plotted on a triangular diagram in Figure 7, where the progresive changes in tetrahedral and octahedral charges may be seen. The circles, which refer to the thick bed, fall in a cluster. The two top samples lie in the direction of the more illitic samples, with a higher proportion of aluminium in both the tetrahedral and the octahedral sheets. By presenting the data in this manner, the total layer charge appears quite constant, as there is no distinction between interlayer charge due to potassium and that due to exchangeable ions.

The next figure (Figure 8) shows more clearly the relationship between tetrahedral silicon and interlayer potassium. The line has been calculated by regression analysis from Kinnekulle samples only. Results from other bentonites have been plotted, and the values fall close to the line, which for zero potassium corresponds to 3.95 silicon at the intercept. This is a clear indication of the montmorillonite character of the smectite unit rather than beidellite as has sometimes been stated.

Calcium is the chief exchangeable ion, contributing about 75% of the total cation exchange capacity (CEC). Magnesium constitutes the remaining part. A minor amount of strontium follows calcium. The next figure (Figure 9) shows the relation between total content of Sr in ppm in the <1 μm fraction and the CEC. The relationship is reasonably linear, indicating that strontium occurs chiefly as an exchangeable ion, being lost when the layers close up due to potassium fixation. Figure 10, a plot of log ppm Sr versus atom % K, is consistent with this conclusion. An increase in potassium leads to a decrease in strontium. The Kinnekulle B-bed samples and those from the C-beds fall on separate lines; this may be a result of the composition of the original volcanic ash. The Billingen B-samples, however, fall in with the Kinnekulle C-bed samples, which is more difficult to explain as the two thick beds always have been considered to originate from the same ashfall.

Figure 11 gives an indication of the crystallinity of the I/S--Structures. The XRD-curves have been run from non-oriented mounts of a few typical samples. The similarity of the curves for the relatively wide range of potassium and thus of smectite units is notable. The top curve is from the very illitic sample, K6, with 8%K_2O. This sample shows general reflections that are somewhat more distinct than the more smectite rich ones, but still the pattern indicates poor crystallinity. The temperature does not seem to have reached the stage where the structure can be reorganized in a well crystallized form.

Although, we understand the smectite to illite reaction to some extent, we do not know the details, nor can we say anything really definite about reaction times and temperatures. To penetrate somewhat more into these problems, I have used the K/Ar technique. Runs were made of the <1 μm fraction of seventeen Kinnekulle samples and of three from Billingen. The Billingen samples were run also as "whole rock" samples. Prior to the extraction of argon, the samples must be "cleaned" by baking to remove air, moisture, etc. Normally, the baking temperature is held around 260°C for one to two days. Trial runs were made to determine whether Ar^{40} was lost at this temperature. By successively lowering the baking temperature to 90°C, it was found that there was an appreciable loss, especially above 200°C for the samples with a higher proportion of smectite. The Silurian samples with nearly pure illite do not seem to have been affected in the same way, which is not surprising, as we know that these layers already were subjected to temperatures around 300°C according to conodont studies by Stig Bergström (1980). For the more smectite rich samples, baking at 170°C shows only a minor loss in comparison to baking at 90°C. Thus the values obtained at the lowest baking temperature may be considered to be comparable.

In Figure 12 extracted Ar^{40} has been plotted versus approximate baking temperature. The calculated age is given at each point. Looking at the Kinnekulle thick bed data (90°C-baking), a decrease in age will be observed from the top sample at 336 My to a sample in the middle of the bed at 300 My. If the ages represent potassium fixation, 36 My would have been the time of potassium transport from the top of the bed towards the middle, a distance of about one metre. According to studies of Montana bentonites, similar but younger, Steve Altaner has found a time span of 3 My only, for a similar distance. Thus local conditions of the potassium potential and of temperature must be decisive for how the smectite to illite reaction proceeds. Determinations by the 39/40 Ar ratio evidently give more reliable age data, free from the influence of argon loss or relict argon.

In Figure 13 the ages have been entered at the sample levels to give better survey in relation to geology. As memtioned above, the Kinnekulle Silurian samples all show ages around 300 My, as do also the samples from Billingen, irrespective of the sample type - <1µ m, "whole rock", or diabase. These bentonite samples all have a distance to the diabase of 30-40 meters. The intrusion has had a strong enough influence to reset the K/Ar clock at these levels. The Ordovician Kinnekulle samples at a lower level have been less affected by the intrusion, and the ages shown most likely depend on a combined effect of an earlier, slow potassium infiltration that ended with the diabase intrusion. The fact that no age less than 290 My has been observed, must be an indication that the illite reaction has stopped at this time and that no further alteration of the smectite units has occured.

In conclusion, it can be stated that first of all potassium must be available for illite to form from smectite, and that then the temperature governs the speed of reaction, which most likely below 100°C is very slow or even negligible.

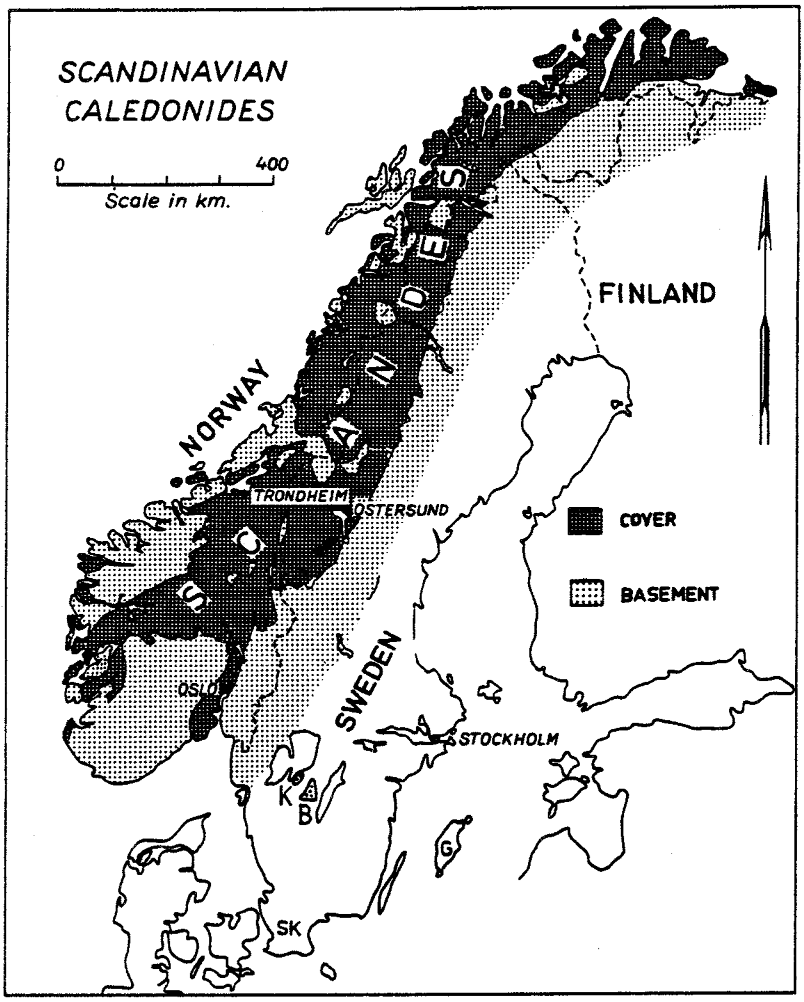


Fig. 1. Survey map of Scandinavia, Kinnekulle (K) and Billingen (B) marked. Modified from a report by Dahlman and Gee (3).

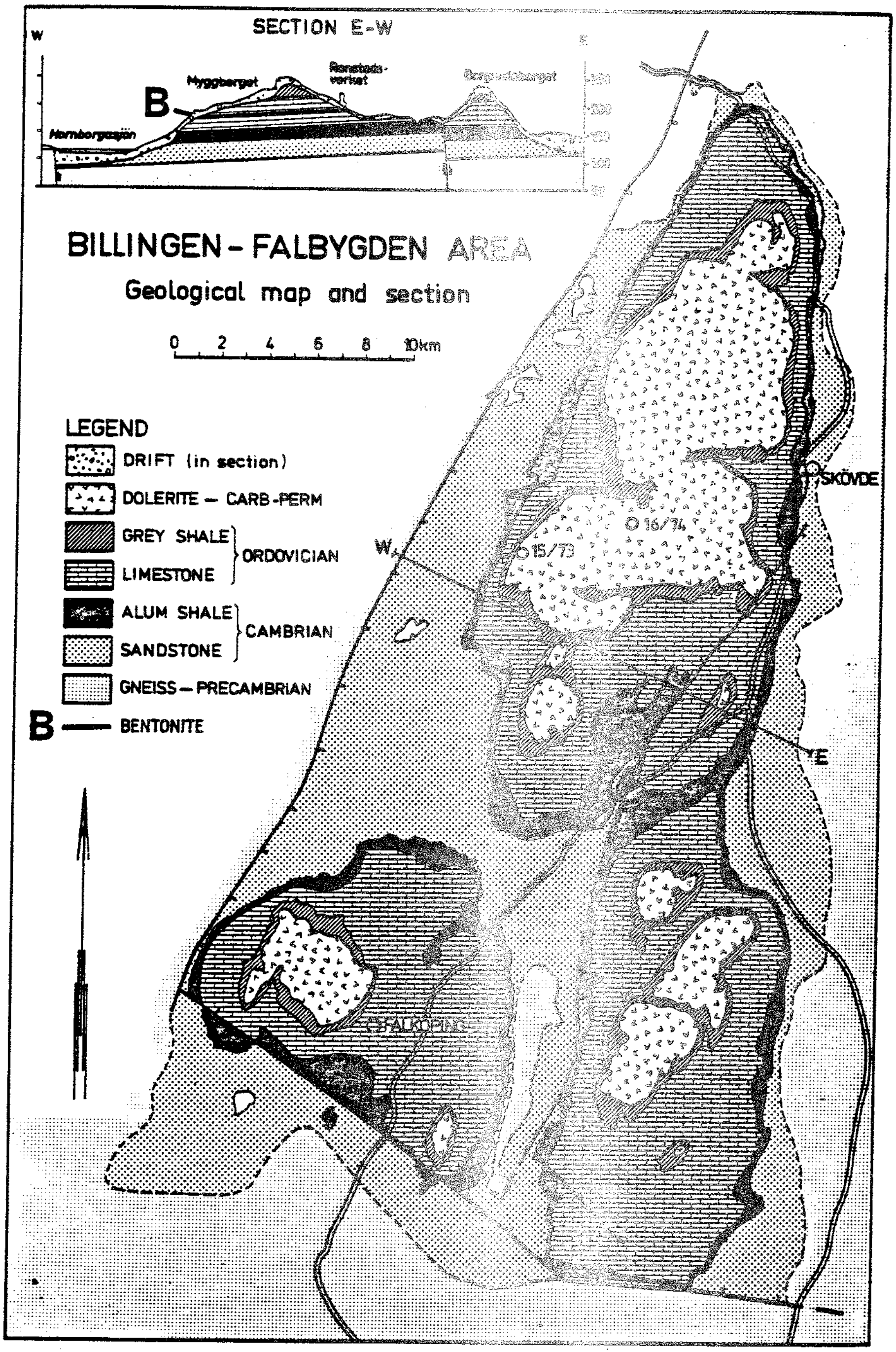


Fig. 2. Outline of the Billingen area, with drill holes marked (15/73 and 16/74). The map is adapted from a report by Dahlman and Gee (3).

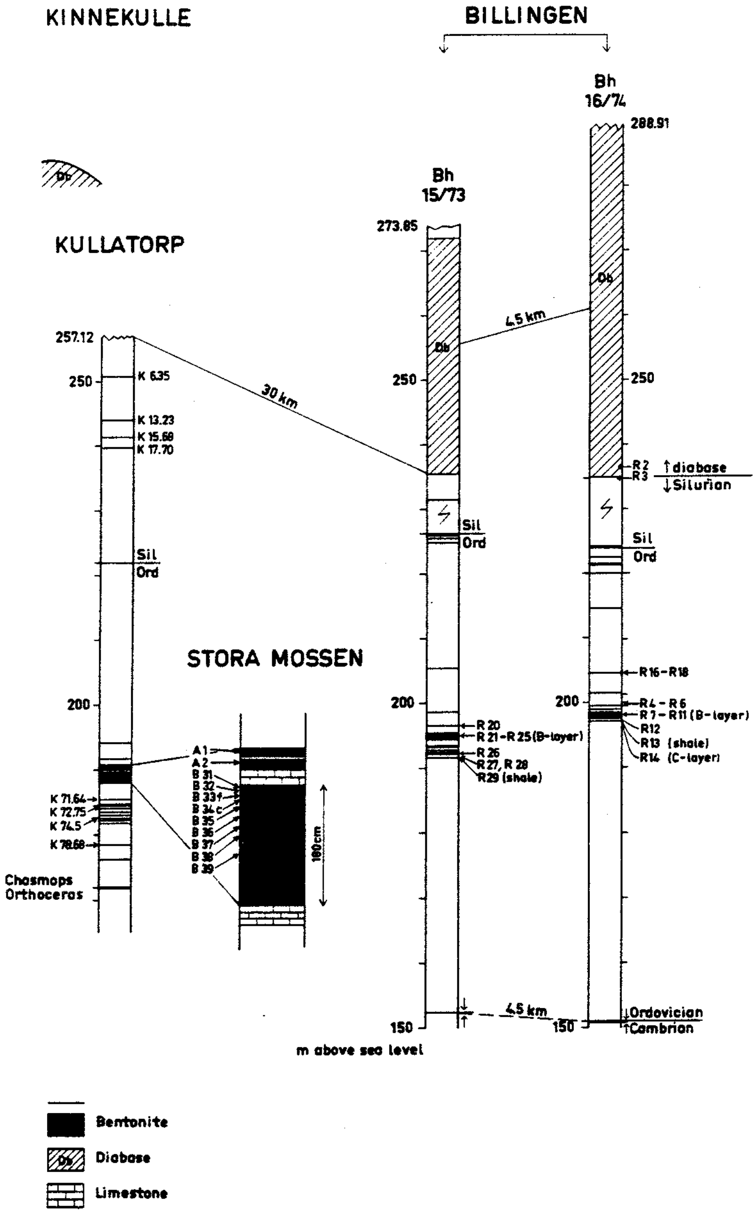


Fig. 3. Schematic profiles of the Kinnekulle and Billingen strata. The Kinnekulle thick bed is enlarged. Sample positions have been marked.

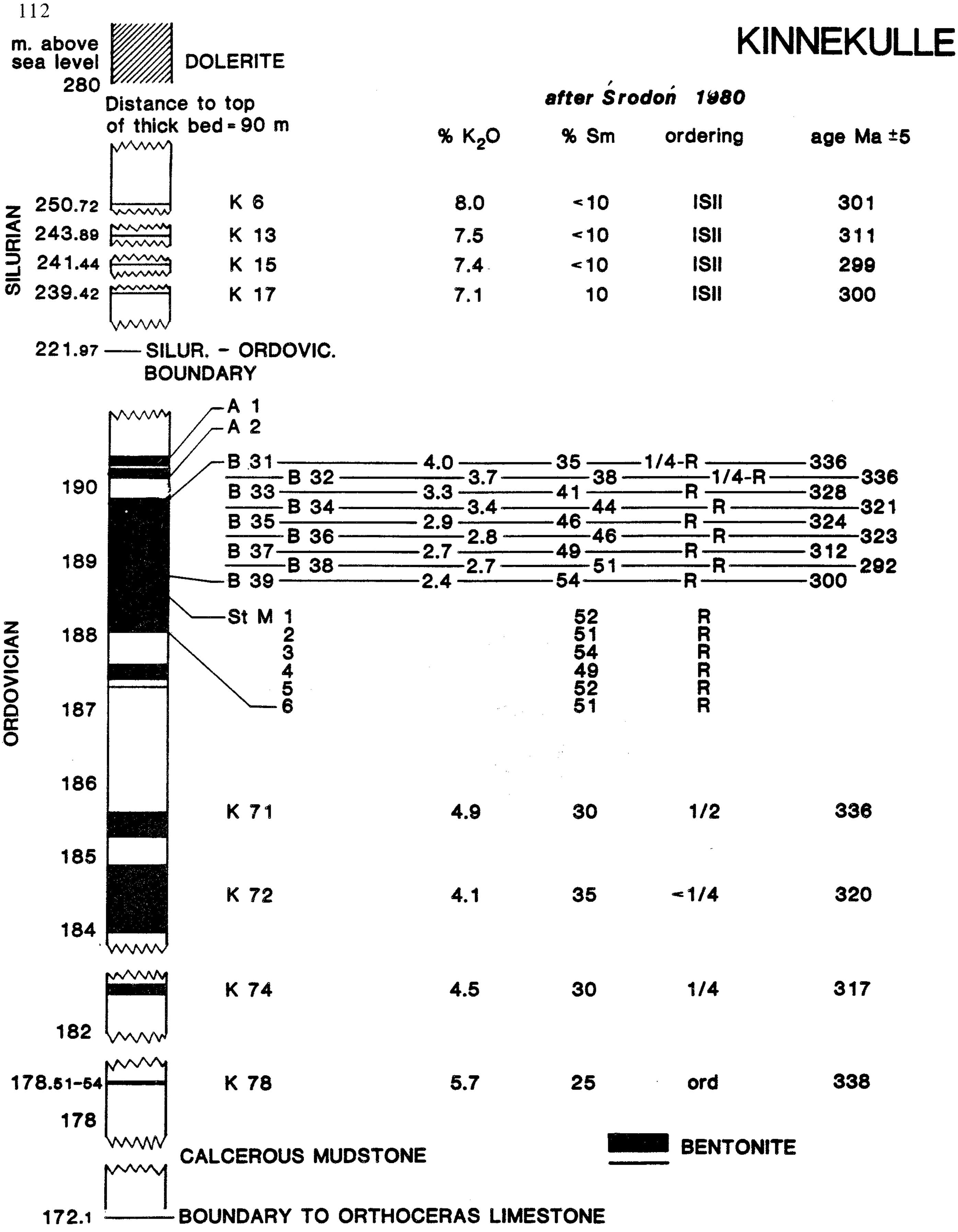


Fig. 4. The Kinnekulle profile, results from analyses of the <1 um fraction, % K_2O, % smectite, I/S ordering, and K/Ar ages.

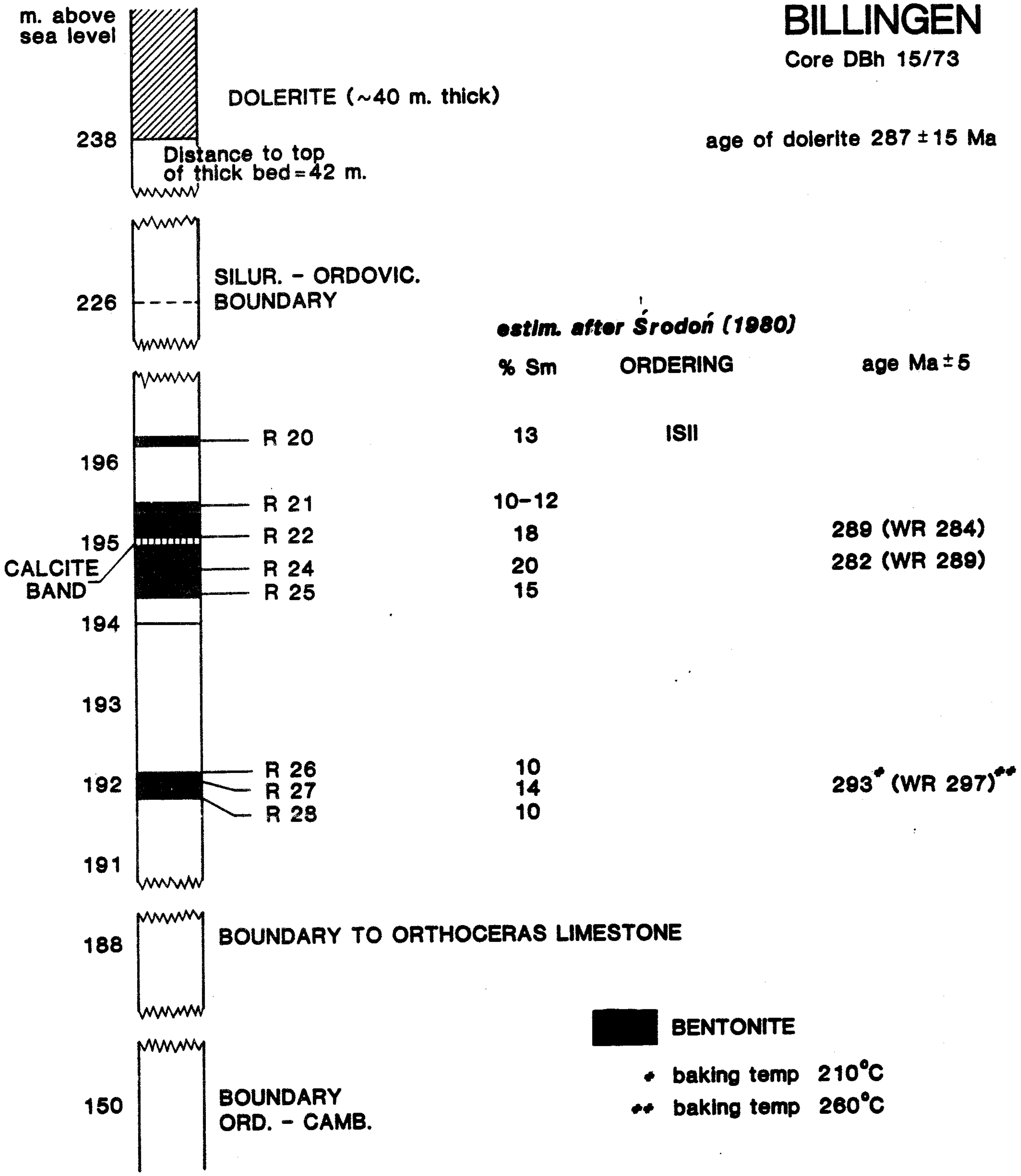


Fig. 5. Billingen core DBH 15/73, samples studied. Chemical analysis was made of the <1 um fraction from samples R22, R24 and R27. Estimated chlorite (autogenous) 25, 30 and 10 % and estimated % K_2O in the I/S phase 6.4, 6.4 and 7.1, respectively.

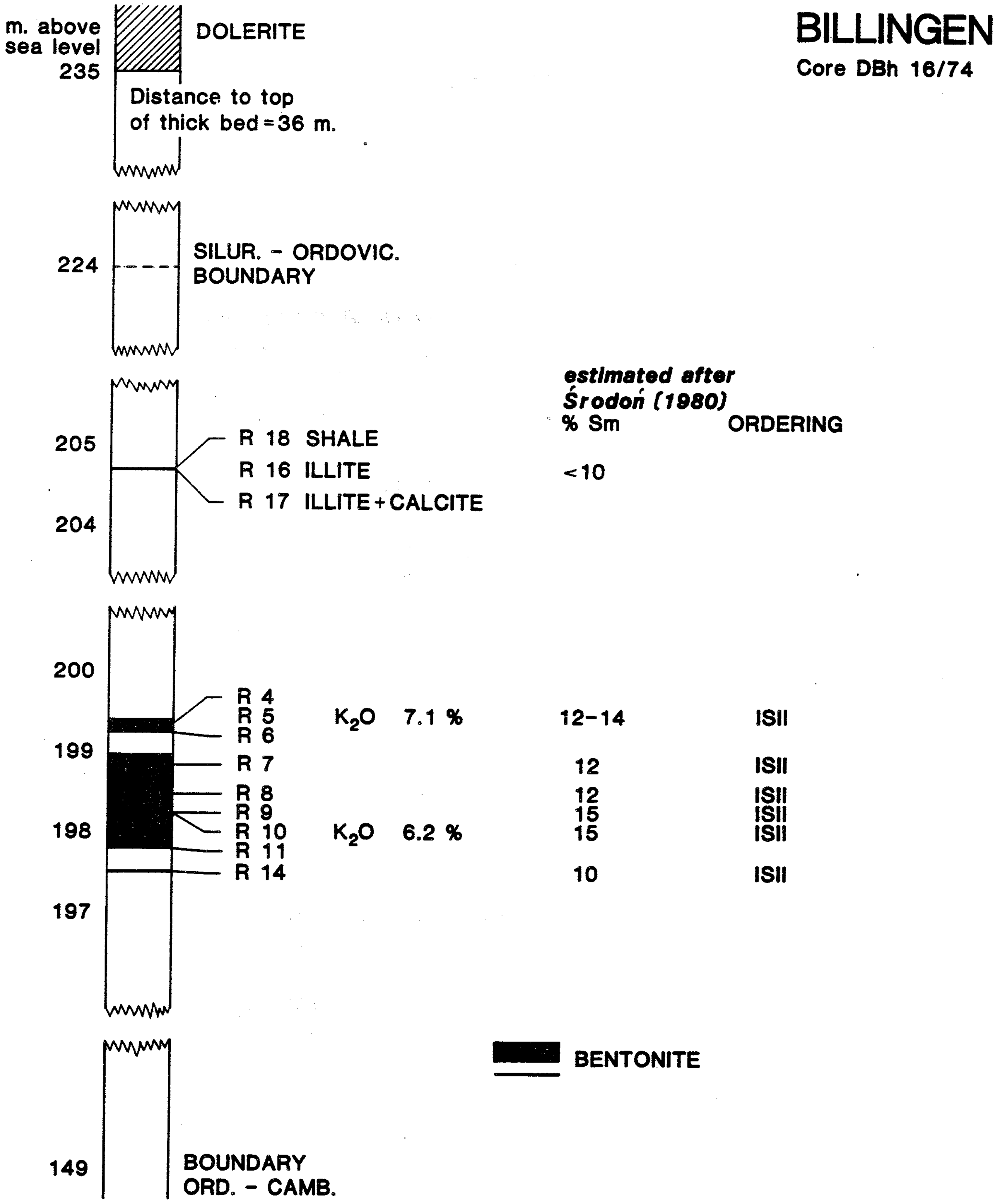


Fig. 6. Billingen core DBH 16/74. Chemical analyses of R5 and R10, < 1 um fraction. Chlorite content ≃5 %.

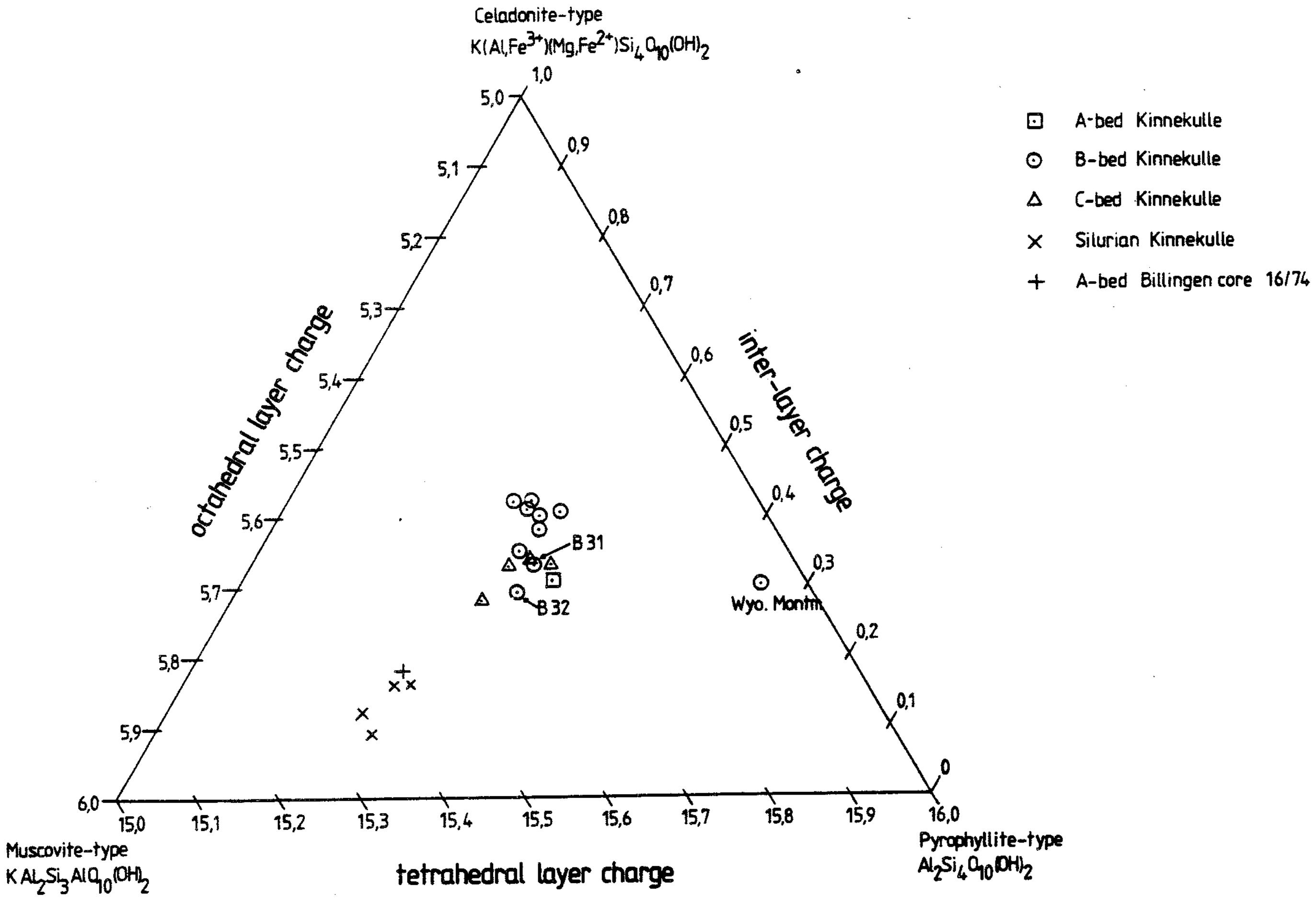


Fig. 7. Triangular plot of layer charges, according to Köster (7) (1977). Sum of charges always amount to 22, from the ideal pyrophyllite structure with O_{10} $(OH)_2$.

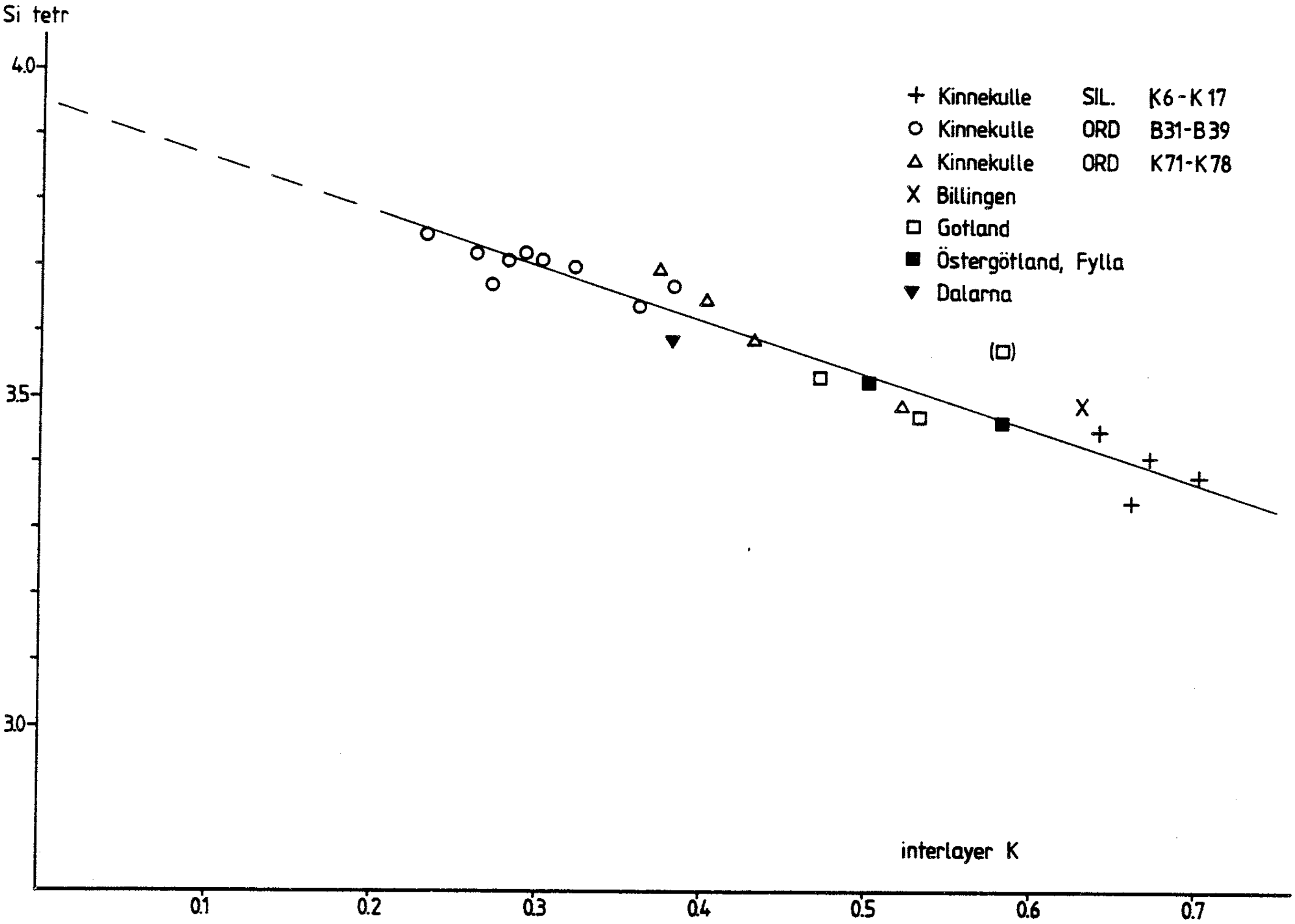


Fig. 8. A plot of tetrahedral Si versus interlayer K. The line is drawn from Kinnekulle samples only, <1 um fraction, corrected for minor amounts of quartz and kaolinite. Data from other bentonites have been added. Gotland samples are from Snäll (1977). (12)

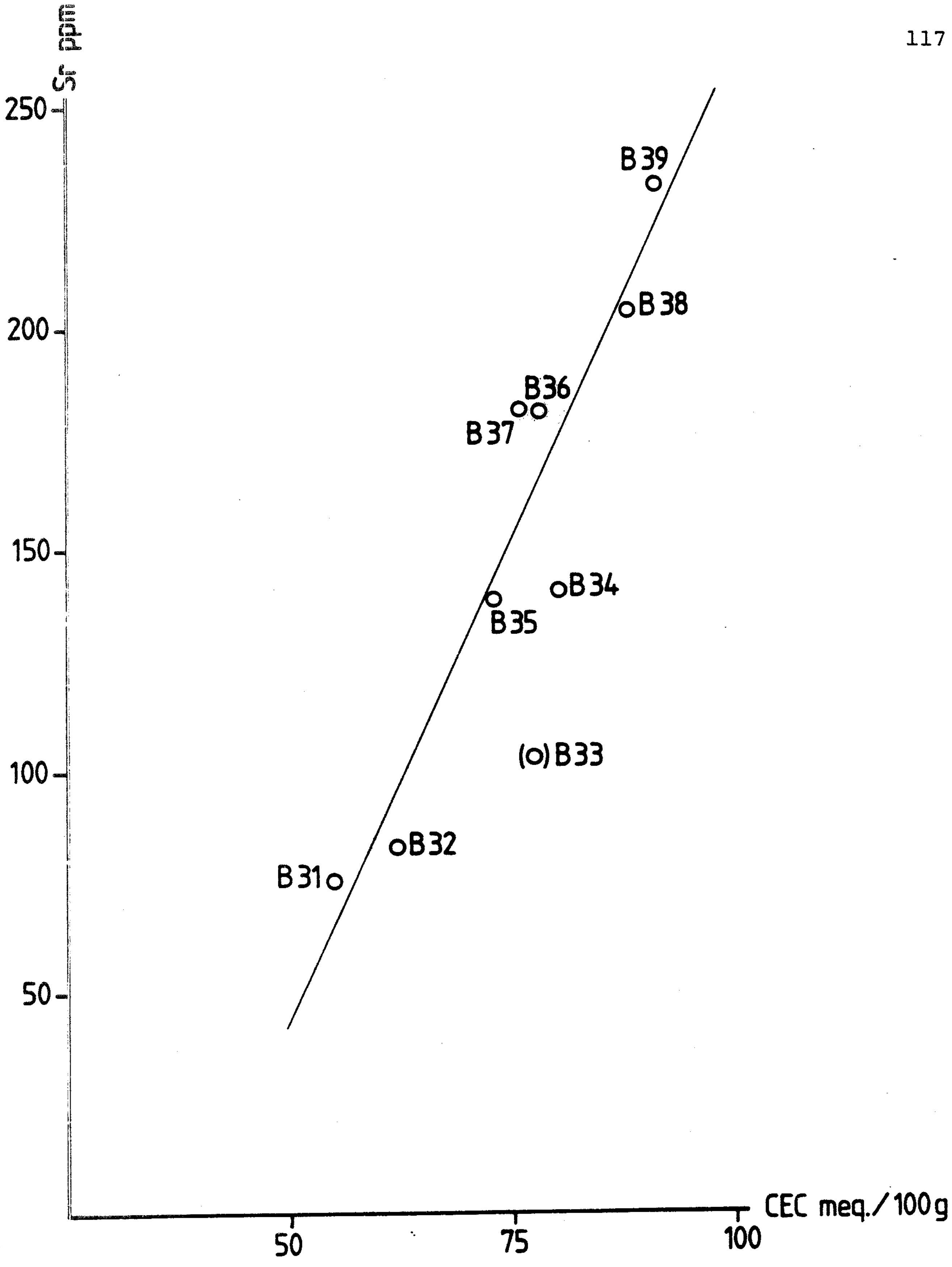


Fig. 9. Kinnekulle thick bed; relation of ppm Sr to CEC meq./100 g. (<1 um fraction). The regression line excluding point B33 gives an r-factor of 0.94.

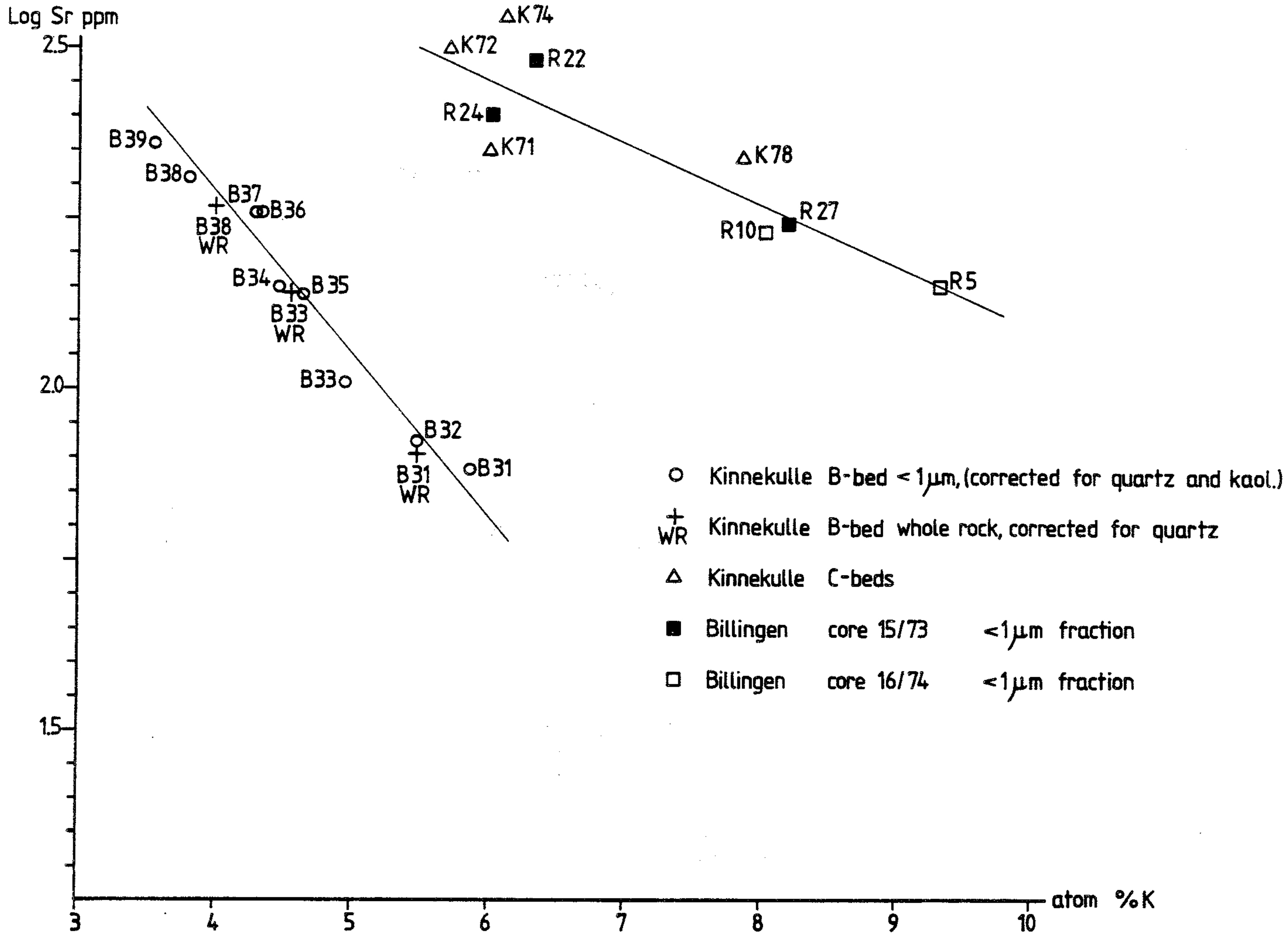


Fig. 10. Semi-logarithmic plot of Sr and K (ppm weight and atom per cent) for the <1 um fraction of Kinnekulle (corrected for quartz and kaolinite) and Billingen samples. Three whole rock values from Kinnekulle B-bed, corrected for quartz, are included. The regression line for B-samples (< 1 um) gives the r-factor 0.98.

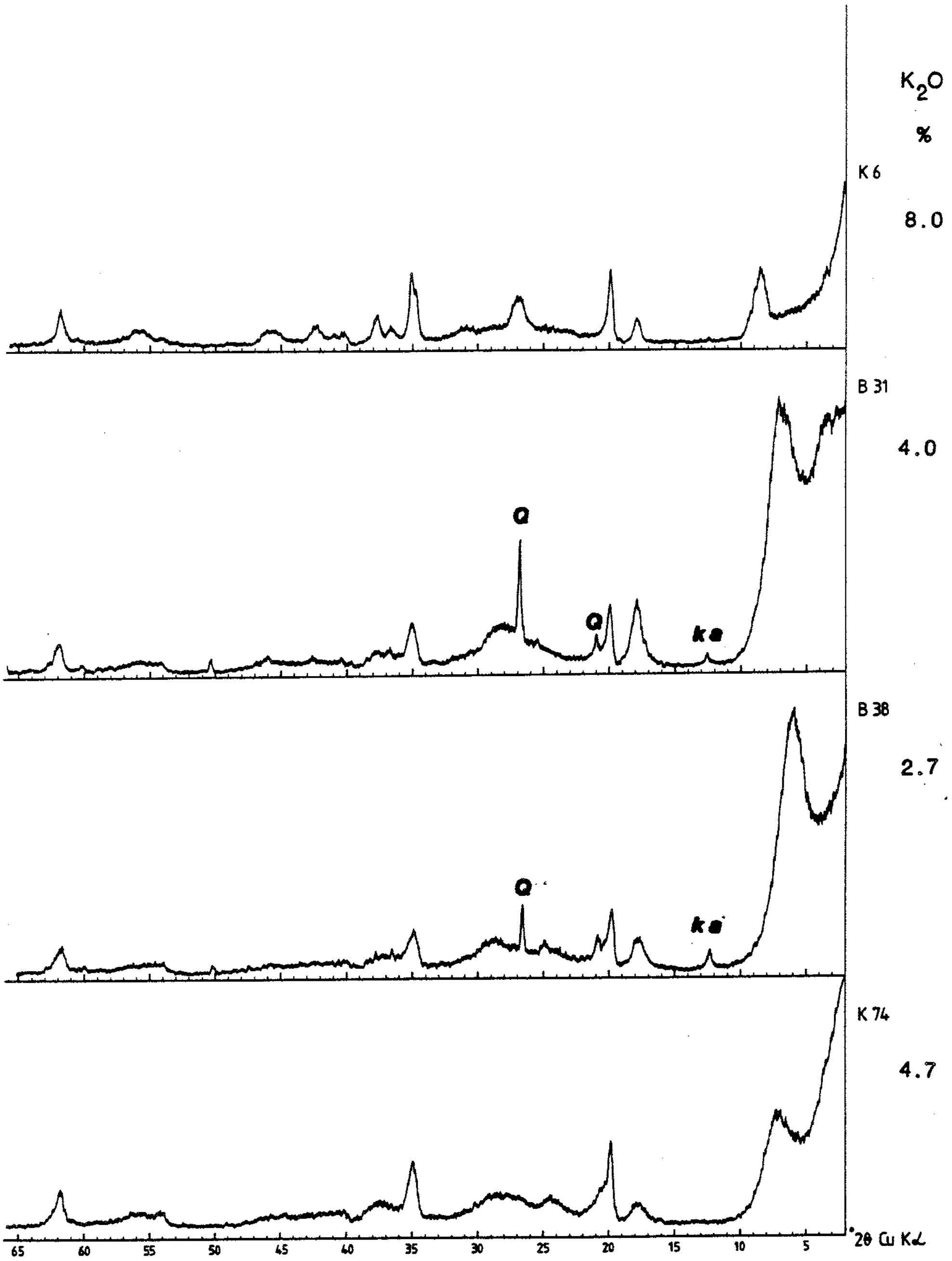


Fig. 11. XRD curves from randomly oriented specimens from Kinnekulle (<1 um). Sideward packing technique, Byström-Asklund (1966). (13)

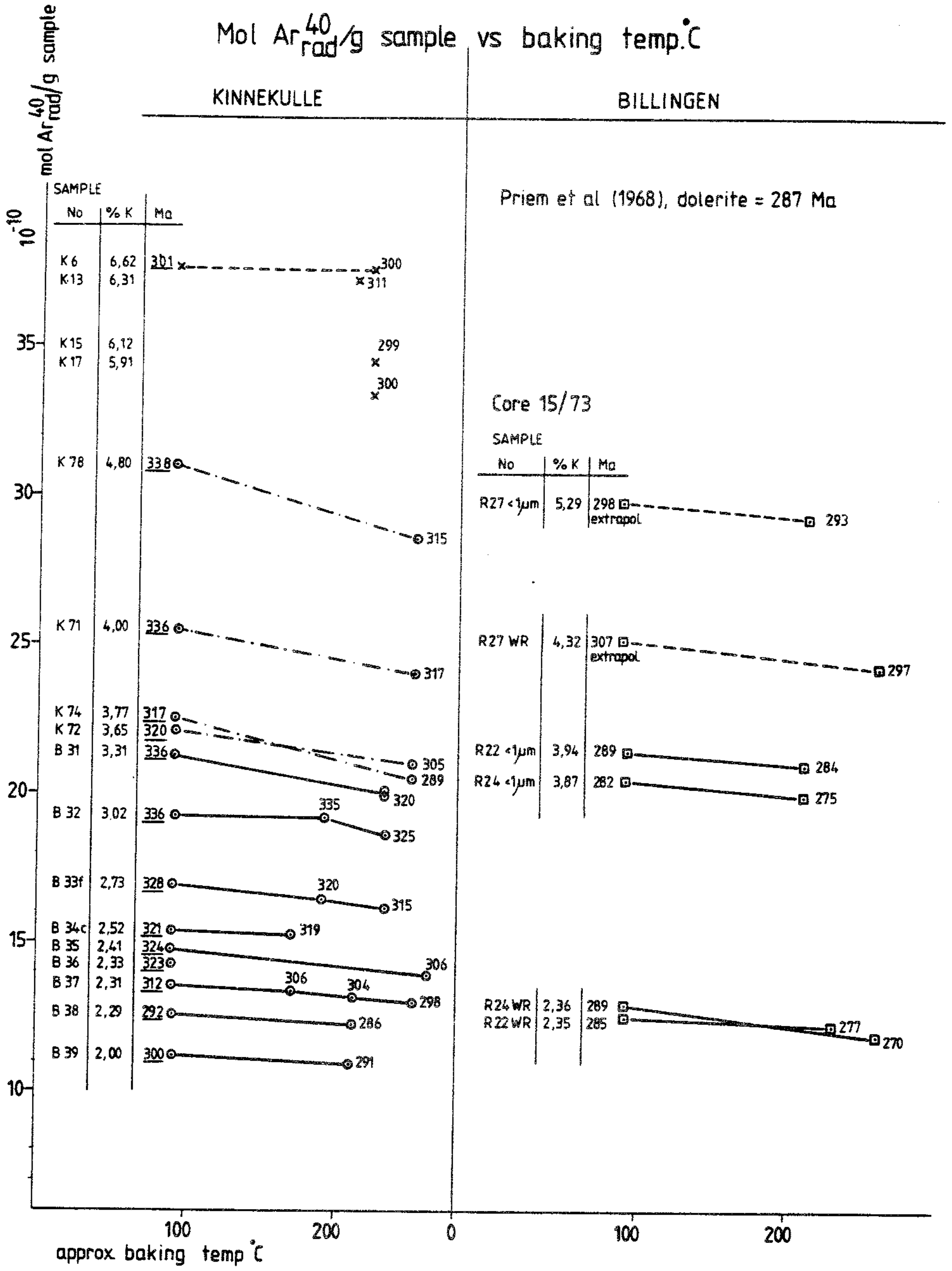


Fig. 12. Ar^{40} rad mol/g sample plotted versus approximate baking temperature. The calculated age is given at each point. The points have been connected with lines, the slopes of which give an indication of the influence of baking temperature.

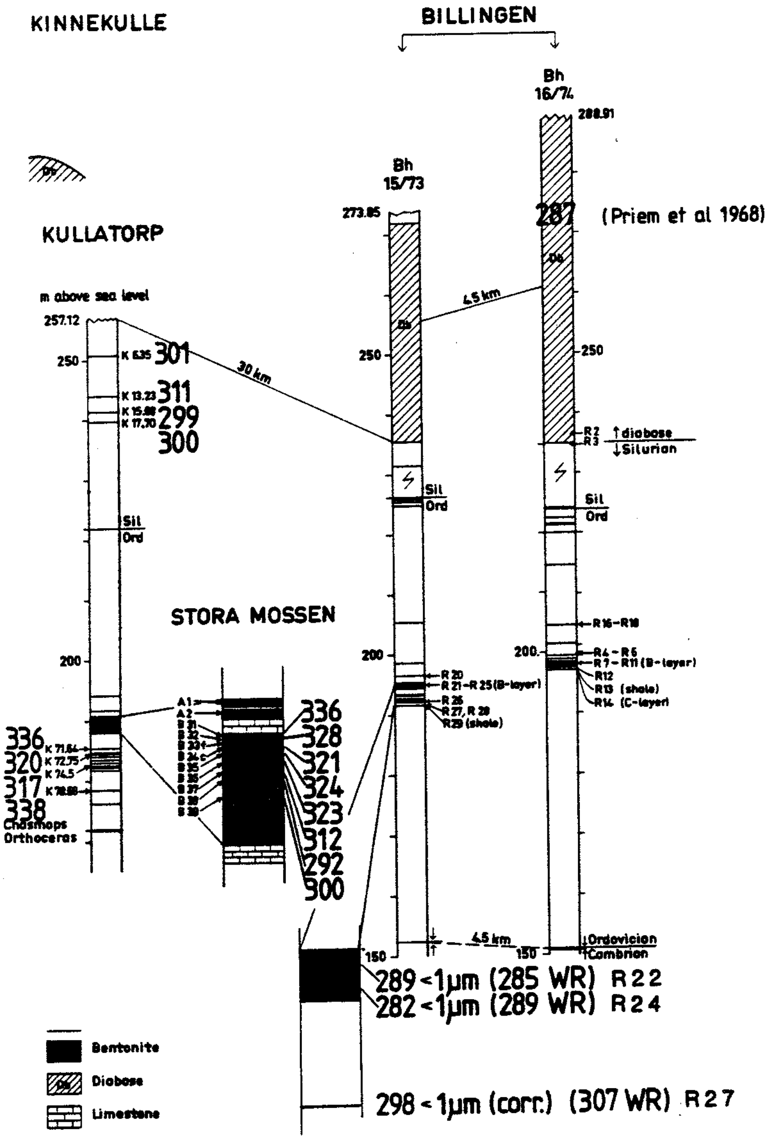


Fig. 13 Schematic profiles of the Kinnekulle and Billingen strata, c.f. Fig. 3 to which K/Ar^{40} ages have been added.

Dr. Pusch:

We took some bore hole samples from the thick bed at water contents up to 35 percent. The bulk density of this water-saturated material would have been somewhere around 2 or 1.95 tons per cubic meter. Now this is a funny thing because the overburden is only about five meters. If the swelling potential is still there, it should have taken up much more water. The present density then would be about 1.3 tons per cubic meters. This suggests that something is preventing the spontaneous water uptake and swelling. It might be some sort of cementation or it might be something else. The clay certainly has had sufficient time to take up water and swell. But actually we should also mention that the whole thing is rather plastic. You can dig it and if you get a piece of clay in your hand, it is sort of plastic.

Dr. Mitchell:

How does it behave if you take it out and rework it and then try it?

Dr. Pusch:

Then it swells.

Dr. Müller-Vonmoos:

The swelling pressure of a metabentonite sample from Kinnekulle has been determined investigating the material crushed smaller 2 mm, and the material after complete particle disintegration by ultrasonic treatment. By the ultrasonic treatment, the swelling pressure increased from 1.8 to 7.2 N/mm^2 at a dry density of 1.74 Mg/m^3, and from 17.7 to 42.3 N/mm^2 at a dry density of 2.02 Mg/m^3 respectively. Forces of particle disintegration by ultrasonic treatment are much smaller than swelling forces. Therefore, bonding forces of cementing material like free silica broken up by the ultrasonic treatment will not reduce the swelling pressure of the metabentonite sample drastically. The amount of SiO_2 set free by Al for Si substitution amounted in the investigated sample to not more than 3% by weight. This SiO_2, determined following complete separation of the mixed layers into the fraction <0,2 m and calculating the mineral formula, will cover not more than half the external surface of the sample as a monolayer, assuming a surface area of 500 m^2/g for amorphous SiO_2 and an external sample surface of 30 m^2/g only. But such cementing material may reduce the water uptake by lowering the permeability.

Dr. Mitchell:

Are you saying that the water did not pentrate the aggregate in the lower case?

Sample	Sieving	Elutriation						Centrifuging	
	>63µm %	63-20µm %	20-10µm %	10-5µm %	5 - 2µm %	< 2µm %	Total %	2-0,2µm %	<0,2µm %
Meta-bentotite B *	1,00	2,69	1,99	4,50	11,08	76,68	97,94	13,59	86,93
	1,30	2,77	1,92	3,85	11,05	76,61	97,50	13,38	87,12
	Ø 1,15	Ø 2,73	Ø 1,96	Ø 4,18	Ø 11,07	Ø 76,65	Ø 97.74	Ø 13,49	Ø 97,03
B 31/32 **	0,39	2,46	2,28	3,01	6,34	81,81	96,29	17,29	83,46
	0,41	2,47	2,27	3,17	6,66	82,37	97,35	16,32	83,88
	Ø 0,40	Ø 2,47	Ø 2,28	Ø 3,09	Ø 6,50	Ø 82,09	Ø 96,83	Ø 16,81	Ø 83,67
B 33 **	0,07	1,23	2,29	4,75	12,56			13,14	85,46
	0,07	1,47	2,03	3,94	12,98			13,27	84,62
	Ø 0,07	Ø 1,35	Ø 2,16	Ø 4,35	Ø 12,77	Ø 75,89	Ø 96,59	Ø 13,21	Ø 85,04
B 36 **	0,33	2,53	2,79	6,33	16,07	69,99	98,04	13,22	84,52
	0,39	2,38	3,03	6,40	16,94	66,24	95,38	13,49	85,53
	Ø 0,36	Ø 2,46	Ø 2,91	Ø 6,37	Ø 16,50	Ø 68,12	Ø 96,72	Ø 13,36	Ø 85,03
B 39 **	2,40	3,05	2,48	5,34	9.06	75,15	97,48	8,27	90,65
	2,84	2,73	2,46	5,09	10,67	72,11	95,90	8,00	91,44
	Ø 2,62	Ø 2,89	Ø 2,47	Ø 5,22	Ø 9,87	Ø 73,63	Ø 96,70	Ø 8,14	Ø 91,05

Ø = mean value

* = pretreatment ultrasonic, soda
** = pretreatment dithionite/citrate, ultrasonic, soda

Dr. Müller-Vonmoos

Yes, if you take a meta bentonite from Kinnekulle, and you compact it and bring it into the apparatus for measuring swelling pressure, then the water is not able to enter completely in the meta bentonite, during two weeks time.

Dr. Mitchell:

If you left it for two months would you have different answers?

Dr. Müller-Vonmoos:

You may. But there is no tendency for an increase; if you follow the two weeks you cannot assume that it will turn up. There is no reason for this.

Dr. Mitchell:

Then do you believe it is a case of cementation, is that what you are saying?

Dr. Müller Vonmoos:

During the determination of the swelling pressure the uptake of water into the compacted <2 mm sample was much reduced and we therefore determined a too low swelling pressure. We do not know the reason. Cementing material may play an important part. But we should not overestimate the part of silica set free by the Al for Si substitution.

Dr. Pusch:

I can add to this a little. If you don't apply this disintegration technique, the ultrasonic treatment and only remold it in the usual way we do in the laboratory, we find a liquid limit of about 75 percent. The clay percentage determined after simple disintegration is only 35 percent.

Dr. Müller-Vonmoos:

Complete separation of the mixed layers into the fraction <0m2µm included complete particle disintegration by ultrasonic treatment and short boiling in soda solution, a complete fractionation by elutriation and centrifuging and freeze drying following precipitation particles <0, 2 m by $CaCl_2$.

Dr. Banin:

Have you looked using the electron microscope, at the clay, before and after?

Dr. Müller-Vonmoos:

No. I have not.

Dr. Banin:

I think there is evidence to show that in some cases you may say that there is some memory in the smectite of the original condition.

Dr. Pusch:

You have referred to microscopy. We have made some electron micrographs of various smectites that have been exposed to various temperatures. This is one of the meta bentonite I have been dealing with, by scanning electron microscopy for many years, and I would say that I have never seen the sort of coating that we can see here; little nodules and coatings which have not been identified with respect to their composition but which might represent the sort of precipitation of silica that we are talking about. Actually, Ann Marie back in 1977 by trying light microscopy, saw quartz precipitation under moderate magnification. I should also add that we have looked at Wyoming bentonite and it does not have these sorts of nodules, nor do the bentonites from Gotland have that.

Dr. Brusewitz:

I think that you should have an x-ray energy dispersive analysis of that region to be sure.

Dr. Mitchell:

Now, we are going to turn to the diffusion governed smectite to illite transformations that have been studied by Dr. Altaner.

Dr. Altaner:

The preliminary program states that Andrew Altaner is going to give the talk. When I came here and saw the program, I was a little surprised because I have a twin brother named Andy but he is in the theater arts and I figured he probably was not going to be giving a talk. I am going to be talking about a field example of a zoned K-bentonite, where the amount of illite formation seems to be controlled by the diffusion rate of potassium into the bentonite. We seem to be going in pairs this afternoon and the data are similar to the data that Ann Marie just presented. The application of my work is in the modeling of diffusion coefficients in deeply buried bentonite/shale systems. I'm going to present mineralogical, chemical and potassium argon data on bentonite/shale system. Then I will describe the modeling efforts that went into obtaining diffusion coefficients. Then I will try to point out possible applications to nuclear waste depository situations. So, if I can have the slides.

The smectite/illite reaction is a well documented mineralogical reaction known to occur in a wide variety of rocks. These rocks include sandstone, shales, bentonites and hydrothermally altered tuffs. The smectite to illite reaction extent is a function of temperature at least in part, and what is involved here is the substitution of aluminum for silicon in the smectite, in order to increase the negative charge on smectite lattice, and the fixation of potassium. The smectite to illite reaction series goes through a mixed clay series where the amount of illite layers in the illite/smectite has been found to be a sensitive function of temperature. Where does the silicon go? Well, sometimes it goes into the formation of quartz and also you get chlorite formation which contains silicon, so it could go there. Generally, it is important to go into silicon cement. Okay, this is illite/smectite compilation data from bentonites in a simple subsiding basin, the Denver Basin, from work by Bob Rathke. Here is a plot of temperature or burial depth versus percent illite layers in illite/smectite and notice the nice direct relation between the two. Here is a plot of percent illite versus age in bentonite, just a compilation of bentonite data that has been reported on in the literature. This red line intersects the median illite/smectite composition for that time interval. The error bars indicate the range of smectite compositions seen. You will see that there is a wide range in some time intervals. But notice that the general trend is that the oldest bentonites are the most illite-rich bentonites. So both time and temperature seem to have some influence on the illite/smectite composition. This same or a similar reaction occurs in shales and sandstone as well.

The field area that I am working in is in western Montana, in the overthrust belt or disturbed belt of Montana, and the structure I am going to discuss is to the east of the sweetgrass arch which is a gently dipping structure and contains cretaceous shells, sandstones and bentonite. Further to the west is the disturbed belt. The disturbed belt formed during the Laramide orogeny at the end of the Cretaceous by the thrusting of Paleozoic and Cambrian thrust slabs over the Mesozoic section. I looked at cretacious rocks in the Mesozoic section there.

This slide is to give you an idea of the style of deformation in the area. This is a thrust plain and these are the cretaceous rocks in the area. Here is a piece of the paleozoic carbonates that are thrust over the Mesozoic section in the area. This is another big Paleozoic block that forms another thrust plate. Now, bentonites, as I am sure you probably all know, form from the near surface, subaqueous alteration of volcanic ash. Here are results from a study done by Kiersch and Keller in 1955. They found a smectite/bentonite with a laterally preserved ash layer. From the chemistry of the two, you can see that the formation of bentonite involves the large loss of cations such as sodium and silicon. It also involves the uptake of water and magnesium, in particular. Kiersch and Keller assumed the aluminum is immobile and there is still a depletion of silica, potassium and sodium. Because you don't know about the volume change, you don't know the exact amount. Potassium bentonite differs from smectite bentonites in containing mixed layer illite smectite as their dominant clay mineral instead of smectite. Here are data from Janet Hoffman's PhD thesis, she looked at bentonite from the disturbed belt of Montana and the sweetgrass arch. These are bentonites from cretaceous rock. Now the cretaceous rocks in the disturbed belt experienced temperatures of 100°C or more, caused by burial underneath thrust sheets. If you'll notice, they are relatively more illite-rich than are the bentonites from the sweet- grass arch, the rock had not been buried to levels experiencing more than 60°C. Hoffman also looked at the bentonite chemically and found that the bentonite from the arch, have very small amounts of potassium relative to their metamorphosed stratigraphically equivalent counterpart in the disturbed belt. So the formation of K-bentonite generally involves a thermal event and in this case, an external source of potassium.

The rocks that I looked at are upper cretaceous from the Marias river shale. This is a marine black shale in which the key member contains many thin bentonites and one calcarious member of the Marias river contains one thick bentonite of 2 1/2 meter thickness. Here is a photo, an outcrop view of some of the bentonites I collected. These are some of the thinner ones. This is probably on the order of five or six centimeters across. Here is another photo of sections which are richer in bentonite. There is a rock hammer to the lower right to show the scale. I looked at 32 bentonites, all of which were less than a meter thick and found that bentonites which form less than 25 percent of the section are significantly more illite-rich than the bentonite present in bentonite-rich sections which form greater than 25 percent of the sections. This is an outcrop view of 2.5 meter thick bentonite, the outcrop is dipping away from you. There is my adviser at the University of Illinois, John Hower and also Gene Witney, who is sitting right here, from the survey in Denver and also Jim Arenson at the Case Western Reserve University at Cleveland This 2 1/5 meter bentonite is bounded by black shale. The lower contact is the relatively sharp contact with the shale whereas the upper contact is a darker grey reworked zone of shale plus bentonite. Disregard the bottom three plots and just concentrate on the top plot. This is the illite/smectite composition. The top figure is a plot of the illite/smectite composition across the bentonite from the lower contact towards the upper contact. You can see that the bentonite is mineralogically zoned and is relatively illite-rich with respect to the smectite-rich center of the bed. The illite content of the shale is about 70 percent illite layers. We concluded from this that the illite/smectite in the shale, the illite present in bentonite and the illite/smectite at the contact represents a complete reaction series for the metamorphic condition that these rocks have experienced. The illite/smectite composition in the center of this bentonite bed and the illite/smectite in bentonite-rich sections represents an incomplete reaction due to a deficient supply of potassium.

This is a blown-up illustration of the K_2O chemistry of the bentonite shale system. Since illite/smectite is the dominant potassium mineral present, the whole K_2O profile mimics the mineralogical zonation, K_2O greatest at each contact and decreasing towards the middle of the bed. The profile is asymmetric, due to a variable quartz to clay ratio across the bed. This sample, here, is very clay-rich hence very potassium rich. This profile is a recalculated profile assuming and homogeneous content of clay across the bed. You can see that it is a lot more symmetric K_2O profile.

If you look at the shale, it also shows a zonation with K_2O decreasing as you approach the bentonite from both sides. If you notice, the depletion on this side of the bentonite is much greater in the shale versus this side. There are three possibilities as to what could cause this depletion in the shale. One is the potassium mineral could be breaking down locally to give up potassium to the formation of the bentonite. Secondly, it could be that in the initial formation of a smectite bentonite from ash (if you remember, this involves a large loss silica) this could be a dilution effect of conversion. A third possibility is that this could be merely a deposition profile. There could be more potassium minerals deposited here in the shale than there. I am going to address that question. If we look at the mineralogy of the whole rock, mineralogy of the shale, I just want to concentrate on the shale and in particular below the bentonite. The potassium mineral phases in the shale are layer silicates. These are muscovite, discrete illite and illite/smectite. There is also kaolinite chlorite but the potassium bearing layer silicates are muscovite, illite and illite/smectite. What we see is a very large decrease in the amount of layer silicates on this side of the bentonite in the shale. This also could be interpreted in any of those three ways; this is just telling us what is causing the potassium depletion in the shale. Two other things to notice is that pyrite increases somewhat, and calcite increases as you approach the bentonite. Now here is clay data from the bentonite-shale system. The boxes are illite. The circles are illite/smectite and the open circles are undifferentiated kaolinite/chlorite. The bentonite is pure illite/smectite. You can see that there is relatively no change in the composition of the less than .7 micron-sized clay fraction in the shale with respect to position near the bentonite, except at the upper contact here where illite/smectite predominates. This can be explained by the large trend with respect to position near the bentonite. Now here, this is a plot of the amount of 2 muscovite in the layer silicates in the total amount of mica present. There are two profiles plotted. Again the bentonite contains no muscovite in the rock. However, the shale does contain muscovite. This is one outcrop and set of data, the squares and the circles are a second set. You can see, perhaps, some trend of decreasing amounts of muscovite as you approach the bentonite. So one possible reaction here is that muscovite is breaking down and releasing its potassium to form illite in bentonite. However, if we write the formula for muscovite with the breakdown recorded by hydrogen attack, here we have potassium and aluminum. If you remember, the original reaction that I wrote in order to form illite, potassium and aluminum need to go into the smectite structure in approximately a one-to-one ratio. So, if we take the two of these out, if we decompose the muscovite and put these into the bentonite, we should be building up the aluminum and silica concentrations in the shale. If you look back at the whole rock mineralogy there are no aluminum phases increasing as you approach the bentonite. This is a possibility that is essentially constant as you approach the bentonite. So from the mineralogies there are no aluminum silicate phases increasing as you approach the bentonite. Chemically, here we have weight percent aluminum in the bentonite shale system and this is the actual profile observed. This a profile calculated if only potassium is transported into the bentonite. Here you would expect no aluminum change at all. If aluminum were transported with potassium, you would expect one kind of zonation, however, we see another type of zonation. Therefore, I've ruled out the possibility of muscovite breakdown in the shale in order to explain the local breakdown of muscovite in the shale in order to release its potassium to form in the K-bentonite. This plot shows the same thing so I'm not going to go into it at all.

The second possibility is that we could be seeing a dilution effect of silica in particular from the bentonite during initial smectite conversion. And you see here that silica is essentially constant in the shale except for very close to the bentonite. So perhaps these samples are affected by the ash to smectite conversion but they can't account for the whole potassium depletion profile. So the only thing we're left is that the potassium mineral profile is just a depositional profile. This brings up the question of where did the potassium come from? The only thing that I can suggest is that potassium came from long-range mineralogical breakdown of the potassium-bearing minerals in the area.

I separated out illite/smectite from the bentonite and dated them. All of the ages are less than 56 million years old, approximately 30-40 million years younger than the age of the ash fall. These potassium/argon ages, then, are reflecting a process of deriving potassium from outside of the bentonite, from mineralogical breakdown. Potassium then migrates through a pore fluid into the bentonite. Within the bentonite the absorption of potassium occurs unto the montmorillonite and there is a chemical reaction to form illite. Before I go on I might mention that Ann Marie Brusewitz also has found a zoned K-bentonite, I believe it is 2 meters thick, at Kinnekulle, and Jan Srodon has done some work on it, I think it is a carboniferous bentonite that is one meter thick, that shows a similar mineralogical zonation with illite rich contact and a smectite-rich center of the bed. So these occurrences aren't unknown to the world.

If diffusion is the transport process, then using the potassium profile in the bentonite and the potassium argon age difference as a measure of the minimum time for the reaction, we can calculate diffusion coefficients for the rate of potassium transport in a deeply buried bentonite. These are the equations that I have used. First, we need to calculate two potassium profiles. One for potassium in solution and that's what would be calculated here. This is the straight diffusion equation with a chemical reaction term. It is a sink term with potassium being taken out of the system by chemical reaction to form illite. Then, the chemical reaction term is written here. This is actually wrong, it should be minus sign here. We also have to calculate potassium profile in the solid phase. Here the changing concentration of smectite is related to K times the concentration of smectite. This is a classic kinetic type of expression, a first order kinetic expression, here K is equal to Ae where A is the frequency factor and E is the activation energy. In order to calculate potassium, you have to relate the amount of smectite in your bed to the concentration of potassium. This is very easy to do and you get this kind of expression. The answers that you get, and I'm going to show some results in the next slide, depend highly on the rate constant that you use. I've used two rate constants, one is from kinetic data from McCubbin and Patton who derive the kinetic expression from the illite/smectite composition in gulf coast shale. The second kinetic expression that I used was from Reynolds and Pytte, who looked at the influence of a dike intruded shale where you see an illite profile, decreasing the amount of illite, going away from a dike with a shale. The difference between the two is that McCubbin assumed a first order reaction and Reynolds didn't; he tried to get at what the order of the reaction was from the data. And Reynolds' kinetic expression found several fits to his data. They included a third fourth and fifth order reaction.

Here is a dimensionless plot of the system. This is the distance along the bentonite, this would be the lower contact and the upper contact of the bentonite, (this should be a minus one here). And this is the concentration of potassium relative to some maximum value. Here is the actual zoned profile observed. This kind of fits (the parameters used to make this fit are the concentration in solution outside, of about 200 ppm potassium, which is a reasonable value for the limited amount of data that we have of potassium concentration in deeply buried shale). Temperatures are about 110°C. The diffusion coefficient that we calculate from this is of the order of 10^{-7} to 10^{-8} cm^2/sec. The other two lines drawn represent changing parameters. This would represent decreasing the diffusion coefficient or decreasing the diffusion coefficient by an order of magnitude and this would represent increasing the diffusion coefficient constant. If you increase the temperature by an order of magnitude you would bet this extremely zoned profile.

So, if we calculate the diffusion coefficient in a highly compacted deeply buried bentonite of 10^{-8}, how do we extrapolate that to a repository type condition. Well, the temperature 110°C is of the order of temperatures that you'll see in a repository condition; so the temperatures will be the same. But the pressures will be considerably different, so what will be different when you try to extrapolate is the tortuosity term in the diffusion equation. Tortuosity is just the difference between a straight path that an ion can diffuse versus the actual path that an ion can diffuse. The tortuosity in a bentonite that is at a lower pressure should be less, so the diffusion coefficient, therefore, should be a little bit greater than 10^{-8}. In order to do a calculation of illite formation in a bentonite in a repository situation, you would need to know the thermal history very precisely, because the kinetics of illite formation is highly dependent on the thermal history.

Also, I think it would be important to look at the possibility of a reversible dehydration. As temperatures get about 100°C (approach 100°C), you are going to reach the boiling point of water and I'm not sure that water is going to stay in the smectite interlayers anyway, at lower pressures. So you'll need to have to consider that possibility also. I guess that's all.

Dr. Mitchell:

During the course of your work did you measure activation energies?

Dr. Altaner:

No, I assumed activation energies from other work. I assumed the kinetic parameters on illite formation from other work.

Dr. Chapman:

The temperature you assumed was 110, what was the justification?

Dr. Altaner:

Well, from the organic metamorphism, there is some organic maturation data which indicate temperatures greater than 100°C anyway, and from oxygen isotope studies on shale in the area and the clay mineral assemblages that have been looked at, all indicate above 100°C, but the upper limit is much less clear.

Dr. Chapman:

And the temperature variations you mentioned?

Dr. Altaner:

Yes, what I meant was you get an order of magnitude variation in the rate constant by changing the temperature by 10°C to 15°C, or maybe 20°C, I'm not really sure about that.

Dr. Chapman:

So the whole process is very, very temperature sensitive.

Dr. Altaner:

Yes, sure.

Dr. Banin:

What is the age of the shale?

Dr. Altaner:

The shale was deposited in Upper Cretaceous times, about 95 million years ago but it contains detrital minerals. Some shale has been potassium argon dated by Janet Hoffman, who worked in the area previously, it was found to be of the order of 200 or 250 million years old. There is old detrital muscovite, illite and authigenic illite/smectite, all in the same rock.

Dr. Banin:

How exactly do you visualize the diffusion of potassium and the alteration to have occurred?

Dr. Altaner:

Well, it was buried underneath a thrust sheet at temperatures greater than 100°C. Smectite is unstable at those temperatures and the potassium derived externally from minerals breaking down, combined to form illite.

Dr. Fripiat:

I would like to come back to the issue I spoke of this morning, about the two phases of water. When you overlap the B phases, by removing the A phase, and calculate or measure the diffusion you have given for potassium movement in the macroscopic bed, I conclude that potassium moves in the hydration layer on the bentonite surface.

Dr. Altaner:

Yes.

Dr. Mitchell:

I think that we should move along now and consider some of the thermodynamic aspects of this business. Dr. Fritz is going to tell us about that.

Dr. Fritz:

My presentation begins with a question; this question was asked to us by Mr. Karlsson a little more than one year ago, when he went to Strasbourg and explained to us the problems of the KBS projects. The question is: in the general simulation of water and rock interaction, can we safely introduce the clay minerals? During the last ten years you have probably followed the results of attempts to simulate the water/rock interaction processes. These simulations involve particularly thermodynamic state of weathering systems at low tempertures. Originally the group in Berkeley who did the first model, (Professor Helgeson) applied it mainly to the study of geothermal alterations and ore deposits. Now the calculation of mass transfer between solutions and minerals is also applied to studies of diagenetic evolution, but the approach is basically the same. Initially one must define the system containing a solution and rock-forming and/or secondary minerals in contact with this solution. Then one asks, is the system thermodynamically stable?

There are some well-known models for detection of saturation states in the solution. They generally apply according to the mass action law. The relations between the molalities and activities of aqueous ionic species are known. From the calculated activities one can calculate for each mineral an ionic activity product generally known as Q, and compare it to a solubility product K for the same mineral. The result of the diagnostic is then oversaturation or undersaturation. I refer to this as a detection step. If you do this for a system and several minerals, you have an indication on the chemical stability of the system. It means that if some minerals are oversaturated, they should be formed in the natural evolution of the system. If they are unstable (undersaturation), they could be dissolved. If we consider all factors together, we have an indication on the <u>possible</u> evolution of the system.

We go then to the next step of this thermodynamic analysis. Let us consider that something which is possible will happen and try to calculate what would be the transfer of each element from the solution to the mineral phase or the reverse. This type of calculation was made first using only pure minerals and is not too difficult: one mass action law equation is used for each mineral phase like calcite for example, at equilibrium:

$CaCO3 = Ca^{++} + CO3^{=}$ with $K(calcite) = (Ca^{++})(CO3^{=})$ in terms of ion activities in the solution (Figure 1).

The mass transfer calculation must include the ion activity product calculation and we have equations to do that. The problem becomes much more difficult if we don't have pure minerals but solid solutions as mineral phases. In that case, the mass action law, which was simplified here in terms of activity of the pure mineral phase (activity equal to one) in only one equation, must contain now one equation for each end-member of any solid solution formed in the system, with provision for the activity of each end-member. That means that calcite and magnesite, for example, have an activity in the magnesium-rich calcite:

$$\mathrm{CaCO3} = \mathrm{Ca}^{++} + \mathrm{CO3}^{=} \text{ with } K(\text{calcite}) = (\mathrm{Ca}^{++})(\mathrm{CO3}^{=})/(\text{calcite})$$

$$K(\text{magnesite}) = (\mathrm{Mg}^{++})(\mathrm{CO3}^{=})/(\text{magnesite})$$

To be able to calculate any transfer concerning this complex phase compared to pure calcite, we must calculate these activities of mineral end-members. If we are then speaking from clay minerals, it becomes very, very complicated.

In fact, we do not have at the moment enough theory and data to make the application easily. Particularly, one might say how can you explain the thermodynamic effect in mineral phases which involve different types of sites? You may say it is impossible by the theoretical approach to solve this problem and one must go back to experiments and observations!

However, we have used clay modeling in our computer program, not only for the KBS program, but in more general studies of natural processes on the surface of the earth and we have had some interesting results by trying to apply the solid solution approach. It is, of course, very difficult because, as you know, differences of dissolution energies of different montmorillonites, for example, are very small. Experimental methods are quite unable to determine these differences in order to give to the model accurate solubility products for a set of realistic clays. Therefore, we used the approach of Tardy and Garrels to estimate the stabilities of the different end-members of these solid solutions. I will not discuss this today, except to describe some of the critical points. To do that I use a simple diagram to compare to possible approaches. Let us consider first the approach developed by Kerrick and Darken (1975) and by Stoessell (1979) for illites and finally by Helgeson and Aagaard for different types of clays. It is a so called "random site mixing model." For a general clay formula like the following simple Al-Mg smectite

$$(\mathrm{Si}_{4-x}\mathrm{Al}_x)_T(\mathrm{Al}_{2-\frac{2y}{3}}\mathrm{Mg}_y)_0\mathrm{O}_{10}(\mathrm{OH})_2\mathrm{K}_x$$

we can consider different ternary sets of pure end-members as constituents in a quaternary unique set of possible end-members (Figure 2). Here is the first uncertainty before discussing any solubility product of these end-members. If you regard the clay mineral as a solid solution, you must be able to define the end-members of this complex phase. Let me show you some examples, in the case of the illite described by Stoessell in a solid solution model of phlogopite, phrophyllite and muscovite: this choice of a ternary set was not unique, but was not discussed. Fritz (1981) has shown that the different choices do not correspond in a general case to the same free energy relations. Not only that, if you take one ternary system, any clay whose composition does not belong to the corresponding triangle in the quaternary diagram cannot be described by the same solid solution. This difficulty to choose a minimum number of end-members among a large number of possible pure minerals will increase largely with more realistic clays with ferric and ferrous iron in iron in octahedral sites and several exchangeable cations... For that reason we have tried to build up a more simple but also more general system (Figure 3). Let us consider, even if this is more or less shocking, I know, that any possible end-member "has a chance" to participate in the solid solution. You can imagine a system with Fe^{++} and Fe^{+++} here in the octahedral sites, and K^{+},Mg^{++} and Ca^{++} or Na^{+} in this interlayer site. If we consider the previous quaternary system only, the four end-members will constitute the solid solution and we decide that each end-member has a thermodynamic relation with the aqueous ion activities:

$$K_i = Q_i \;/\; (A_i) = Q_i/(X_i\lambda_i)$$

If we do not have here the problem of the choice of end-members, we still have to estimate the solubility products (K_i) of all the end-members. By doing this and using the multicomponent solid solution in the simulations we found that it was very important to use these constraints: they act not only between the constituents of the solid phase and the aqueous activities but also inside the solid phase. This makes the solid solution of clay minerals (several substitution sites) very different from pure minerals, of course, but also from other binary or ternary solid solutions (only one substitution site) with respect to mass actionlaw equations. For pure minerals, the equilibrium condition concerns only ion activities, it is a a constraint only for the aqueous phase. But the solid solution gives both constraints between activities in the aqueous phase and activities in the solid phase. In order to illustrate the problem of choice of the solid solution set of end-members, let us consider a clay with increasing complexity in the formula. The total number of possible end-members increases progressively (Figure 4). If you try to choose the minimum number of necessary end-members to build up a simple solid solution, you see that the number of possible choices increases dramatically and you will not be able to justify one choice. For that reason we decided to build a model with all these end-members. I would need alot of time to explain more deeply our model and the results we have obtained applying it. I will just discuss one result concerning the occupancy of octahedral sites at low temperatures. The competition between Al, Fe and Mg is controlled by the chemistry of the solution, particularly by the magnesium to proton activity ratio $\log(Mg^{++})/\log(H^{+})^2$ (Figure 5). For increasing magnesium activity in the solution (or increasing pH), you see on this figure that the importance of magnesium in an octahedral position is increasing. But what is interesting is to see that you can find different chemical environments where you will have opposite relations between the different cation contents of these octahedral sites. If you have here an increase of ferric iron in the octahedral with increasing tetrahedral charge, this corresponds to a decrease of aluminium in the octahedral charge. But you can also have both increasing, depending on the characteristics of the system. This is the kind of mechanisms we

TRANSPARENT 1

1) DETECTION

AQUEOUS SPECIATION ------= SATURATION STATES

MASS ACTION LAW Q_i / K_i

2) EVOLUTION CALCULATION

PURE MINERALS : 1 EQUATION / MINERAL PHASE : Concerns only the aqueous solution : $K_i = Q_i/(A_i = 1)$

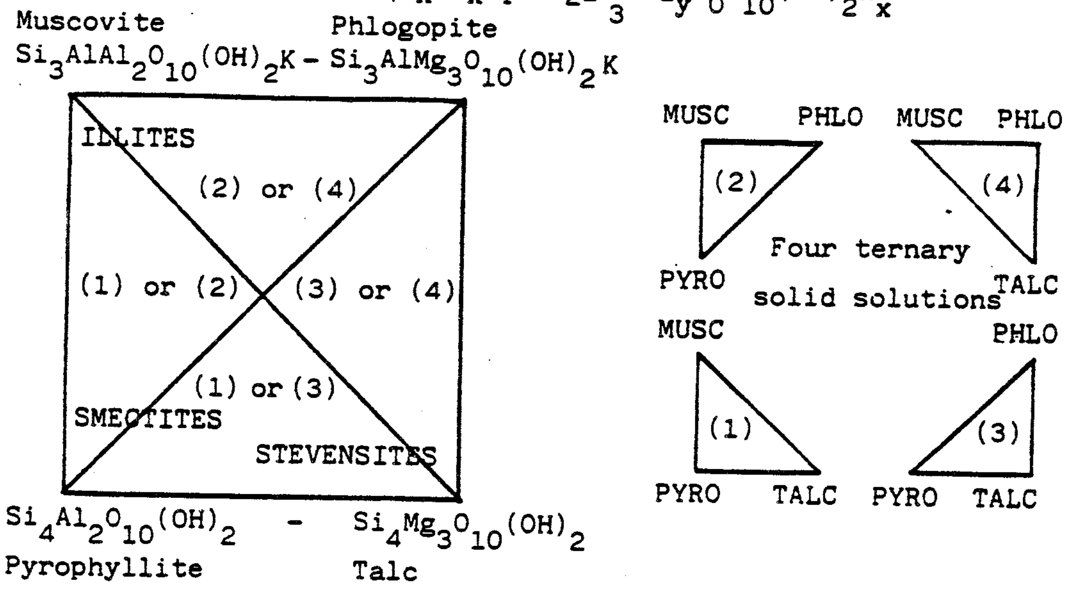
" REAL MINERALS " : solid solutions : 1 EQUATION / END-MEMBER : concerning both aqueous and solid solution

ex. :-$Ca_{1-x}Mg_xCO_3$ $K_i = Q_i / A_i$ for each end-member i
1 type of substitution only

-Clay minerals
2 or 3 different type of substitution

TRANSPARENT 2

General formula :$(Si_{4-x}Al_x)_T(Al_{2-\frac{2y}{3}}Mg_y)_O O_{10}(OH)_2K_x$



Possible ternary solid solutions in the pyrophyllite-muscovite-talc-phlogopite system.

TRANSPARENT 3

- general formula : 2:1 clays

$$(Si,Al)_T\ (Al,Fe^{II},Fe^{III},Mg)_O\ O_{10}(OH)_2\ (K,Na,Ca,Mg)_I$$

- end-members

  only one type of cation in each site

- Mass-Action Law : 1 equation / end-member

  $K_i = \frac{Q_i}{A_i} = \frac{Q_i}{X_i \lambda_i}$ with Q_i = I.A.P. ; A_i = end-member activity in the sol.sol.
  X_i = " " mole fraction
  λ_i = " " activity coefficient

- for an ideal solid solution $\lambda_i = 1$ and $A_i = X_i = Q_i/K_i$ (= saturation index)

=== EACH END-MEMBER PLAYS ITS ROLE IN THE SOLID SOLUTION PROPORTIONNALLY TO ITS SATURATION INDEX IN THE AQUEOUS SOLUTION

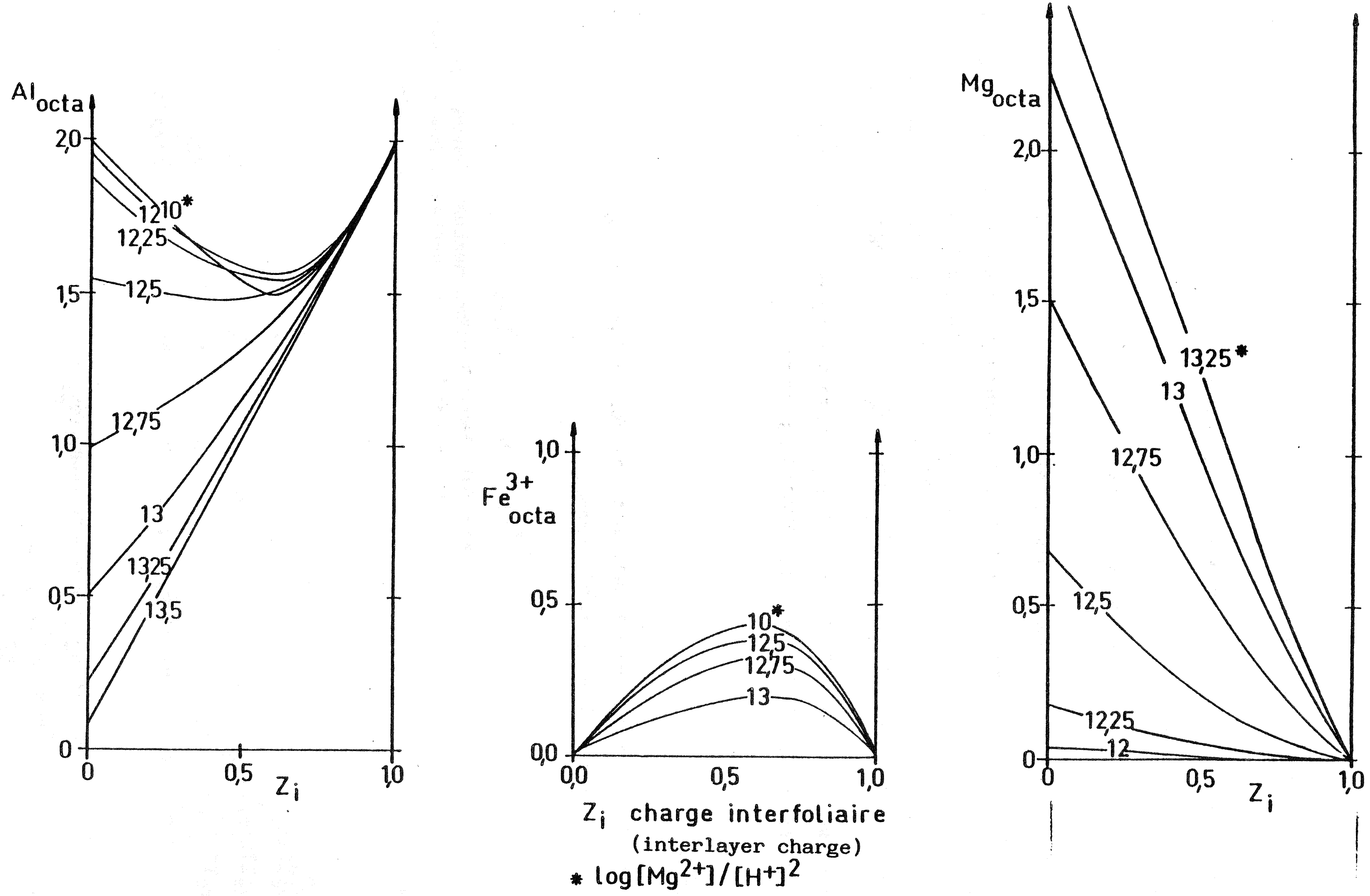
TRANSPARENT 4

Number of possible end-members and possible solid solutions as a function of the clay mineral composition

Clay mineral composition	N_{min} minimum number of end-members	N_{max} total number of end-members	N^* number of possible solid solutions
pyrophyllite-muscovite			
$(Si,Al)_T(Al)_OK_I$	2	2	1
$(Si,Al)_T(Al,Mg)_OK_I$	3	4	4
$(Si,Al)_T(Al,Mg,Fe^{III})_OK_I$	4	6	15
$(Si,Al)_T(Al,Mg,Fe^{III},Fe^{II})_OK_I$	5	8	56
$(Si,Al)_T(Al,Mg,Fe^{III},Fe^{II})_O(K,Na)_I$	6	12	924
$(Si,Al)_T(Al,Mg,Fe^{III},Fe^{II},Mn)_O(K,Na,Ca,Mg)_I$	9	25	2042975
"real clay"			

N^* = number of choices of N_{min} minerals among N_{max}

$$= C_{N_{max}}^{N_{min}} = \frac{(N_{max})!}{(N_{min})!(N_{max}-N_{min})!}$$

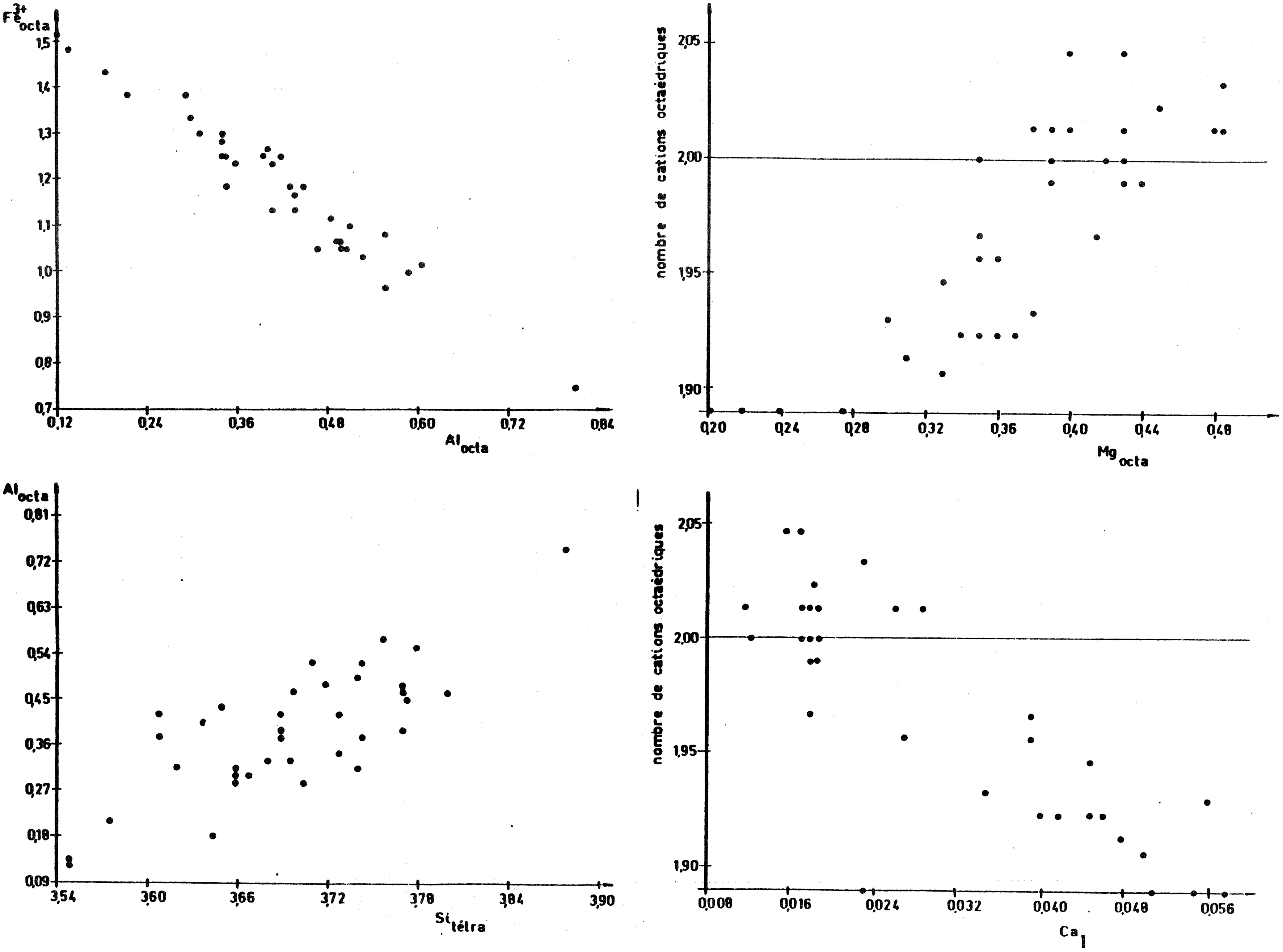


Octahedral and tetrahedral composition in a simulated clay mineral

(After Fritz,1981)

TRANSPARENT 6

Chemical variations in a population of 38 particles of one sample of glauconite



After Fritz,1981

try and hope to solve using this modeling and comparing the results with the analytical data on population of clay particles produced in a same environment. I give you one example from the work of my colleague Duplay, for a glauconite. The chemical variations in the composition of 38 particles studied by scanning electron microscope and microprobe are very important and unexpected for one sample of clay, let us say, one gram of a unique sample, as defined by x-ray pattern (Figure 6). These kinds of differences in the composition can be explained, if we accept that the solid solution effect can play its role.

Dr. Anderson:

When we had our first workshop last year, we considered two possibilities. Would it be possible to predict the stability and the alteration rates of smectites from theory? That is Point 1. Point 2 was: Is it possible to derive useful information on the stability of smectite clays from field evidence? The concensus, which was expressed in the report, was that there was no theoretical procedure by which one could predict the stability and the alteration rates of clays. Therefore, the only possibility has to do with interpreting field evidence. What is your reaction to that?

Dr. Fritz:

I would never apply this model without field observations first. I do not know how to call this approach correctly in English; you have information from field observations and you try to understand it; this gives you some information for a theoretical approach. You try then to apply the model and you go back again to the field for complementary information, and so on... I do not apply a computing "black box" that explains all the clays in the world. Such an approach, blind and disconnected from field observation (or experimental work) will just give nothing. What I have tried to explain at the end of my talk is that the kind of relation that we found by this model, between the different cation contents of clay minerals as functions of solution chemistry may be related to what is given to observations and analyses of real clays, for which the reacting solution is generally unknown. The modeling approach cannot be developed alone, it is a discussion tool using experimental results, field information and modeling trials.

Dr. Anderson:

Isn't it possible to say yes or no on this question?

Dr. Fritz:

I do not think so.

Dr. Mitchell:

Isn't he saying that you have to use everything together? Yes.

Dr. Anderson:

Yes, that is what he is saying but my question is, do we have a sufficiently sound theoretical basis for making accurate predictions?

Dr. Fritz:

To make the ideal model I would dream of I would say, no. Definitely no today.

Dr. Anderson:

That was our conclusion last year.

Dr. Fritz:

I know, I have read this report last week. I cannot say that we have now information to make the ideal theoretical thermodynamic model we need and it is not possible to do for the clay-solution interaction what some people did ten years ago between calcite and the solution.

Dr. Mitchell:

That is not to say there may not be a model which can accommodate all available evidence. You do not know.

Dr. Fritz:

When you try to apply the model, you see some problems. It can be a tool just to see the problem.

Dr. Anderson:

I have no difficulty in accepting the fact that theories are useful, even when they are not complete and even when they are imperfectly known. And the usefulness of combining theoretical deduction and field evidence, I have no problem in accepting. The question that we are considering, right now today, is that if we have to make predictions, are we better off making these predictions on the basis of a theoretical model or are we on sounder ground if we depend mostly on field evidence and deductions from field evidence?

Dr. Fritz:

I am not sure I can answer the question. I am not sure that the field evidence will help you to solve the problem of KBS, for example.

Dr. Mitchell:

You have got to have compatibility between such field evidence as you have and whatever models have been proposed.

Dr. Fritz:

If field evidence would give the answer, my place would not be here at all. I know the weakness of these models. I do not apply them just separately.

Dr. Mitchell:

Well, here we are Mr. Chairman. The time is 9 before five. Arne Gustafsson has agreed that tomorrow morning would perhaps be a better time to make his presentation because it is probably going to take 20 minutes or so. We have the possibility of two short ones. We could have those tomorrow too. It looks like we have enough flexibility to schedule or we could stay later now. I leave that up to you because you are the one who made the schedule.

Dr. Anderson:

We might as well stop now.

Dr. Mitchell:

Fine.

Adjourn

Dr. Mitchell: (Next day)

It is now 8:30 and the schedule says that it is time to start. As you recall from yesterday, we fell a little bit behind our schedule. We are going to accommodate the speakers that we could not hear from yesterday. I might point out that in this room which is so big that we may have to speak rather loudly in order to be heard. I think that it will get worse because I peaked through the curtains and see that that room is all setup for a large group. I expect that in due course it will get loud over there too.

We are still working our way through session II and I am going to call on Dr. Gustafsson to present the material that he has on alteration scenarios from the stoichiometric and geological points of view.

Dr. Gustafsson:

Good morning everybody. I will begin with making an approach to this problem from the point of view of feldspar weathering. The comparatively little difference in size between silica and aluminum allows both to coordinate and so on. This is elementary, written in the paper that is available on the table there. Written for everyone to get an introduction into this problem. The pure clays, as well as mixed forms of them, are not stable at all temperatures and pressures in the forms they had at the moment they were created.

You will notice that there are two positions with a pyrophyllite. These two pyrites seem to be quite equal but it is suspicious. I believe there is a difference between them, in behavior, in the later contact with cation. We can discuss it later on perhaps. It is essential to have those reactions, especially in the neighborhood of these repositories, with respect to electron transport that may take place around them. The ground is full of electric currents, different voltages and directions and so on and often we do not notice it so much, but in the geological and surveying activities and when we are searching for ores we come in touch with them, and we understand a little about how to evaluate them. You have heard, for instance, about a gossan deposit where sulfide ores and polyralent metal elements have their little game between their coordination states and transform between different metals. Copper deposits, for instance, have several stages of valence. Practically, you notice that too when you get troubled with your water pipes with corrosion; that it is electrons working against you just under your feet.

In clays and clay deposits there is movement too that is of importance to us and for our clays. I also say that in clays there is a sharing of oxygens that can be understood as a scarcity of oxygen in the surroundings. Four coordinated aluminum transfers to six coordinated aluminum, the most favorite form of aluminum. At low pH we can regard Al3+ as an end member and Si, as you know, forms the proto-acid and perhaps later on it crystallizes.

The solubility diagram is well known to all of you. You see that to have a quiet area between pH5 or 2.8 or a little more, alumina will not go into solution. Through silica, the quartz increases constantly at up to higher and higher solubility as pH goes up. But at both sides aluminum is very well able to go into solution. Here is a simplified approach to the question of stability of smectites. Fewer feldspars, clean water and air are thought to be present. A thorough described oxidation of feldspars we saw how the annual mu, mow and peat were developed and how, for instance, an origin in plagioclase is suggested by now. One way to look upon these minerals is to regard it as an increasing contest. Up there we have margarite at over 1.2, that means an origin in the plagioclase. It is very essential for us to know the source of the deposit. We are very glad to be able to represent five clay minerals of that type, to point out the part the welding has gone in, and an area that is well settled with equal conditions all over it. There have been streams, there have been inclines, there have been swampy areas with the vegetation and so on, and then reducing conditions. With the help of this we can say something plausible about the origin.

Here we have margarite and there pyrite, pyrophyllite, muscovite. From the best analysis we can get we tried to find out if there is a relation between aluminum and the silica. Down there all the tetrahedral aluminum is finished. Now we turn to the smectites and their stability. My opinion is that the better the weathering, the compositions that make up a forefold coordination of alumina, the better we are. An alteration we should not like in the repository. Irrelative materials occur in the form of debris, aggregates, etc., that behave in a balanced collaboration depending on potential, shape, distribution of charge, dispersion, pH, redox, and so on. A lot of conditions are represented here.

Phrosilicates have a tendency to grow in plates and they can join another. They need not be of the same composition. Two minerals of little different type can find another if the tetrahedral layer is of the same construction. What is there on the cation plane that is a secondary thing? They can be joined in the combinations like, for instance, glauconite, which corresponds to one more plus 5 pyrophyllite. Some of the chlorites that I had up there on the illustration you see are indistinct with respect to the cation member. But these, you see here, are distinct minerals. They have a distinct composition. They have found an order that fits and satisfies. But as I say, these in that group are variable. They are more or less equipped with iron. Iron +2 and iron +3 make it possible in the cation position to transfer charges. The illite-layer is a little troublesome for me still. But I believe, that we have in reality that mica goes to hydromica. And by hydromica, I mean where water molecule has substituted and potassium, then one hydroxyl or more in the aluminum layer, is substituted for a water molecule. But where is the mineral remaining after heating, in nature, of such hydromica? Where is the mineral representing the calcination, in nature, of hydromica? Isn't it illite? Calcination of hydromica can go up to 100 degrees, 200 degrees, 300 degrees, or up to some 500-600 degrees when muscovite decomposes. We need a lot of analysis from illite and a lot of ability from illite to absorb water and to swell. There are often discussions among scientists about this. I believe it goes the other way. Hydromica is formed, the potassium has left but then heat has come and then the water goes away and what is left is illite. That is one thought you can get from these diagrams.

If you take labradorite, about 67% andorite and plagioclase can be brought through weathering and form a beidellite. It can be created, I believe, in other ways too but it is important to remember if anyone makes this observation you must have your eyes open to that phenomena. What has been mentioned here may be an introduction to the phenomenon of regular and irregular interlayering of clay minerals and the stacking of these with limited symmetry. How the mechanisms behind the formation of these complicated and mixed-layered and stacked aggregates must be explained. Smectites exit, the main, depending on small differences in charges that cannot be exactly satisfied by one cation. I know there are swelling clays of types with unsaturated cations but that is another thing. Let us regard this one first that has built up an aggregate using the cation and itself.

I understand that we had better shorten this talk and let you study the printed papers and discuss it later on if necessary. I thank you people for your attention.

Dr. Mitchell:

Thank you, I think you have given us a few points that we could debate and discuss for some time. But as I interpret what you say you are beginning to provide for a framework to move through a whole series of transformations from one mineral to another. I think this will be very useful, and I personally look forward to reading and studying this in some detail even though I am neither a mineralogist nor a chemist. I think there are some concepts there that will be useful, and I think it will help in understanding the stacking and the interlayering and the consequent effects on the swelling. It is interesting that you have some difficulties with the concept of potassium and aluminum in this smectite/illite transformation. I suspect that we could debate that for awhile. Unfortunately, we don't have the time but that was one of things that I thought had been reasonably well agreed upon at some stage, at least it was one of the building blocks I was beginning to think about and evidently there is some question there.

Looking back now on an admonition that Duwayne gave us yesterday which was the main purpose of the workshop is to deal with the behavior of the smectite and its alteration. We have two short things to do, before we get more in detail into the behavior and in that regard, I would like to call on Robyn Johnston who has some things to present from yesterday and that will be followed by Dennis Eberl with his comments.

Ms. Johnston:

The point I would like to bring up deals with the pH of the clay- water system. The pH buffering capacity of the clay is very important. I have been wondering if that can be assured because in all the experimental work that I have done with clay, the pH has consistently fallen in chloride solutions. When you start with clay which is distilled water and have pH of up around 9 in chloride solutions, at 150 degrees for 30 days, the pH falls considerably to 5 or 6 and at 275 degrees it falls even further. I don't know what the mechanism for the pH change is. I was talking to Dennis about this yesterday and he wrote me an equation where the hydrogen ion was balancing the potassium ion in the formation of illite. But it is observed very consistently, and Dennis can bear me out that in all the experimental work he's done, as well, the final pH's at the end of the run, are always very low (Figure 2). I would like to hear what people think about this. Whether this is an effect that only comes in at about 100°C, whether it is not important below a hundred. This is something I don't have a lot of feel for, but I found in my experimental work that the final pH for the system has a profound effect on the product. If I allow the clay to control the pH the product is very much along the lines of what everyone has found. At very low potassium content, I developed a high-layer charge on the smectite with very little collapse to the 10 Å phase, and at the higher potassium contents the product is a mixed-layered illite/smectite (Figure 3).

With the pH being controlled by the clay and final pH down around 3 to 5, the layer silicates are preserved and the results are not really terribly controversial.

I did a few runs where I controlled the pH using either bicarbonate or potassium hydroxide, so that final pH's after runs at 275 degrees were between 8 and 10 for the bicarbonate systems and between 5 and 12 for the hydroxide systems. In these cases the run products were very different. If the final pH was above about 8 the run product is really quite complex, and by no stretch of the imagination were the clays (Figure 4).

There is still a clay component in there, but what I think I can identify in these are feldspars and an analcite phase with bits and pieces of things like that. But large amounts of feldspar and of the illite phase, so that there is destruction of the layer silicates, almost completely and formation of framework silicates. For the sort of middle range of pH with pH higher than if it had been controlled by the smectite alone, but still in the neutral range, I do not find any zeolites but there is still abundant feldspar. So that even when the pH is really quite low, in the neutral range, I am still finding destruction of the layer silicates and formation of framework silicates (Figure 5).

I think there is plenty of evidence in nature that layer silicates will form in the sorts of conditions we are talking about (Figure 6). But in the sort of regime we are looking at, acid to neutral system, smectites may form (Figure 7). In the neutral to alkaline regions feldspar and zeolite may form. At some pH, you're beginning to dissolve the layer silicate and precipitate framework silicates and presumably that would be a function of temperature. Then at some much higher pH you get the formation of zeolite. In natural systems there is plenty of evidence for low temperature feldspars. Potassium feldspar is very stable, even in the acidic conditions of surface weathering (Figure 8). And orthogenic alkali feldspar is very widespread, so there is a lot of evidence for stability of these framework silicates under low temperature conditions. I feel that conversion of the smectites to something other than clays is an option that has not been considered very much and it is a distinct possibility. There is plenty of evidence as well for zeolite formation mainly in volcanic sequences. The formation of zeolite is favored by conditions such as high silica activity and alkalic activity; and in closed systems, with restricted flow. And I think especially in the Canadian program where we are looking at very saline brines, the formation of zeolite is distinctly possible (Figure 9).

I've found it useful to look at some stability diagrams. I know that there is a lot of controversy about whether stability diagrams mean anything, but I think it's worth looking at them just from a point of view of trends. This diagram is at 25 degrees, quartz saturation in a sodium potassium systems. The different colored dots represent the shield brines, the highly alkaline brines. This is the more normal granite ground water.

For quartz saturation at 25 degrees, they are all plotting well down within the clay stability field.

You can look at the diagrams more in terms of clay stability down in this direction and framework stability up in this direction, rather than looking at the separate phases (Figure 10). If you move into a system where silica activity is higher, then you can prove that you are moving, especially the brine up further towards the stability field of the framework silicate. And the other point is that this is very pH dependent, as well. If you change the pH by one unit, you move these bars up in this direction to about here. But by increasing the pH even by one unit, you get a considerable effect on the stability of the framework silicates as opposed to clays. And if you look at higher temperature plots for the same system, again the effect is to move the ground waters up into the stability field of the framework silicates as opposed to the clay. This has relevance if you are thinking of a system where concrete has been used in the vaults. There has been quite a lot of talk using concrete in the vault as bulkheads, grouts, seals, and things like that (Figure 11).

Canadian Nuclear Fuel Waste Management Program

Bentonite - buffer (+ 20-50% Sand)
- backfill (+ 50-80% sand or crushed rock)

T - 150°C (at cannister surface)
- spent fuel (>100,000 ur)
- reprocessing wastes (10-100,000 yr)

Swelling pressure <hydrostatic (10 MPa)

Max pressure - lithostatic at 1000 ~ 30 MPa

Groundwaters - shield brines
Ca- Na- a

Figure 1

pH of Montmorillonite Suspensions

	Na-saturated	Ca-saturated
25°C		
DDW	9.5	8.5
150°C		
DDW	9	8
A^-	5-6	5-6
275°C		
DDW	5-6	5-6
Cl^-	3-4	5

Pembina montmorillonite, <2µ

Solid: solution = 1:50 (by weight)

$[Cl^-]$ = 0.1 to 1.0 M.

Run time = 30 days

Figure 2

Smectite-Chloride Systems

pH controlled by smectite

275°C

pH^f = 3-4 (Na-montmorillonite)

~ 5 (Ca-montmorillonite)

$[K^+]$ <0.1M

- development of high layer change
  (Mg-glycerol- peale shift to 14 Å)
- little collapse to 10Å phase

$[K^+]$ >0.1m

- development of mixed-layer illite-smectite
- proportion of illite increases with $[K^+]$
- Na-sm -more extensive reaction
  (Na-sm at $[K^+]$=0.1 Ca-sm at $[K^+]$ =0.5
- smectite partially beidellitic
  (Li-glycerol - peale shift 12Å)

Figure 3

pH controlled by solution

$HCO_3 + Cl^-$ pH_f = 8-9 (Ca) 10(Na)

$OH^- + Cl^-$ pH_f = 5-12

275°C $[K^+]$ = 0.1M

$pH_f \geq 8$

V. little smectite preserved

Some formation of 10A layer silicate

Complex reaction products

- feldspar
- analcime/wairakite
- boehmite/gibbsite
- ferrihydrite

pH_f = 5-8

Smectite preserved

Formation of illite (I/S 12A)

Feldspar abundant

Figure 4

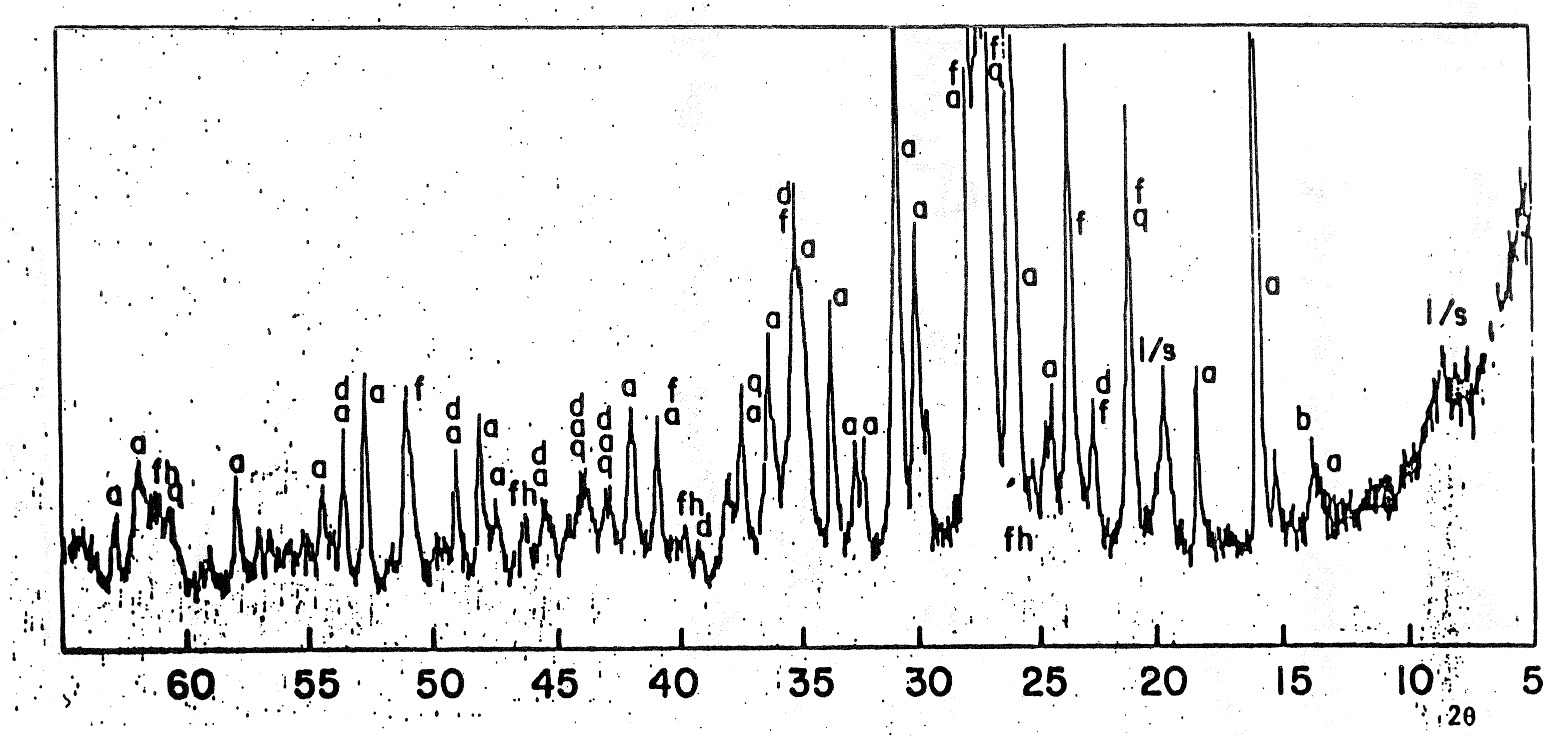


Figure 5: XRD Trace of Pembina Bentonite (Na-Smectite) After Hydrothermal Treatment at 275°C for 30 Days in 1 mol.L^{-1} K^{+} (as KCl and KHCO$_3$), ph Buffered at ~9. (Conditions as for Figure 3.1.1(4)1).

a	analcime/wairakite
f	feldspar
b	boehmite
q	quartz
d	diaspore
fh	ferrihydrite

2 REGIONS

1. pH controlled by clay (pH low)

   Layer silicates preserved

   $a_{Si^{4+}}$ low

2. Higher pH imposed by fluid

   Dissolution of Al-Si sheets

   Precipitation of framework silicates

   $a_{Si^{4+}}$ high

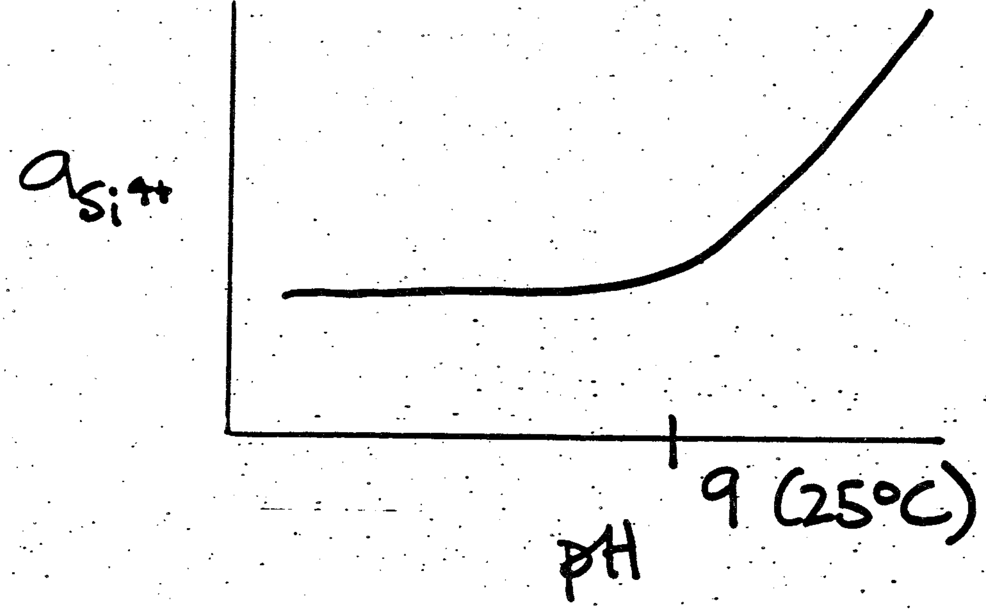


Figure 6

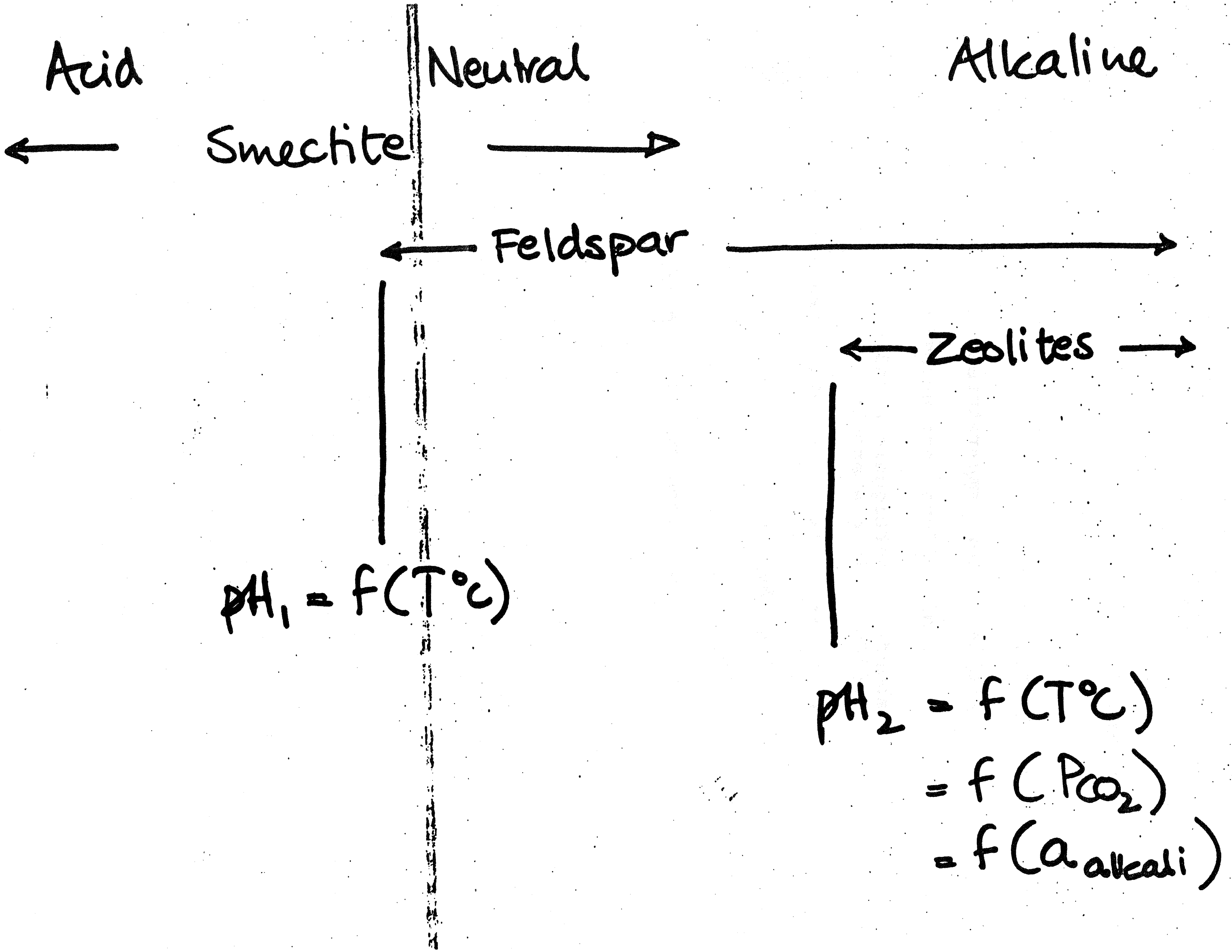

Acid
Neutral
Alkaline
Smectite
Feldspar
Zeolites
$pH_1 = f(T°c)$
$pH_2 = f(T°C)$
$= f(P_{CO_2})$
$= f(a_{alkali})$

Figure 7

Feldspars

$(K,Na)\,Al\,Si_3O_8$

- $Ca\,Al_2Si_2O_8$

Alkali Feldspars

- stable at low temperatures
- detrital feldspar not uncommon
- abundant, authigenic alkali-feldspar in diagenesis
- stability relative to clays favoured by
  1) high $A_{Na,\,K}$
  2) high pH
- sanidine produced experimentally at T = 150°C

Figure 8

Groundwaters

	WN - 1		SCS^3	
Na	1910	83	5050	220
K	14	0.36	50	1.3
Mg	61	2.5	200	8.2
Ca	2130	53	15000	370
Sr	24	0.28	20	0.23
Fe	0.56	0.01	-	-
Si	-	-	15	0.54
HCO_3	68	1.1	10	0.16
A	6460	180	34260	970
SO_4	1040	11	790	8.2
NO_3	33	0.53	50	0.81
pH	~7		~7	

Mg/litre

Millimoles/litre

Figure 9

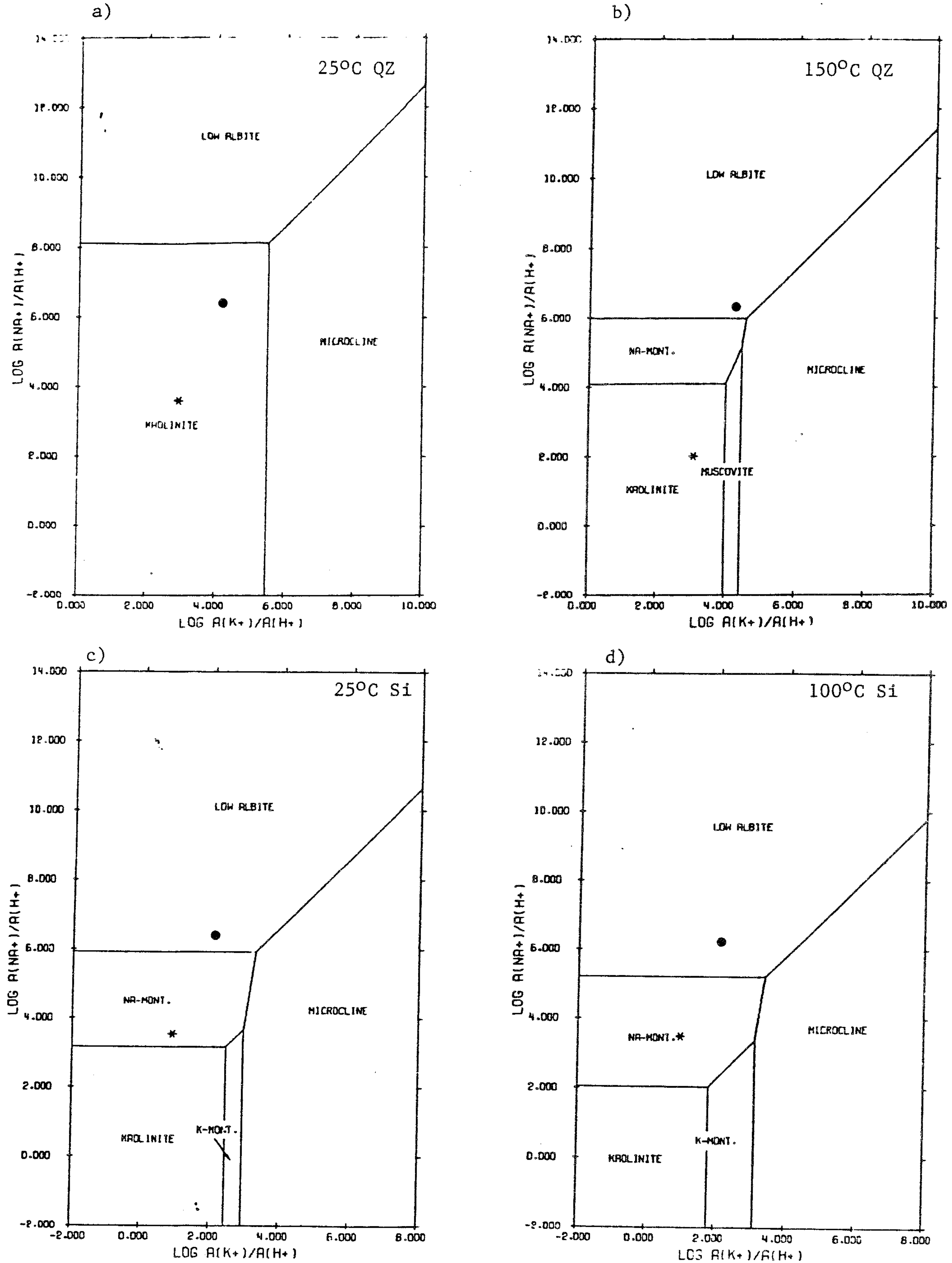


Figure 10: Theoretical Stability Fields in the System $4Cl-H_2O-Al_2O_3-SiO_2-K_2O-Na_2O$ (after Helgeson et al, 1969)

QZ: quartz saturation ● Standard Canadian Shield Saline Solution

Si: amorphous silica saturation * Granite Groundwater

CONSEQUENCES

1) Cementation
   - zeolite
   - feldspar all brittle
   - quartz

2) Loss of swelling potential

3) Volume change
   - expansion ?

Figure 11

One should because of the possibility of considerable volume changes during the reaction.

Dr. Anderson:

When you refer to the groundwaters in those stability diagrams, are those groundwaters in Manitoba?

Ms. Johnston:

The red and blue both refer to the Canadian shield sort of brines. The black dots which always plotted much further down, in towards the clay stability field, are typical of granite groundwater in general. And they're all plotted for pH of 7. And as I've said, this is very pH dependent. If you take the pH down, they move back into the clay stability field.

Dr. Anderson:

But, do the two colored dots correspond more or less exactly to your conditions?

Ms. Johnston:

The shield groundwater is almost infinitely variable. There is a variation from ordinary granite groundwater to waters of 30 thousand ppm calcium. So you know you can't say that.

Dr. Anderson:

Will you be searching for a favorable groundwater?

Ms. Johnston:

No, we'll be searching for a tectonically favorable and geologically favorable region. But we have found that almost everywhere they've gone, below 300 to 500 meters in the shield, we have found saline brines. So, this is a situation we're going to have to deal with. It looks like the groundwater will be saline brine. If the pH is rising in a system containing concrete, then I don't think you can guarantee that you're going to retain the layer silicates. There is the possibility of framework silicates in almost any situation where pH is increased.

Dr. Chapman:

At what temperature do you start to be concerned, then?

Ms. Johnston:

This is the problem. I've run most of my experiments at 275°C and I don't know how far down this effect would go. Maybe Dennis will be able to tell.

Dr. Eberl:

In nature, it seems to start at 60 degrees.

Dr. Chapman:

But there must be a big kinetic factor involved.

Dr. Mitchell:

With regard to some of these transformations you're talking about, are these occurring in an excess of brine?

Ms. Johnston:

I have done my experiments in chloride solutions of .1 molar.

Dr. Mitchell:

But what about the relative proportions of solids and fluids?

Ms. Johnston:

I've been using 1 part clay to 50 parts solution, by weight.

Dr. Mitchell:

Okay, whereas in the repository, this is more likely to be the reverse and that may well be a factor that we can't overlook.

Ms. Johnston:

Yes, the things that you have to look at that are going to affect it are solution ratio temperature and rate of flow. But rate of flow is likely to be very low and that is going to favor framework stability rather than layer lattice stability. Since it's going to keep the alkalinity high.

Dr. Chapman:

I think the kinetic factor has been ruled out in this case because of the generally low rate of flow.

Ms. Johnston:

I've run some experiments at 150°C, in those I don't find the framework silicates but I do find that there is destruction of the layer silicates. That the x-ray patterns after reaction in 30 days at 150°C have lost a lot of their definition so that even though I'm not forming framework silicates, the layer silicates are suffering.

Dr. Fripiat:

I would like to offer an observation that I think is relevant to the discussion. We have tried to increase the charge of montmorillonitic minerals, such as bentonite, to exceed a differential change and we have observed using sodium nitrate, not fluoride, you increase the amount of the hydroxyl content.

Well, I found this in the runs I did with the pH controlled by the clay. Even at low temperatures, 150°C, and without very much potassium in the system, I built up a high layer charge in the clay. I get something that is almost vermiculitic in charge. I don't know about composition, but in charge.

Dr. Eberl:

I would like to say a little more about the smectite to illite transition. And then I would like to talk a little about ion selectivity. I hope this will only take about 10 minutes.

There are several ways of getting from smectite, in this case potassium beidellite, to illite. One way is if you have potassium beidellite, potassium as the interlayer ion. This will react to form illite. If it goes all the way, of course, it forms illite/smectite on the way. If you have extra potassium in the system, beyond the cation exchange capacity, and in this case there is no need to form kaolinite, just go to form illite plus quartz giving off hydrogen ion. This causes the pH to become low. You could have another system where you have not only excess aluminum but also extra potassium in the system, plus beidellite. In this case, you form a different amount of quartz. Less quartz and no need to form kaolinite. So these are three different reactions and it's not always clear which reaction is going to happen in the system.

Next slide. Now this is the reaction we studied when we started out with the gel of beidellite composition with just enough potassium to fill the cation exchange capacity, so we're looking at a system which will make kaolinite at lower temperatures and pyrophyllite at higher temperatures, and quartz. This amorphous gel reacts first to form 100 percent expandable smectite. With time it goes on to form illite/smectite, kaolinite, or pyrophyllite and quartz. The illite/smectite gets more and more illitic with time. This is what we find generally when we study clay reactions in hydrothermal systems. They don't go immediately to the stable phase, but rather they pass through a whole series of other phases on their way to form a stable phase. This is called Ostwald's step rule.

Now here is a reaction at 390°C. Of course, we use elevated temperatures so that these sluggish reactions can happen. These reactions occur in nature at much lower temperatures where you can wait a thousand years or a hundred thousand years instead of one year for your reaction to occur. As you can see, starting with this beidellite gel, using either potassium as the interlayer ion or sodium as the interlayer ion, you get much different reaction products. First of all, with time, three days, 23 days, 169 days, you can see that the potassium clay decreases in expandability regularly with time, everything else is constant, you're only changing the time. The sodium smectite, however, stays expandable at this temperature. This is very nice if you plan to use sodium smectite, it looks like it stays expanded. I don't have the data here but the interesting things is that when we ran the reaction at 250°C, the sodium gel reacted to form smectite and it stayed smectite with time. Why this, is I don't know. The lower temperature reacted to form a mixed layer of clay and at the higher temperature it stayed expanded. We ran these experiments for a very long time 200 days, and saw this pattern of behavior. At a higher temperature, still, it reacted to form a mixed layer of clay. It looked like at an intermediate temperature it collapsed. So you may run into problems running clays at higher temperatures to try to predict what will happen at lower temperatures. Maybe you will be surprised.

Here is a reaction at 490°C and, of course, in this case, the potassium gel reacts faster, going towards pure illite. By the way, these numbers are expandabilities. So that this is 35% smectite, 25% and then 10% smectite layers, is going towards forming illite. Now you can see at the higher temperature, the sodium smectite is reacting downward to form a mixed layer of clay. So with potassium saturated Wyoming bentonite, starting with gels, we formed this series of mixed layer clays with time. In nature this seems to start at about 50°C or 60°C.

Now, this potassium series here is just one example of a more general reaction trend. You can form mixed layer clay, different kinds of mixed layer clay, by simply switching the interlayer cation. Starting with potassium, with sodium, or magnesium or something like that, you get different series of mixed layer clays. If you start with a sodium smectite and reacted it 400 degrees you form this regularly interstratified chlorite smectite. Finally, if you get the temperature up high enough, it reacts to form chlorite, a pure chlorite. If you add lithium chloride to this system, instead of reacting to form a mixed layer chlorite/smectite, it actually forms a mixed layer mica-smectite. Why this is, I don't know.

Magnesium smectite forms Hectorite. Magnesium smectite plus magnesium chloride reacts to form this regularly interstratified chlorite smectite, finally all the way to chlorite. Calcium smectite also forms these mixed layer clays with time.

If you have a calcium smectite and add aluminum to the system and react at 150 degrees, you form a mixed-layer of kaolinite smectite which gradually reacts to form kaolinite, passing through these mixed layer phases. At a higher temperature, we formed a mixed-layer pyrophyllite smectite, a phase that hasn't been found in nature yet, but it has been found in our gold tubes. This reacts to pyrophyllite. These, of course, are happening in a closed system so that the reaction products don't have a change to migrate away.

Now the next thing I would like to talk about as far as this reaction of smectite to mixed-layers is concerned is the effect of pressure. We can see that in these experiments we're starting with different kinds of smectite here: sodium saturated smectite, lithium saturated, calcium saturated, and potassium saturated. This means simply autoclave pressure, or low pressure. The other experiment was carried out at 2 kilobars. You can see for the sodium smectite, 400°C 7 and 30 days autoclave pressure react to form this rectorite mixed-layer clay, kaolinite and quartz. Higher temperature, here and 21 days. At low kilobars pressure, smectite stays smectite. See the same pattern with calcium: low pressure, mixed-layer clay, high pressure stays smectite. And, likewise, here although the results are not as spectacular. What we are seeing here is that increasing pressure favors the expandable phase. In other words, if you increase the pressure and you favor staying with smectite rather than reacting to form mixed-layer clay, this is understandable in terms of LeChatelier's principle. It must be that interlayer water, in hydrothermal systems, is denser than pore water. This makes sense because interlayer water is under electrical fields in the innerlayer where it can be held in a denser state.

I would like to emphasize what Dr. Weiss said the other day that trioctahedral clay is more stable than dioctahedral clay. If you're worried about thermal effects, then perhaps it would be best to use trioctahedral clay. There are large deposits of trioctahedral clay in the Western United States. Perhaps this is the clay to use. Now Dr. Weiss was talking about both dry systems, where the water has a chance to migrate out of the system and a wet system, where it is confined. I'm going to talk only about a confined system where these reactions were carried out in welded gold tubes. Here we see montmorillonite untreated and here we ran a potassium montmorillonite, this is the Wyoming bentonite, for a week at 400°C. You can see that the reaction has been profound. This is reacted to form a mixed-layer clay. When these layers collapse, they expel water which is the last thing you want in your repository to be moving around, and also there is a change in volume so that this can lead to cracking. It loses a lot of its cation exchange capacity when you form mixed-layer clay, so this is something that we need to be concerned about. Let's see what happens with saponite. Here is the untreated saponite and saponite after one week at 400°C. You can see that there has been little or no reaction. Saponite is much more stable in hydrothermal systems. We think this is because saponite contains so little aluminum that there is no way to build a layer charge in this system, the layer charge needed to form a mixed-layer of mica smectite structure. You want to keep aluminum away you can stay highly expanded even in hydrothermal systems. Of course, a week isn't very long.

Here is another example, just like the last two. These were run in gold tubes side by side in a hydrothermal bomb and the temperature in the bomb varied due to a failure of a thermal couple, but they were run side by side so they were treated exactly the same way. After 34 days at some temperature between 300°C and 500°C the saponite, starting with a gel this time, the other one starting with natural saponite, stays highly expanded. The K-montmorillonite gel reacts to form almost completely formulite. Here is a K-saponite gel, run for seven days at one kilobar at 300°C. You can see from this pattern that it is highly expanded. There might have been a little reaction here at 350°C. You can see that the low angle scattering here has gone up a little bit. The same here at 400°C, but not much reaction really. But then we get up to 550°C, after a week, we can see now that the saponite is beginning to react. It is probably beginning to react to form a mixed-layer of talc saponite. So we can get saponite to react if we take the temperature up high enough. Here is a K-saponite gel at 450°C one kilobar. After seven days, good smectite; thirty days, still good smectite. After 120 days we're starting to get reaction to a mixed-layer clay; 200 days later, the reaction has been profound. The mixed-layer phlogopite smectite and mixed-layer talcsmectite. So the thing here is that if we wait long enough, we can get the trioctahedral clay to react, if we raise the temperature or if we increase the time.

This slide emphasizes the idea of the Ostwald step rule. We cannot simply use short-term hydrothermal experiments to tell what is going to go on, because these things react in stages. As an example, we start out here with a talc composition. We have temperature on this axis and time on this axis. Let's talk about say 400°C. The first thing we form is a good talc. With time, this talc seems to decay. There is sharp x-ray peak, then this peak gets broader and broader with time and then this reacts to form stevensite, curolite and stevensite with time, and if we let it go far enough, we begin to get corensite showing up and crystobalite. So all we're doing is changing time here, keeping temperature pressure the same and see these sluggish silicate reactions, who knows what the stable phase is? Here we have reacted for over 200 days and we still haven't reached stability. What is going to happen in the repository over the course of a million years? It is hard to predict from these experiments.

This is nothing new. In fact in zeolite synthesis, the idea is to interrupt the experiment at the time when most of the phase you want has formed. In zeolite systems one phase will form, and perhaps if you are interested in the second phase, you wait that amount of time, then you can extract that phase.

Now a little bit about selectivity. This is a little bit speculative. We have two ions here, sodium and potassium, being attracted to the clay surface which is this negative surface. Of course, this can be described qualitatively by Coulomb's law, where the energy of absorption equals the charge of the cation, which is +1, times the charge of the annion, which is -1, times the constant divided by the radius of the cation and the radius of annion. The radius of the annion will be constant, so that the energy absorption goes up as the radius of the cation decreases. We have potassium with its hydration shell, sodium with its hydration shell. Hydrated potassium ion is a little bit smaller, so it's absorbed with a greater energy and so it's preferred on the clay surface. Potassium is always preferred over sodium. But thinking about the forces involved here, potassium has an attraction for its water hydration and also has an attraction for this clay. Now if the attraction for the clay exceeds the attraction for its water of hydration, then the potassium ion will dehydrate. We can change this attraction by simply increasing the layer charge or shrinking this plate. So then we have a dehydrated potassium ion competing with the hydrated sodium ion. Potassium is very much preferred over sodium.

We can continue to increase the charge here on this plate and we can reach a point where sodium dehydrates. Then we have dehydrated potassium competing with dehydrated sodium; here sodium is preferred over potassium. This would be the case of a smectite of low charge, where hydrated ions are competing. This would be the case of sodium and potassium competing, say a case of vermiculite where potassium is very much preferred over sodium. If we have both of them dehydrated, as happens in some zeolites, sodium is then preferred over potassium. This can be represented qualitatively here by the free energy for this exchange reaction. Where both ions are hydrated, then the exchange free energy is close to zero, it is a little bit negative, so potassium is slightly preferred over sodium. When the field strength increases by increasing the layer charge, you reach a point where potassium dehydrates and then potassium dehydrates and then potassium is very much preferred over sodium. When both dehydrate, then the free energy for that reaction becomes positive, it moves to the left, and then sodium is preferred on the clay over potassium.

Now what would be nice to be able to do, if we could design our clays properly, and if we wanted to remove a certain element, would be to pick a charge that would dehydrate that element and not the other elements.

One other point here, this is data by Warren and Jacobs. It has been repeated in a more elegant fashion by Maes and Kramers in Belgium. We have the different kinds of clay here. Illite, montmorillonite a mixed-layer biotite, vermiculite and kaolinite. The CEC of the clay is here. You might think that if you want to remove, in this case, cesium, the thing to do is to get a high

CEC, get a Wyoming bentonite. This will remove most stuff. But actually what we should think of instead of CEC is selectivity; what ion is selected by the clay? Let's look at proportion of the exchange sites. This is filled by cesium on the clay. This is run in six molar sodium nitrate solution with 10^{-4} 4 molar cesium. In other words, an enormous amount of sodium in the system and just a little of cesium. This is the proportion of the exchange sites; one would be all of the exchange sites filled by cesium; zero would be none of the exchange sites filled by cesium. You can see on illite more than all of the exchange sites are filled by cesium. That is enormous selectivity of the illite structure for cesium. Montmorillonite is not too good at removing cesium from this concentrated sodium solution. The group in Belgium is proposing that in order to remove cesium we should surround the canisters with illite. This is so selective for cesium that even if we have other ions in large concentrations, cesium would be removed quantitatively.

Dr. Banin:

Is it milligrams cesium or ...?

Dr. Eberl:

It is milli-equivalents. There are a couple of explanations for all this. We don't know which is the right one. One is the frayed edge theory where we have the illite structure with a frayed edge here and a hydrated cation here. Cesium goes in for this hydrated cation and collapses the layer around it so that it is fixed in the illite structure, the frayed edge theory. Here is the theory that I favor, it is called the "weak force fixation." We have some sort of defect in the structure giving rise to an extremely diffuse negative charge around the illite crystal that needs to be balanced. And we have two cations competing to balance this charge. One is a hydrated cation and one is cesium, which is thought not to be hydrated in solution. This one is so insulated that it can't see this extremely diffuse charge and so cesium is fixed by this diffused charge because it doesn't have a shell of hydration around it. In other words, cesium is fixed because the force is so weak that the water insulated cations can't see it.

Dr. Mitchell:

We turn now to the physical, chemical and rheological properties of smectite and extending that to what the implications are for the long-term stability of the clay as a sealant in the waste depository. I was called on to say a few things about this. Hopefully, there will be a few points here that are relevant and I hope that it all isn't too simplified for what we are trying to do. They suggested though that some of the very basic considerations would be appropriate to discuss.

Can we rely on smectite? This question is appropriate because just a few days ago I learned of this book, which many of you have probably seen. One of the authors of the book, Vif Lindblom, is spending the year at Berkeley with us. He is a very good friend of mine for ten years standing, but I didn't know that he had written a book until he gave a seminar on it a couple of weeks ago. The basic issue here is nuclear waste disposal, "Can we rely on bedrock?" Of course, if the answer to that is no, then we are going to have to rely on smectites, aren't we, because the rock won't do the job. If you haven't seen this, it is an extremely interesting book. It is done more for the layman to understand the problem of nuclear waste disposal and the illustrations in this are absolutely marvelous.

In looking at this question, it seems to me that here are essentially four aspects of behavior that we have to be particularly concerned about. First, the volume change properties. We need to know whether it's going to expand, shrink, or crack, as a result of these volume change properties. We're going to need to know if they are likely to change during the life of the repository. We're going to be very much interested sometimes in the stress-strain-time and the strength properties. But of the four main categories of behavior that I think are important for the study of engineering problems involving clays, I would put this one perhaps as least important, at least the strength part when it comes to packing smectite into a repository. Although there are some aspects of stress-strain-time that relate to what might happen if there are some deformations that could be important.

One of the most important considerations will revolve about the conductivity characteristics and when I get to this we'll see that there are several aspects of conductivity and several types of flow that have to be considered; they have extremely important ramifications. In a fourth category we could mention durability or stability, and what we can anticipate in the way of changes with time. The bulk of the discussions that we have had over the past day and half have been focused on these changes with time. I think that from the standpoint of repository sealing that of these, one, three, and four are going to be our major concerns. We have talked about this indirectly. the properties will depend on both the compositional and the environmental factors. We're going to be in deep trouble if we try to deal with one to the exclusion of the other. Compositional factors as I see it are essentially these items: (1) The types and the amounts of the minerals. We have heard talk here about many different kinds of clay. There are proposals that will involve mixing clays with other minerals for filling the repository and so on. They are going to be important considerations. But that is not enough. In the system there will also very likely be some amorphous material and some organize material. These can have a very profound influence on behavior. There has been discussion in the past few days, at the party last evening, about the amorphous quartz and everything else that can be there and the effect that it can have. (2) The pore fluid. The pore fluid is the water phase and whatever is dissolved in it. There conceivably could be a gas phase. In fact depending on how one might use a smectite for a buffering material in a repository, it could go in with air present, it might not be fully saturated. That can have effects. (3) These are the compositional considerations also that we have to worry about, what are the density and structure of the material? Clays, in general, really are an infinite variety of materials. You can take a given clay and from a physical and mechnical standpoint, cover a range of behavior from here to here. But practically everything is in between and this depends a lot on the water content and the density and on the structure for given values of these other things. That really is simply to say that the compositional factors establish the possible range of property. They do not identify the specific property. So to know that a soil is a 100 percent trioctahedral smectite tells you part of the answer but you cannot be specific as to what the actual strength, or compressibility, or hydraulic conductivity will be until you know something more about it. For assessing the compositional characteristics of these materials, we have a couple of things that are very useful to us. The grain size distribution and the Atterburg limit. And these are good classifying properties but they won't tell you by themselves, of course, whether the actual situation will be one of lower or higher conductivity or swellability or whatever. Of course, with the grain size distribution, what we commonly do is to develop some sort of a gradation curve. I want to make the point here that very often the result we get is more an artifact than the real thing. We can get whatever grain size curve we want very often in a laboratory test and it may or may not bear a relationship to the effective gradation in the clay material as you encounter it in the field. That is because we can break down clays, we can break ions and we can do a whole lot of things just by how we go about doing the test. Those are compositional factors. Also the Atterburg limits are compositional factors. The liquid limit, the plastic limit and the plasticity index, these terms I think are familiar to just about everybody here, they have been used over the past couple of days, but we should note that they depend on the type and amount of clay, the absorbed cations and the pore fluid composition. We have some pretty good ideas of the ranges of Atterburg limits of the different common clay minerals. For the kaolinite we are looking at the least plastic. The kaolinites will usually be down to less than 50 percent. The illitic material will be higher in the range of 50 to 100 percent and the smectites can go to several hundred range percent water content, corresponding to the liquid limit. The liquid limit is an arbitrary thing, both of these limits are arbitrary things but they are quite reproducible if the procedures are controlled. The liquid limit can be viewed in another way. It can be viewed as the shear strength corresponding to a certain condition because it is a dynamic slope failure test that you do to measure it. You have the material in a dish and you cut a groove in it and bounce it up and down until it closes. There is a general range of shear strength that corresponds to this but at the liquid limit, a clay material is far wetter than we had ever been dealing with in the repository. It's a pretty soft, mushy material. At the plastic limit where the arbitrary boundary between where it behaves as the plastic type of material can be deformed without cracking or without rupture and where it is brittle and falls apart, perhaps the plastic limit condition would be more representative of what we would encounter in a repository. If one follows the Swedish approach, at least as they are looking at it now with the densely compact smectite, it is far drier than that.

Now these limits reflect both the type and the amount of clay in the system. And these came out of general soil mechanics and soil engineering where we have materials that are commonly made up of clays and silt sand, and so on. And it recognizes that when you have the clay materials present, they can have a very pronounced influence on the behavior, and plasticity is important. If you think about it for a bit, you come to the conclusion that what these reflect are the type and the amount of the clay. You cannot distinguish clay types just on the basis of Atterburg limits alone. But there is a way that can be done which is very useful and that is to make use of a property that we call the activity, A. The activity is simply the plasticity index divided by the percentage of clay size material which is the percentage less than 2 micrometers.

We get this kind of a relationship for kaolinites and illites. Smectites can cover an extremely wide range. We could have a narrow range there for illites, but the important thing is to note that the smectites can have activities that range anywhere from say 1 up to 7. Usually these other materials will have activities that are less than 1.0. Again the plasticity index is the water content percentage difference between the liquid limit and plastic limit. Where you are here can vary greatly for a given smectite depending on such things as the type and the amount of pore solution, electrolite and the types and amount of the absorbed cations. Simply by varying the pore fluid characteristics, you can go here to here, let's say for some of the clays.

A good comparison, of course, would be a sodium and a calcium montmorillonite. The liquid limit of some of the sodium montmorillonite is up around 700, the activity up around 7. Some of the calciums may be down around 100 liquid limit and an activity of 1. That gives us some cause for concern and consideration when dealing with these materials for repository use. We consider the environmental factors, the temperature, the pressure, the availability of the water, and chemical factors. I don't know if it is going to be important or not, probably not, biologic factors; there may not be any. These wastes will probably take care of that concern. But in any event in some other problems that we run into, biological factors can be more important than we have given them credit for in the past and now we are learning alot of things that we hadn't noticed. And, finally, radiation which was discussed briefly yesterday. I think there still remains some questions about radiation. With respect to these environmental factors, we have to realize that they determine the actual property value. The compositional factors give us our range, the environmental factors give you the specific focus as to what it will be. Both have to be given careful consideration.

Well now let us turn to these four classes of properties that I started out with and make a few brief comments. Volume change: Generally speaking, the relationship between either water content or void ratio or porosity whatever you'd like to use to characterize your volume, and pressure or depths of burial if you are looking at something in a geological column, will be something like this. If the pressure gets high enough, these things get packed into a system that is more or less independent of what the material originally was. If you densify any of the clay materials simply by pressure compaction, you get down to some low porosity or some low water content or some value of bulk density. I suppose I could have put bulk density with a reverse arrow on the axis or if you go to a high enough compaction stress, they all come to more or less the same thing. But at the lower stresses, you can have quite a range and in general the higher the plasticity index, or if you wish the smaller the particle size, or again if you wish the greater the specific surface, the higher up you are likely to be on your particular curve or the higher up it is likely to be that the particular curve. For the application of clays that we are looking at, say the Swedish system, we are down here, it is dry packed. Well, it is not really dried, it is almost like brick. It has been pressed under such high stresses. So we are down here. And again as I pointed out yesterday, this pressure corresponds to the swelling pressure of the material if you want to look at it that way. If you unload it then presumably it would swell. Now which curve it would follow on swelling depends on what the material is and what your environmental conditions are during the swelling process and again a given material like a smectite can swell a lot or little depending on those factors.

Also we need to keep in mind in dealing with this, that temperature, pressure and composition affects solution composition. Affects are the greatest at the low pressures and for the high activity clay. You can get big changes here by changing these things, not so big changes over here. We have to keep that in mind. If we want to examine further the swelling pressure of smectites, as I have already stated the electrolite, cation and so on can be very important. There are some theories for working out this swelling pressure. They have been around now for a while. Particularly, the double layer theory which thirty years ago was given a great deal of attention and seemed to explain very nicely some things that went on in pure clay systems with extremely small particles. They will also work for clay systems with extremely small particles with some silt sized and sand sized tossed in, provided that you don't have the granular materials interfering with each other. But we have done experiments that show reasonably good agreement with double layer predications for sodium montmorillonite, half sodium montmorillonite and half silt for example. This has worked out pretty well. There are some problems with it so you will find that there are also some other approaches to the problem. I know that Phil Low has put together an interpretation for swelling that looks extremely interesting and promising from the standpoint of surface area consideration. This suggests that the double layer is not the issue at all, but it is the surface area. But on the other hand if you change your solution composition, why then your effective specific surface changes too and we get into questions of tactoid sizes and distributions and all that kind of thing. In any event, there may or may not be a mean for looking theoretically at what the swelling pressures are going to be. Dr. Pusch, you did that with your experiment but how did you calculate the swelling pressure? Did you do it phenomonologically or based on double layer theory?

Dr. Pusch:

We did it several ways, we applied the Bolt-Warkentin type of theory and if the bulk density is below two tons per cubic meter, you have a reasonable agreement between theory and practice.

Dr. Mitchell:

Now let me speak of stress-strain-time and strength. I said I don't believe strength is a major issue because we are not trying to support anything. The stress-strain-time behavior on the other hand may control the ability of the clay mass to adjust to volume change and/or distortions of the repository without cracking. That we have to be careful about, because we wouldn't want any fissures and cracks to open up. Smectites will exhibit both creep and stress relaxation behavior. That is if you sustain a stress on them and there is room for them to deform, they can steadily move as a function of time under a deforming shear stress. Or if you put a stress on them and hold them in the deformed state, the stress required to maintain that deformation can relax with time. And phenomenologically there are some relationships that can be used to study creep and stress relaxation behavior. I would say we would be most interested in maintaining ductal rather than brittle behavior. That has come up a couple of times in the discussion and what we mean is we would like the material under stress to be formed without breaking.

Now we get to a really important consideration. I would say probably this is the most important consideration in the use of smectites in a repository conductivity. After all, the whole name of the game is to keep any waste that may come from the canisters from coming into contact with the surrounding groundwater or the ground surface. Conductivity can be an extremely complicated thing in clay. There are four kinds of flows at least that I think we would want to be interested in. Fluid flows, chemical flows, thermal flows and electrical flows. We haven't said much about electrical flows but as Dr. Gustafsson said, we have lots of currents and voltages and things in the ground and over a period of a hundred thousand to a million years, I think those small potentials that might be there could be a factor. The direct flows are simple in concept. We have a hydraulic gradient and water flow, hydraulic pressures drives water, temperature difference drives heat, chemical difference drives chemic diffusion, and so on. We treat those most usually using Darc's, Fick's and Ohm's law. And of great concern in all that, of course, is the coefficient. Here we have our conductivity coefficient. We can in the laboratory very often make measurements of this. The question then that arises in the field is will the conditions be the same and will they stay the same. This is the nub of the problem here. So we have to think about that and there are a lot of things that become important there, a lot of concerns. Just trying to predict the hydraulic conductivity can be one of the most challenging things that we run into, at least the problems I have come up against. Like whether a storage pond will have a leak rate that is less than a certain amount. We are going to put in a clay liner and compact it and we try and estimate the hydraulic conductivity. We can miss by a great deal, a very great deal, and the consequence can be rather major. The mathematics of these kinds of flows are now quite tractable because we follow similar patterns for each of these. The equations are not that complicated and with numerical methods we can work out, even for complex flow systems, what is going on. We also have though coupled flow and these have to be considered where we have temperature gradients and we have chemical gradients and we have hydraulic gradients, and we have now identified we can have electrical gradients. That is, a flow of type can be caused by a gradient of type J depending on the magnitude of this coefficient here. For example, we could have thermal osmosis, electro osmosis, chemical osmosis; a whole host of things could go on here. With four basic flows you have a combination of sixteen. The four direct flows and three cross flows for each type.

Irreversible thermodynamics has a major role to play here. It can get complex, but at least it serves as a basis for organizing our thinking and trying to understand what goes on. It turns out from experience that the kinds of fine grained materials in which coupled flows may be important are likely to be clays and of them smectites may have the most significant effects of all. This may need some further consideration beyond what evidently has already been done for the repository problem. Hopefully, Amos Banin will commment some on this later because I know he has worked much with the coupled chemical hydraulic system.

Coming back to the direct fluid flow, which is going to be probably the major transport mechanism will be the direct fluid flow. We're most interested in pore size and in pore size distribution. There are various theoretical approaches for deducing what the hydraulic conductivity should be in terms of the composition.

The bulk of the flow is going to go through the larger channel. And here the homogeneity of the clay pack is going to be absolutely essential to prevent there being large flow through certain channels. The small hole effect, I wrote that down simply to point out that little holes in an otherwise dense material can have one whale of an effect. One of the courses that we teach in our program in engineering about seepage and groundwater flow has to do with cutoffs and leakage through barriers and so on. You can do an analysis which will show, for example, if you want to drive a sheetpile wall into the ground to cutoff flow and you have a layer that is this thick, if you miss 10 percent of that cross sectional area, 90 percent of the flow will still go through, compared to the flow that would go through if you did not put anything in the ground. So those kind of things have to be thought about.

So those are the flows and there are some other aspects of these fluid flows. If stuff gets through, then we release waste into the environment and it is important, of course, that we prevent that. But there are going to be as they go through a clay barrier, if that is what we wind up using, various absorption/desorption phenomena. That is important, in its own right, because then we could perhaps count on the clay to pick off some of these bad things before they get out. But on the other hand, we have to give some thought to what is being replaced and what the consequences would be if that replaced material gets out.

Finally we come to the fourth category of property, the durability and the long-term stability. Not much I can say about that, that is the purpose of this meeting. That is really what we are here for. However, in looking at that, I think it is always useful to come back once in a while and ask ourselves, does it matter? Keeping in mind that we are likely to be dealing with the stuff when it is densely packed and we have to take a lot of the considerations that we have been talking about for the past day and a half and bring it to bear on that particular situation. The stuff is in there at relatively high density, the flow rates are low, etc. the access of different chemical solutions and so on will be prolonged rather than a continual flushing and so on. Another related question that occurred to me as the discussions proceeded this morning is this. If the clay is unswollen initially, does loss of some of the swelling properties matter? Maybe it does, maybe it doesn't. I raise as questions for discussion and, Mr. Chairman, that concludes the remarks that I wanted to make in getting us into the next phase of the program.

SESSION III

Dr. Chapman:

I'm going to begin by putting down some things to show you how I would like to conduct things this afternoon and then I am going to introduce the first of our speakers. The first things we need to do is to state the problem that we might see with regards to future generations. I think that this states the problem, as other people might see it in the future, quite distinctly. I think the first thing that I want to point out and it is something that we have not really talked about at all is where exactly the smectites are going to be used, and in what scenarios. They are going to be used eventually under a wide range of conditions, in a wide range of environments. We are talking about using them within repositories as buffer material around canisters, within tunnels as tunnel fills, within shafts as shaft fills, and that is something we have not talked about at all. We are going to use them perhaps in deep borehole disposal facilities, to seal the boreholes. We are going to use smectites to seal investigations to the repository. We perhaps are going to use them to seal major fractures which run through the repository zone.

Some of these smectites will be then placed in areas which you are going to see quite high temperatures and some of them are going to be placed in zones in which you are not going to see any appreciable temperature variation at all. In some cases, they are going to be placed in rock units which are dissimilar to the actual disposal formation in which you might see much greater flow rates of water, and consequently faster transported cations to and from the sealing materials. In other places, you are going to see very very limited transport to the bentonite material. So the thing I would like to sort of drive home is that we are looking at their use or their potential use in a wide variety of physical/chemical environments and we shouldn't just concentrate on one. Long-term stability will be very important in all of these situations.

The problem as I see it for all of these environments in which smectite will be then placed, is predicting the longevity of the properties of the clays. And it can be divided into three areas, the first of which is how long do we really try to predict these properties for? How long are we interested in them for? Some people might say that it is a relatively short period, perhaps only ten thousand years. As far as the KBS proposal is concerned, I would think, a million years is the limit, no more but certainly no less. Because part of the program is that you must be able to predict the canister behavior for a million years. So we have to look at that kind of time scale. How hot are the smectites likely to be? And that varies from concept to concept. KBS and for the proposals in Italy and in Belgium and many of the other countries which are using smectite as host rocks for backfills, the temperature is not likely to exceed about 80 degrees. In the Canadian concept, we hear that temperatures may be 100 degrees or slightly more. And for the other projects, well, I don't know what the temperatures are, I put down about 200°C, maybe more. So we have quite a wide range of temperatures to look at.

And the third thing is which properties are we really interested in? I think we have demonstrated that absorption in the backfill material and certainly in seal material is of no practical interest. As far as the geosphere is concerned, that will act to pick up any of the shorter half-lived isotopes which the backfill would tend to stop. And as far as the long half-life nuclides is concerned, the backfill will not add to the general retarding behavior of the geospheres. So, the absorption is not a property of any interest. We are interested in the hydraulic properties, the buffer and seals and mainly this is from the point of view of Bonley. We are not particularly interested in the hydraulic properties of the seal because we know or we are considering that there is going to be no flow through the seal as far as the water availability to the waste form is concerned, or as far as subsequent transport of nuclides is concerned. So I think we can say that the permeability of the clay is not important under normal conditions.

Now, if the permeability of the rock is about the same as the permeability of the clay, in other words, if we are using clay host rock, then the hydraulic properties of the buffer are just not important under any conditions. But if the hydraulic conductivity of the rock is greater than that of the clay, which it is in the case of crystalline rocks, perhaps 2 orders, 3 orders of magnitude higher, we have got then to consider the long term clay properties. Under normal conditions, again, it is not of interest but hydraulic properties become important in the long term.

The main thing I think we are interested in is diffusion in the transport of corrodents through the buffer and the transport of nuclides out of the buffer. That is not certainly the case for the near field. Now of all the things that everybody has been talking about over the last two days, we have to try and isolate something from all of this information so as to go about solving the problem and we have heard about using thermodynamic models. Perhaps I am being unfair to say this, but the consensus was that by using these, alone, there is little hope of ever being able to make any reliable predictions. We need kinetic data; we have not really talked about this. I think it is something that we ought to have a discussion about later this afternoon. I think that is important. Linked together with the thermodynamic model, it can become very very important, very very powerful, but only, I think, if you link it with these other two, either natural analogues or of large scale field data. The difference being that in natural analogues you are looking at small systems like Steve was talking about. With field data you are looking at perhaps regional data on clay properties in large basins and we have got to find out how they evolve with time. But you can interpret both of these by using thermodynamic models with the kinetic data, if we have got it.

From all of this, I have distilled a few questions which I think we need to ask. I'm going to put them up now and then I am going to put them all up again later. Just look through them and then we are going to go back and try to talk about each of these, plus any more which anybody else can think of after we have heard some further discussion. The first of these is, will cation exchange, particularly calcium, sodium and copper, which we heard might be important, will that significantly affect the long-term properties? This is one of the crucial issues. If it does affect the long-term properties, do we really care? And I think that is something which varies from concept to concept, whether it actually matters whether the hydraulic conductivity changes or how much it can change before we do become concerned.

Laboratory data show very high temperature stability for the smectites. This is something we were shown yesterday. Up to 100°C or 600°C, but we have very little information on what is the effect of time if we are considering a million years. We really have to think about the kinetics again. We cannot use the laboratory information alone. Look, for example, at this kind of data which show the accepted expandability as a function of temperature for natural clays. You can see a very wide range in the expandable as a function of temperature where time has been an obvious factor in controlling it and we are not looking at temperatures which go up to 600 degrees or more, we are looking at much lower temperatures and a wide range of expandabilities. So this time factor has got to be looked at, and to my mind, natural systems are the only ones which are going to give us that information.

The third question, which is the one the meeting is all about and which we haven't actually answered is, what is the long-term stability of these minerals? I think it is going to be slightly specific, obviously it is going to depend on the groundwater chemistry, host rock chemistry, but are we actually any nearer predicting, for example, rate of illitization against time. Are we any nearer doing that than we were yesterday morning? Other questions are: Should we use calcium or sodium smectite or mix smectites with other clays? What is going to be the best approach? The question which Roland put forward is, what is the most conservative or the most reasonable; the two things are not synonymous, I don't think? What is the most conservative alteration product of smectite that we can use for modeling, what is the worst we can expect in other words? It doesn't mean what is certainly not the most reasonable approach, but let us try and identify what is the worst scenario? Are there other reasonable conditions and then define the properties of that alteration product. We want to look a little bit further into the effect of pH both bentonite dissolved. If so, when and where are we likely to expect these extreme pH conditions? Is there a reasonable limiting temperature for the various disposal concepts? That again is very important. It is certainly politically very important as to whether you decide to go above or below this magic threshold of 100°C. A group like this can put forward some of the answers to that question and again it is going to be site specifics. Are there any advantages to high temperature not given earlier? Can you tell us something about that? A small question is whether activated calcium bentonite is going to be better or worse or equal to natural bentonite and its properties?

Finally, on the physical behavior of the clay, does the long-term plasticity remain? Is it preserved after heat treatment or cation exchange or mild irradiation. If it isn't preserved, what controls any possible fracture development in propagation in stiff clays? That is something which is also of interest to those that are using clay as a host rock rather than just simply as a bufffer. Do we ever actually get to the point where we would anticipate any fracture development in clay?

I think I'll stop here. What I would like to do is to put Gary Beal on who is saying something of interest to Rob. He wants to hear it before he goes at 2 o'clock. It gives me a little break. Gary has something to say about radiation stability which he says is worrying him so it should worry us too.

1. Will cation exchange (Na Ca, , etc) significantly effect longterm properties? -If so, does it matter anyway?

2. Lab data show very high T°C "Stability" of smectites (100-600°C)-But what is the effect of time? (Where do we get kinetic data from?)

3. Long-term stability is site-specific; but are we any nearer predicting ilutisation v. time behaviour now than 2 days ago? (i. e. General longterm)

4. Should we use Ca or Na smectite (or mixed smectite/other clays)?

5. What is most conservative (reasonable!) alteration product of smectite + what are its properties?

6. Effect of pH: Bentonite dissolves? When/where do we expect extreme pH's?

7. Is there a reasonable limiting temperature for various disposal concepts? Should we be conservative: advantages to high T°C?

8. Soda-activated/bent: =, better, worse than
   Ca- natural bentonites?

9. Is long-term ductility preserved (plasticity) after heat treatment, cation exchange, mild irradiation, etc. If not: what controls possible fracture development & propagation in semi-stiff clays?

OTHER ISSUES

(Not covered here-but could be topics for future workshop?)

- Geotechnical properties
  particularly where smectites to be used in mixed clay backfills-swelling, bonding, pore fluid chemistry

- Smectites as major host rock components
  - effects on mining propetios, swelling, role of atomospheric moisture

- Chemically tailored buffers-necessity,?
  do they differ in long-term response and stability

- Micro-organisms: Presence in clay, effect of pre-treatment on
  (a) bugs
  (b) smectite
  - role in SO_4^{2-} reduction + corrosion

- Economic backfills
  - developing more realistic mixes with adequate properties
  - smec/illite/kaolinite mixes

- Numerical requirements of seal properties
  - especially borehole sealants
  - what exactly is required of them, for how long, and how do we test them
    in field
    in lab

- Radiation damage: is it (where is it?) important?

Dr. Beal:

Yesterday I was talking to Rod about alpha radiation effects. About six years ago, I did some work in which we loaded Einsteinium on clays to see if we could accelerate the alpha and atom recoil effects. Einsteinium has about a twenty day half-life and about a 6.6 MEV alpha, so if anything is going to show up some effects, that should. We loaded the various clays with the Einsteinium up to about the total cation exchange capacity. The kaolinite had an exchange capacity of about ten equivalents per hundred grams, the attapulgite had something like thirty and the montmorillonite about 100. We found that montmorillonite after one day, and the dose at one day is about 10 to 18 alphas, was completely destroyed. We could not pick up anything that we could identify as montmorillonite. The attapulgite was completely destroyed after about three days of exposure, the kaolinite was destroyed after about four days. So it seemed to fit the cation exchange capacity fairly well.

If I could have the first slide. These slides are not real good so I will probably pass around some of the original prints so that you can see the destruction better. This is after one day for attapulgite. What you see is the rods start to get little holes eating in the surface. You get a lot of material like this that looks fairly amorphous building up on the thing. This is after two days, and you can see how this is more of the amorphous material building up. The rods are less well defined. I will pass around the actual prints so you can see better. The next one shows kaolinite. On exposed samples, ones you can see little pits eating into the kaolinite. By the third day, you really couldn't identify any morphological features that you would say was kaolinite. The total dose after about four days would be close to 10^{19} alphas.

When I did this work back about six years ago, I did not have any idea of what the inventories in the U.S. would be before the alpha-active material. But now we have some fairly specific requirements that we must meet, one of which we really can not take credit for, our canister more than a thousand years. Last night I sat down and figured out what the inventory of alpha-active material would be in a thousand years. We also have another requirement: we cannot allow more than 10^{-5} of that inventory to leach per year from the canister after it is breached. So I made the assumption that if we allowed 10^{-5} of this inventory to migrate out of the canister it would take about 80 to 150 years to reach the equivalent of the doses that I see causing total destruction of the clay. But the assumption I made was that each year's inventory that came out then moved to the next segment of clay. In fact, if you look at it chemically, that is not what is going to occur. You are going to get chemical concentration of the Americium and Plutonium. So the first year's inventory will have the second year's additive and you are going to get a buildup. My preliminary calculations indicate that you may see total destruction of the montmorillonite within a month of leaching the canister. The more calculations I did the more concerned I have become about this effect.

Dr. Anderson:

When people go target practicing with rifles, they shoot into a sandbank or gravel bank that has the properties of being self-healing with respect to impact. Is it possible to design some kind of material for that purpose?

Dr. Beal:

Well, Rod can probably talk a little bit better about this. He has looked at a lot of crystals over a long time period that have been exposed to reasonably low doses of alpha. A lot of them do not survive, they do not self-heal.

Dr. Ewing:

There is a forward reaction of the damage and the backward reaction of the annealing kinetics and some structures evidentally anneal as fast as the damage is infused. Other structures don't anneal so you find them after millions of years, amorphous to electron diffraction. The problem with this is that this event say is one thousand years after the emplacement of waste and the thermal event that you would need for the annealing of the damages has long gone past, so this damage is permanent.

Dr. Beal:

But you know that is a question that these experiments really do not answer.

Dr. Anderson:

One other question related to that. There is, I believe, a sort of a natural radioactive or uranium powered power plant in Africa, is there not, South Africa, where these processes have been going on for a long long time? Has it been determined whether any of the materials at that location can be studied to answer this question?

Dr. Beal:

Rod would just say give me some money; we will study it.

This occurrence has been looked at very carefully by the French and the people at Los Alamos, mainly in terms of radio nucleide migration. As far as looking at structures and materials and making conclusions about damage, they do not know anything.

There have been many transformations of the clay minerals depending on the distance from the natural reactor, in the first system. The first meter contains a lot of amorphous material, but I have not seen this result. I know that in the distance of one meter, which is considered as the distance where most of this damage happened, all silica phases are amorphous and a lot of silica has been washed out by the hydrothermal system that moderated the system. Farther away, the clays have been transformed. It is a complicated transformation between illite and an illite/chlorite association with the uptake sodium, potassium and magnesium and the release of silica. I have never seen this description published. These transitions could be the end result of damage from recrystallization so it can relate directly to the damage. Since the main nuclides that caused this problem are Americium and Plutonium, they are going to be localized fairly well. They are not going to migrate much of the adsorption process. So they are going to be fairly concentrated.

Dr. Wood:

I think again you really must take this sort of study and look at it in terms of the specifics of geology. For those geologies which are quite reduced, for example, solubilities of these elements are extremely low and you are not going to get anywhere near that dose rate in months or years. I mean it is going to be higly dependent on how much of those alpha producing nuclides can actually get into solution and migrate. I realize your concern and I understand that, but I think that we must first consider each site specifically as to how much of an alpha producing nuclide we expect to get into solution in a backfill material.

Dr. Anderson:

How much would the container itself cut down on the dose rate because of shielding for these alpha particles?

Dr. Beal:

For alphas, it would depend on how many pinholes it would reach in a canister, obviously.

You have to remember my assumption or just following the law that we have to meet and they say that you cannot take credit after a thousand years for that canister. And that your leach rate cannot exceed 10^{-5} the inventory at that time. So those were my assumptions.

Dr. Wood:

That may be an assumption but you have to be realistic. You have to predict for each site what you think the real situation would be and base your conclusions as to the known behavior of these minerals and not on assumptions that the canisters disappear magically, etc.

Dr. Beal:

But I think that the point I would like to make is that this is significant enough that we ought to study it.

Dr. Wood:

Oh, I am not disagreeing with you at all about that. I am just saying that we need to be very careful when we look and study this in terms of applying it to the real or expected situation.

Dr. Beal:

The only problem that I have, and I think the only problem that Rod and I share is, it is very easy to do the gamma experiment but it is very difficult to do the alpha experiment. Consequently, there has been a lot more work done on the gamma ray effects than on the alpha.

Dr. Anderson:

I, for one, think that it is just unacceptable to go on the assumption that a canister cannot be designed and built that will last more than a thousand years or ten thousand years, I think that is ridiculous.

Dr. Chapman:

I think it is an interesting discussion as to how long the canister should last and whether you are overly conservative of it or you make the basic assumption that the canister is of no importance. It's interesting, I like talking about it.

I have a list of additional speakers. The first is Marc Wood.

Dr. Wood:

What I would like to do first is rather briefly describe the situation I am in, actually working in a repository project, and how we need to complete our goal of determining whether or not a repository is suitable for the geologic medium that we are in, and in my case it is the basalt. The U.S. program, for those of you who are not familiar with it, is rather diverse in that we have three rather large efforts going on in three very different rock types, basalt being one, salt being another and tuff being another one. The crystalline rock project is in its very beginning stages. ost of the work has been done in the three sites that I mentioned. I want to stress that out of the three sites I mentioned, all are quite different in terms of their geologic characteristics. The basalt site is the only potential repository location which will be saturated. Both the tuff and salt sites are proposed as unsaturated or partially saturated media. So right there you can see there is a tremendous difference in emphasis and the sort of work that needs to be done.

Let me describe briefly the methodology we are using to identify the need for and usefulness of smectite in a basalt repository backfill. First, it is necessary to define the functions of the backfill material. That is, what should a backfill material do? Until that is done, decisions about which materials to use and what properties they should have cannot be made.

Three major factors affect the choice of backfill functional criteria. The first factor is regulatory criteria. A regulatory agency is going to issue requirements which they expect a repository to satisfy. This will be a goal that must be met by a site if the repository is going to be built there. Secondly, and I cannot emphasize this too strongly, the characteristics of the site geology are going to affect how developed a repository is. It is most unfortunate that sweeping generalizations are often made based on a set of experimental data which is applicable to one situation, but totally inapplicable to another. It happens all too frequently. And then, thirdly, the functions of the backfill material must be considered in the context of an engineered barrier design. Most systems are very similar to the Swedish KBS concept in which a series of barriers are devised which act together. The functions of one component cannot be defined without considering the functions of all the other components. It makes a lot of sense.

Let us suppose that backfill functions have been defined. Then it is necessary to identify the material properties which are needed to perform these functions. Having completed that analysis, materials can be selected which seem most likely to be characterized by these properties. The last step then is to quantify these properties through testing progrms in which site specific conditions are simulated as realistically as possible. Because time and money are important constraints in our program, it is necessary to be careful about choosing the most useful experimental and testing techniques. In the next few minutes, I want to describe the most important data needs for our particular repository environment.

The American concept of what an engineer barrier system has to do is defined now by the NRC (Nuclear Regulatory Commission) in a formal document. There are basically two requirements. One is "complete containment of waste for three hundred to a thousand years" and by complete they are not saying one has to predict absolute containment of waste. That cannot be done. What can be predicted is a reasonable assurance that a substantial portion, of the waste, however, defined will be contained during that time period. The second part of the requirements are that "a controlled release of radionuclides to the host environment must be achieved by an engineer barrier system." The Nuclear Regulatory Commission has set up a concept that one part in 10^5 of the inventory at 1000 years cannot be released over a period of a year; more than one part in 10^5 cannot be released. There are also other regulatory requirements. The EPA has a set of requirements which NRC will abide by. The EPA requirements apply to the whole repository system, not just the engineer barrier system; the engineer barrier system plus the underground facility plus the host rock out to some perimeter. They have defined a cumulative release rate over 10,000 years on a nuclide by nuclide basis. So really we have a couple of different kinds of radionuclide release related criteria which have been proposed.

Dr. Mitchell:

If complete does not really mean complete, how do you do it?

Dr. Wood:

You have to define what you mean by complete. In other words, you are going to have to predict the performance. And you have to predict a probability. I mean, essentially, it comes down to saying, "I have this degree of confidence that I can contain these radionuclides." There is no way you can say, "I absolutely know that for 1,000 years not a single radionuclide is going to get out of this engineer barrier system." Actually, the wording is "substantially complete." You have to define, quantitatively, what substantially complete means and you are going to the regulatory agency and say, "well this is what I mean by substantially complete containment, is this an acceptable way of defining quantitatively substantial containment."

Dr. Mitchell:

This leaves the regulatory commission in a position to be able to say "no" depending on the political climate at the moment.

Dr. Wood:

This is the framework in which the American repository development is set. And it has a great deal of effect on how we try to design a repository. Given that background, we have gone through several years of figuring out different kinds of engineered barrier concepts that we think might work. What criteria and based on the basalt geology, is this set of functions which we think are important and can be achieved in a basalt repository. I think I have also listed these in the order of the importance we place on them.

First of all, we want the backfill to be chemically reactive so that it promotes moderate pH and low pH. In other words, what we want this backfill to do is act as we think the host rock will act. And the reason we are doing that is because the basalt, at least potentially, has very promising geochemical capabilities to isolate or to control the release of radionuclides. By imposing a reducing state on the system, you reduce the oxidation state of multivalent radionuclides is reduced, particularly the actinides and selenium. This means that the solubility of these radionuclides is minimized, so that there is a maximum concentration in solution which is quite low. Secondly, we would like to have diffusive control of mass transport. That is the minimum rate of transport that can be achieved. This has both the effect of minimizing canister corrosion, because aqueous species take longer to diffuse in and out, and secondly, diffusive control of mass transport, we feel, will allow for the greatest residence time in the backfill to allow the completion of chemical reactions which we want to occur. And, finally, we would like sufficient strength to support the canister in the backfill. This is, to our way of thinking, the least important component and is considerably different from the Swedish approach. In fact, in our current concept for waste package for support we're looking at horizontal implacement. We are actually considering placing the canisters on metal supports in the backfill so that there really is no need for the canister to sit on the backfill material. That may change. The design concepts are still in a state of flux.

Dr. Mitchell:

Is that a discussable issue?

Dr. Wood:

Well, we could if you want.

Dr. Mitchell:

I have really serious reservations about putting it on supports.

Dr. Wood:

Oh yes, I know what you mean. There are certainly problems with the canister corrosion and stress corrosion, cracking, etc.

Dr. Mitchell:

And the movement of the backfill material from under it leaving yourself a big void.

Dr. Wood:

Well, if you don't get swelling, yes.

Dr. Mitchell:

We have run into that in some field tests where we do the performance of heated pipes in specially placed backfills. When we did our postmortem, we found gaps underneath.

Dr. Wood:

Do you have a large smectite-type component?

Dr. Mitchell:

No.

Dr. Wood:

We rely on the smectite to prevent that sort of thing from happening. But this model is by no means fixed and I suspect rather shortly it may be changed.

As I stated, the expected results from this kind of a functioning backfill will result in a minimization of a canister corrosion and the minimization of the solubility of radionuclides. The primary material we are now considering is a mixture of 75 percent crushed basalt and 25 percent sodium bentonite, by weight. I think you can see reflected in our proposed backfill composition, the importance we place on chemical reactivity because its the interaction of crushed basalt and groundwater which is going to both moderate the pH and impose a reducing condition. The only really important smectite properties are physical, mainly low hydraulic conductivity and moderate swelling capacity.

I guess this is a good time to talk about temperatures. We are proposing relatively high temperatures, compared to the European programs. There are two parts to this. First, there is a good possibility that groundwater will exceed its boiling point early in the repository lifetime because that is the time when temperature is highest and pressure is lowest. That is, shortly after emplacement, system pressure should be close to atmospheric as a result of communication between the atmosphere and the underground workings. System pressure will not begin to increase until resaturation begins to take place. Consequently, a post emplacement scenario is expected where the backfill is initially dry or partially saturated as water flowing from the rock flashes to steam and is transported through the backfill as a vapor phase. As time goes on, temperatures will decrease and resaturation will commence as soon as water becomes stable in the liquid state and a wetting front is established. Consequently, it is necessary to determine the stability of smectite under both dry and wet conditions.

To consider the effects of dehydration on smectite, we heat sodium bentonite for periods of up to a year, isothermally at temperatures ranging from 250°C to 550°C. We have discovered that between 370°C and 440°C all of the structural water is lost. In other words, the clay could no longer swell again after dehydrating at 440°C. Thus, it appears that if peak temperatures are kept below 370°C, no permanent alteration of smectite will occur under dry conditions.

In the bentonite water system at 300°C, the reaction products we see are albite and quartz, suggesting that a breakdown of bentonite to albite and quartz is occurring. In the basalt system, we tend to see the formation of the reaction product zeolite, primarily mordonite which is an alkaline-rich zeolite, iron smectite and crystobalite. Occasionally we see illite formed, plus hydroxide. These are discreet reactions that are always observed, in all of our experiments and are very repeatable. The solution compositions are also very repeatable and even the concentrations for repeat experiments. So, it's our suggestion that the dominant reaction in a basalt water experiment is the basalt glass dissolving and these secondary mineral products forming.

If we add bentonite to basalt, we see pretty much the same set of reaction products coming out; zeolite, iron smectite, crystobalite. What's happening to bentonite? We are not sure at this point. We haven't done sufficient characterizations yet to understand what is going on. What appears to be happening, is iron enrichment in the bentonite itself, and there is also some limited substitution of potassium into the clay. The clay is by no means gone; there is still a smectite present. We are just not quite sure what the reaction is. I'd like to ask your opinions of what might be the reaction that is going on. The potassium that is released from the glass or elsewhere in the system, is found in a zeolite secondary product. It is found in discrete illite. We may even have got some sort of substitution of potassium into a feldspar. What I am suggesting is that once potassium goes into solution, that it does not necessarily react with the bentonite. It appears to be just as easily going into a zeolite phase or something else so that substitution of potassium for sodium in bentonite is limited. Again, the occurrence of illite in the fracture mineralization of basalt is pretty rare. These observations suggest that illitization smectite is not a significant or highly favored reaction.

If the smectite remains stable in the system, then the swelling properties and low permeability characteristic of bentonite will be maintained during the lifetime of the system.

Dr. Chapman:

So what you are saying is that you are actually expecting it to be dry, in which case you will maintain the expanded properties when you get up to 300°C. It will be a nonsubstituted bentonite. But if you got water in your system, for some reason, you would get an ion-substituted bentonite or smectite.

Dr. Wood:

That is correct. What we'll have to do is complete enough experiments so that we can actually measure the swelling properties of altered basalt and bentonite mixtures and see what kind of change we are getting. With regard to the swelling properties, it is a question of how much do we need. I am not sure I know the answer to that yet. I think all we really need is the capability for it to expand enough to fill fractures and voids that need to be filled up. Other than that there is no great need to have a large swelling pressure. Also, swelling reactions are probably important only during the resaturation period. After resaturation, the potential for introducing more voids into the system seems rather remote. For example, it is difficult to devise a scenario where a wetting-drying cycle could occur.

Speaker (not Dr. Wood).

Geotechnical properties are something we have not really talked about in any great detail today and particularly where we are using smectite in mixed clay backfill. We need more information on the swelling properties of that kind of material, the bonding properties to other types of clay and the effect of pore fluid chemistry. Smectites, where they are going to be acting as major host-drop components, rather than just as backfill, we need more information on the effects on mining properties, the swelling after excavation, the role of atmospheric moisture in interlayer swelling around an open excavation, these are all engineering or geotechnical problems maybe for people other than ourselves.

We haven't talked about chemical control of buffers. We did begin to mention it. Are they really necessary? Maybe there are some circumstances where they could be considered necessary. My own opinion is that perhaps they are not necessary at all. If we do use them, do they differ in long-term response and stability? If we put so much vivianite in the buffer, is it going to affect its physical properties?

Microorganisms, I think, is something which definitely needs to be looked at. We know that these clays which are going to be excavated from near the surface are going to have a microorganism in them. The clay is possibly going to be pretreated to reduce the content of organic material and microorganisms. How is that going to affect the properties of the clay? What happens if the microorganisms remain in there, if they are tolerant to the treatment conditions? How will they affect sulfite reduction and consequently possible container corrosion?

We haven't really talked about economics. What is an economic backfill? We need to eventually think about developing more realistic mixes which have adequate properties. Smectites with illites, kaolinites, and so on. We haven't talked about smectites as seals, for example, as I said in the cold regions and exploratory boreholes and shafts and so on. We haven't talked about what is required of them in terms of their longevity. How long do they really need to last for a seal? We fix the lifetime of the backfill material, for technical reasons, for the lifetime of the canister, but for a borehole or a shaft seal there are other factors which control the length of time in which the seal is required to function. And the groundwater flow parameters, we need to think about those and how we may test them in the field. This is a whole new area which we haven't considered.

Radiation damage we have covered. You may want to add something to those on to the list of questions that we want to see answered today.

- Coffee Break -

Dr. Chapman:

This is from Gulf Coast shale. And there we have dated for

110°C and 90°C and this information predicts 10 percent collapse of the clay at 110°ᴬC after one million years. So that the experimental and the field base give different answers. I think what we've got to try and do is assess how we can use both of these things together. I know the two are not comparable, but I am just putting them up here as examples.

Dr. Eberl:

I have a question as to just what that plot means. That is just a first order kinetic plot for reaction extent, the way you would plot a first order kinetic equation.

Dr. Chapman:

And, the conclusion is that after the first 20 million years, you actually are on line for the first order kinetic reaction. after that they will fall off.

Dr. Eberl:

But is that 100°C...

Dr. Chapman:

This is the predicted temperature.

Dr. Eberl:

Yes, it is the predicted temperature, but it has not reacted for 20 million years at 100°C so it is more complicated. There are so many things that affect the kinetics of that reaction, like solution chemistry and pressure that until it's all been worked out it is hard to say what it means. Maybe you can get the maximum rate.

Dr. Chapman:

So, you think we are going to lie somewhere between the experimental base and the field base. A compromise.

I have a list of questions. I am now going to attempt the impossible which is to bully you all into a consensus opinion, so that we can make some relatively simple answers to these questions. It probably won't work, but we will try anyway. We have just less than an hour to do it.

First of all, are there any additional important questions which people think ought to be added to this list? Question one: Will cation exchange significantly affect long-term properties, and if so, does it matter? Does anyone have anything to say on this which isn't going to be site specific? Or are you going to let me put words in your mouth? Will cation exchange significantly affect long-term properties and if so, does it matter?

Dr. Weiss:

You answered yes.

Dr. Anderson:

Is it possible to ask that question a little differently and restrict the question to highly compacted bentonite or smectite. What would be the answer in the case of highly compacted smectite?

Dr. Müller-Vonmoos:

If you change from the calcium to the sodium form, the swelling pressure maybe in the sodium form a little bit higher, but not much I think. If you have aluminum clay you will lose swelling properties.

Dr. Pusch:

Some clay material that you put around the canister is consolidated and under the high swelling pressure of the hydrated highly compacted clay. So you end up with something which is continuous and very dense.

Dr. Chapman:

This touches on the question of modifying, or using an optimized composition for the backfill material you use, rather than using pure sodium bentonite; using a mixture of local material which is partly exchanged anyway, and then accepting the properties of that material, or modeling, or designing the site around the properties of material that is available rather than doing it the other way around.

Dr. Anderson:

Let me ask again in the case of question 4, is there an advantage in having highly compacted smectite as opposed to loosely packed smectite?

Dr. Wood:

I would say that the reason for the highly compacted clay is to assure diffusive control of the mass transfer and that once you can determine at what density you can achieve a satisfactory hydraulic conductivity, at that point, you have achieved a satisfactory material. It is simply a matter of determining what that density might be, one that gives diffusional transport. If you can get better fine, but I would say that you should not try to spend a lot of money and effort in the lab to decrease your hydraulic conductivity at that point if you do not have to.

Dr. Chapman:

It is another case of optimizing the material properties to achieve exactly what is required.

Dr. Mitchell:

Yes, but you would want to have it dense enough to cope with potential volume changes. In other words you would not want it so loose that, it could contract, shrink and crack. You want it to be densely packed, in order to keep the spaces filled. If you have the ion exchange they tend to collapse and you don't want to do that, I don't think.

Dr. Wood:

That will happen under saturated conditions okay. I am just not sure it can.

Dr. Pusch:

On the question of compacted clay. Exert a swelling pressure, that is the pressure on the rock which can be tailored so as to fit reasonably well with the original stress exchanged from the rock, so that you actually come back to what you had before. At least it tends to be that way.

Dr. Chapman:

And in your concept, you would not be worried about a certain amount of sodium calcium exchange, in terms of the long-term performance. What is your general feeling about all the other ideas? Do you think that would be acceptable, that you could balance these out, that you could assume a certain amount given the groundwater chemistry and design accordingly?

Dr. Pusch:

Yes, I think it wouldn't be impossible.

Dr. Banin:

Over a long period of time there may be a slow movement of the clay matrix itself, in response to some of the other gradients. Those that Dr. Mitchell described in terms of thermodynamics. If you have a compacted matrix, this mechanical field will prevent much of that, and there may not be any redistribution of the clay.

Dr. Anderson:

When I think in terms of the advantage of highly compacted bentonite, I think in terms of the hydration properties of the clay, those that I spoke of yesterday, and would prefer to see an interlayer spacing of roughly six Angstroms, two molecular diameters, and no more, when it is fully hydrated. That is the point at which you get the maximum advantage of swelling pressures and low hydraulic conductivity. It is almost impossible to compact bentonite to a degree that the lattice spacing is less than the figure that I gave, the two molecular diameters. The pressures required to compact the bentonite and force that interlayer of water out are so enormous that they are not within our capability really to utilize. So the point I am making is, the more densely you can compact it, the better.

Ms. Johnston:

But you know when you say let us accept the highest compaction we can get, what values should we try to attain?

Dr. Pusch:

You must define what kind of density you are talking about. Is it dry density or is density fully water-saturated? What we said yesterday was it would probably be very difficult to get to a dry density exceeding 1.6 ton per m^3.

Dr. Chapman:

So we are talking about 1.6 ton per m^3 dry densities.

Dr. Pusch:

This is not so easy, actually, because if you have a large bentonite content then you have the bentonite confined in the pores of the larger grained material, the sand, etc. Thus, the density depends very much on how much bentonite you put in it, the degree to which it is filling up the pores. This is a very important function of the exchangeable cations. Sodium bentonite will actually fill up even larger pores than calcium bentonite. So we will have a larger difference in hydraulic conductivity between calcium and sodium bentonite.

Dr. Chapman:

If I summarize that, could I say that 1.6 seems to be critical for sodium montmorillonite but that there is adequate scope for using other types of smectite minerals as long as their swelling properties and reactions are likely to be well understood. There is no reason always to opt for the sodium montmorillonite.

Dr. Pusch:

These questions have been dealt with by KBS and are reported in a KBS report which is entitled, "The Use of Clays in Repositories."

Dr. Chapman:

Is sodium activated calcium bentonite going to be as good as, worse or better than naturally occurring bentonite? Why does one ask that? Because as you pointed out in your diagram, when we come to the point of the whole thing, we do not refer to a sodium Wyoming bentonite for all the mixtures. We have to use cheaper materials. In Europe, for instance, you can buy Sardinian bentonites for say 1/3 or 1/4 or 1/5 of the cost of sodium Wyoming bentonite. Then it comes to the question of whether this soda treatment has any significant negative influence. And if it does, can it be minimized by double the treatment or something. It turns out that most companies that do this, on an industrial scale, add two or three to five percent sodium carbonate to the bentonite and make a one time, one process treatment of the whole thing. And I think that we do not get a complete or a very efficient ion exchange by that. Maybe if we repeat that it could perhaps be only by lowering the cost very little, but we might arrive at practically the same properties as we have of the Wyoming bentonite.

Dr. Chapman:

But, bearing in mind that we have just been talking about the acceptability of other than pure sodium bentonite, does it really matter? I mean are there likely to be any adverse properties introduced by the soda treatment?

Dr. Pusch:

Yes, well what we add is actually kaolinite. And kaolinite is present in Wyoming bentonite and it is present in the Sardinian bentonites also.

Dr. Chapman:

In other words, the answer to question 8 is; it is probably equivalent.

Dr. Pusch:

I would say so.

Dr. Weiss:

I think that if you have a soda activated bentonite it would improve thermal stability. But it is not so important, but you do have a small improvement. You avoid the distortions by free iron coming in and so I think the soda activated would be better.

Dr. Pusch:

I got the impression that you said that yesterday.

Dr. Weiss:

Yes, in this soda activated bentonite you do not have a quantitative cation exchange. Most companies try to arrive at the point where you have about 60 percent to 70 percent sodium clay, the rest is calcium. This is where you have the best dry strengths and most of the properties are optimized.

Dr. Chapman:

It seems to me, too, it is reasonable if not a good thing to do. However, whether it is economic to treat 250,000 cubic meters of bentonite in this way or not, I don't know.

I think we are proceeding toward the same answer. The consensus of the group last time was that if the environmental temperature did not exceed a certain level, and this level was generally taken to be about 100°C to be on a conservative side, that there would be no illitization, to speak of, for a million years.

Dr. Chapman:

Does anybody want to differ with that?

Dr. Altaner:

Well, I'm not sure I would necessarily differ with it until I sat down and did some calculations. What I think is perhaps the best natural analogue situation to what we are dealing with is a dike-intruded shale. In a dike-intruded shale, depending on the exact width of the dike, the thermal event as you get away from the dike, say a foot or two into the shale, the thermal event maximum temperatures will be on the order of 300°C to 100°C as you move away from the dike. The heating time is on the order of hundreds to thousands of years. From that it is possible to get at the kinetics of illite/smectite reactions in natural systems. Bob Reynolds and Tony Pitta at the Dartmouth College have done this. They have tried to model the exact thermal history. It is very easy, applying pure heat conduction type models to get at the exact thermal history. That is the most important aspect, I think, knowing the thermal history. Then they calculated kinetic parameters from that, not assuming that it was first order reaction which many people have done, but they just calculated what the parameters were that fit their data. It appears that those parameters are pretty good at fitting gulf coast type illite/smectite, as well. I think that that is a very good start, using their kinetic type parameters to model this system.

An additional calculation that I think may be necessary, is the kind of calculation that I showed you at the end of the talk that I gave. Marc has told us that if we get at a certain density, and therefore a certain low hydraulic conductivity, that we can assume diffusional type transport. So, if we have a reasonable value for the concentration of potassium in the solution, at a given temperature, in a granitic groundwater system, we know what the thermal event is with time. And knowing a value for a diffusion coefficient, in a compacted bentonite, we can then calculate what the illitization would be as a function of time using Reynolds and Pytte's kinetics.

Dr. Anderson:

I think in order to give everyone here a maximum opportunity to comment on the earlier conclusion and to perhaps contradict it, I should elaborate a little more. The group regarded the illitization reaction as a two-step process. One in which a high lattice charge was created and it was this step that requires a high temperature, over 100°C perhaps 150°C or more. And the second step is the influx of potassium by some mechanism and then eventual lattice collapse. That is the general process as it was envisioned.

Dr. Pusch:

In the Swedish granite where the maximum assumed concentration of potassium is 10 ppm, it would require much more than 1 million years because there is no concentration gradient. You have got to have groundwater flow through the buffer mass to bring this amount of potassium to the clay. That would require more than 1 million years, that was your conclusion, also.

Dr. Altaner:

I would disagree that there is no concentration gradient for potassium because inside the bentonite there is essentially no potassium if you have gotten rid of the potassium mineral phases. Outside there are potassium minerals in the groundwater and once you get up to elevated temperatures, illite is a more stable mineral and so there will be a concentration gradient and the diffusional transport will be more rapid than the hydraulic conductivity type of transport. So I think that some of the calculations made in the original paper might have to be redone, because they were assuming a hydraulic conductivty transport of potassium into the system. Diffusional transport will be much more rapid in a compacted bentonite.

Dr. Brusewitz:

I think in the two-step process, the two steps are almost simultaneous.

Dr. Wood:

In my presentation, I suggested that the process is not a favorable one in a basalt environment. Whether or not that is true probably remains to be studied some more, but I would at least like to suggest that we consider the fact that the occurrence of illitization is to some extent site specific, considerably different in shale, granite and other systems.

Dr. Pusch:

I just have to comment again. If 100°C is the critical temperature, or temperatures higher than that, then we won't have this first step at all; we won't have this high charge and potassium coming in and out, it is not essential. And that is an important question to ask here. Can we still signify 100°C as a safe temperature to avoid illitization of smectite?

Dr. Altaner:

In my opinion 100°C is not a magic temperature. It would be a question of time at the temperature. At 80°C for a very long time that could certainly produce illitization and 100°C for 100 years may not produce any illitization, 150°C at 100 years may not.

Dr. Chapman:

This is where we are trying to link it into the time-frame that we are interested in. I think that a half million years is the time-frame we want to know about, so we have got to try and fix some sort of temperature. It seems if we adopt this, I think what Roland is saying is to look at the two-stage process and see whether it still applies. I mean how can you summarize what you said in three words? Do you think that still works?

Dr. Pusch:

What I said was, can we still stick to the conclusions of the Buffalo meeting, that temperatures of 100°C will not produce a charge change in a heating period, of say, a couple of thousand years?

Dr. Anderson:

Could I quickly state the conclusion in the reverse form? The conclusion of the Buffalo meeting was that if the temperatures did exceed 100 degrees for a significant period of time, then it was certain that significant alterations of smectite would occur and it was advised that this is to be avoided. In this particular system, potassium was available and known to be available to contact the smectite for one million years, with a heating period of a couple of thousand years. It was considered to be a two-stage process. The first stage of heating producing a high charge lattice. The length of time may be a hundred years or a thousand years, but a small period of time compared to the million years in which potassium would be expected to diffuse in and cause lattice collapse. That is the way the problem was viewed at the Buffalo meeting.

Dr. Altaner:

I am not sure that I would agree with the hypothesis of a two-stage reaction, because I am not sure that the data that this is based on actually proves a two-step type reaction. But I do not think it really matters in that situation, because I am not sure what the high charged layer would alter to. Most people at the Buffalo meeting believed that the temperature effect was measurable and significant beginning at, say 60 or 80 degrees. So the choice of 100 degrees was arbitrary but necessary to arrive at because some number has to be specified, ultimately, in a design. The group there felt that 100 degrees was a reasonable number to specify knowing or feeling strongly that 150 degrees was too high and that 60 degrees would be difficult to attain and very expensive to maintain and the rates would be sufficiently low; 100 degrees was the figure they chose to give. So it was not an ironclad view of the process or the problem.

Dr. Fripiat:

I think it is a very, very difficult reaction to try to specify.

Dr. Chapman:

I am having difficulty getting this down. My difficulties are shomewhat mitigated because Duwayne is getting it down on tape. So, I suppose we are going to make some sort of sense out of it at the end but this is the crucial issue, I think, for this meeting. It seems to be a different, slightly divergent conclusion from the last meeting.

Dr. Anderson:

No, I have not heard anything in the nature of a strong objection to that conclusion. Steve in fact has elaborated on it in a way, in my mind, that does not negate that earlier conclusion unless you want to say differently.

Dr. Altaner:

I would say that I would have to do the calculation in a site specific situation to see whether or not the problem is displayed; there are no grave errors in what has been said thus far. I think both the relative lack of potassium in the system as a whole, plus the apparent preferable reaction which consumes potassium in other minerals, are both factors which inhibit illitization.

Dr. Weiss:

I think we should make a careful choice of the bentonite if you use a higher charge bentonite, say if you take a bentonite like Bavarian or Wyoming with the net charge of not more than 0.3 meter, then you will not have illitization below 100°C.

Dr. Chapman:

Is there a reasonable limiting temperature for various disposal concepts and should we be conservative? Are these advantages to high temperature? I think from what Marcus said that there is a limiting temperature above which you would not want to go which would be about 70 degrees above where you are at the moment.

Dr. Wood:

With regard to smectite stability a safety margin must be utilized to account for experimental, especially kinetic effects.

Dr. Anderson:

Why do we not state clearly what the advantages are? Is it an advantage to be able to pack more into a small space?

Dr. Altaner:

Yes.

Dr. Anderson:

Are there any other advantages to having a high temperature? Well, chemical reactions which I mentioned, that you would want to induce one easier.

Dr. Chapman:

That brings us on to item 5. What is the most conservative, within reasonable limits, the alteration products of smectite and what are its properties? Roland did you pose that question? You have got a specific site.

Dr. Pusch:

Yes, considering what has been said before, I think we have had the opportunity to hear that not only phyllosilicates may be the end product, perhaps under the repository conditions, we consider at least, in crystalline rock with known composition of the groundwater, would not the transformation to illite be the most conservative end product we can define?

Dr. Chapman:

In your condition, yes. But at the lower temperatures you couldn't pose framework silicates as being a reasonable alteration product. They may be very conservative but not reasonable. So in your case it would be illite.

Dr. Anderson:

Except that I think that we should consider more now, after hearing Rod Ewing and Gary talk about radiation damage. I think it should be recognized that if there is not a sufficient barrier shielding, the radiation damage could produce essentially amorphous materials next to the canister wall. I believe that is what they said.

Dr. Ewing:

I guess what I am trying to say is, that maybe we should not automatically suggest that we have to have significant shields, because of the potential for radiation damage until we have determined whether that really is truly a very deleterious effect.

Dr. Eberl:

Another reaction that a few of us were talking about over lunch was that, as you increase the temperature in the presence of quartz or amorphous silica, the silica concentration and solution will increase and then as your thermal pulse dies away, silica will precipitate if it has not been transported away. So the possibility of silica cementation in the bentonite and subsequent fracture is there, it could damage the bentonite.

If we start up with a high density of the bentonite with a specific gravity of the smectite of the order of 2.7 grams per cubic centimeters and eventually arrive at a complete illite which has a specific gravity of 2.67 grams per cubic centimeters, then those would not be a contraction. Actually, there may be two-water hydration layers, and if the hydration properties of the illite standing overnight are like the smectite, we would not expect any change in the physical properties.

Dr. Chapman:

What you say, in fact, goes someway towards answering question 9 about the preservation of long-term plasticity; after cation exchange or heat treatment, as far as you are concerned, it does not make very much difference, because your most conservative alteration product would expect to have the same fundamental properties as the original smectite. Does anybody else feel differently?

Dr. Anderson:

I have a memory of something that Jim said earlier today that causes me to be somewhat alarmed. He mentioned that in the laboratory it is not too difficult to get very low hydraulic conductivities with smectites, but in the field it is very difficult. I recall seeing quite a number of field occurrences of bentonites, highly swelling bentonites, that were compressed to an interlayer spacing of 6 A, a water content of 25 percent by weight and these materials had a very stiff consistency, something like leather or hard rubber, they would bend and deform but with great difficulty. I have seen some like that and then I have seen others that were actually fractured because of dehydration. So it is possible, I think, to form fractures in this highly compacted bentonite, if dewatering occurs. And very often in nature that must be what you get, that must explain why your ponds leak, Jim.

Dr. Mitchell:

Well, it is that and nonhomogeneities and it is a good point. Roland had a picture of his clay. One of his micrographs showed an aggregate. If you pack a bunch of those aggregates together, you can have channeling between the aggregates.

Dr. Banin:

This is the point I was trying to make. Illitization would result in an increase in the interlamellar spacing and increase the volume.

Dr. Pusch:

Do we have the bulk density preserved? So the question is if we have an illite clay with a bulk density of 2 tons per m^2, what hydraulic conductivity does that clay have? I would say that this may be one or two orders of magnitude higher than the smectite, but we would still be 10^{-11} or 10^{-12} meters, say.

Dr. Mitchell:

Oh no.

Dr. Pusch:

With smectite we have 10^{-13} and 10^{-14} meters per second. These are meters. You know what we have in our stock of illitic clays in Sweden, with a bulk density of the order of 1.6 tons per cubic meter, we have 10^{-9} meters per second.

Can I put the question another way? Can we agree that if we get a complete alteration from smectite to illlite and have the bulk density preserved, that this would increase the permeability but not by more than say 1 or 2 orders of magnitude. That would be my suggestion.

Dr. Chapman:

Okay, I put down what you have said. It summarizes it reasonably. I don't think anybody is going to disagree by a couple of orders of magnitude, in which case it probably, as far as you are concerned, has very little effect. I think we have gone through all the questions now. I had a few other summary points.

Dr. Anderson:

Before leaving this question, let me ask it another way again. Is there anyone here who would have difficulty with obtaining the specific answer to the question we have just been considering on the basis of laboratory determinations of the hydraulic permeability of illite compacted to the same bulk densities that are being discussed? In other words, if laboratory measurements show that the permeability is no more than 1 or 2 orders of magnitude different from the original smectite, would you accept that, do you think, as being the answer to that question?

No objections stated.

Dr. Chapman:

Fine. These summary points were written before we had the discussion so they preempt anything that we have just said. I still think some of them still stand, the first one is another hard statement really. I think everyone would agree with that.

The second one that we are mainly interested in is the chemical transport properties of corrosions in the buffer, but the seals as the hydraulic properties of the bond that is important, these are additional points that are of interest.

Smectite will collapse, at least partially, on the kind of time scale we are interested in, perhaps even less will we discuss that one out. Another point which is not in those answers to the question is the point which is being said several times over, that trioctahedral smectites appear to be much better, are much more stable than dioctahedral ones and ion substituted smectites have been suggested as being possibly something worth further consideration or perhaps a little bit more work.

High pressure temperature laboratory work is ambiguous. I say this as having been a high pressure temperature experimentalist myself. I think another important thing to have come out is the fact that we must use more field data, and this idea of looking at small scale natural analogues of illitization, in particular, is something we should press for more work on; that is going to be very, very useful. It has got to be tied up with the thermodynamic work. But I think by themselves the data from laboratory experiments are rather difficult to interpret. We have seen an example of that earlier this afternoon.

QUESTIONS

1. Will cation exchange (Na Ca, Cu, etc) significantly effect long-term properties? - If so, does it matter anyway?

2. Lab data show very high T°C "stability" of smectites (100-600°C) - but what is the effect of time? [Where do we get kinetic data from?]

3. Long-term stability is site-specific; but are we any nearer predicting illitization v. time behaviour now than 2 days ago? (i.e., general long-term)

4. Should we use Ca or Na smectite (or mixed smectite/other clays)?

5. What is most conservative (reasonable!) alteration product of smectite + and what are its properties?

6. Effect of pH: bentonite dissolves? When/where do we expect extreme pH's?

7. Is there a reasonable limiting temperature for various disposal concepts? Should we be conservative: advantage to high T°C?

8. Soda-activated/bent: =, better, worse than
   Ca- natural bentonite?

9. Is long-term ductility preserved (plasticity) after heat treatment, cation exchange, mild irradiation, etc. If not: what controls possible fracture development + propagation in semi-stiff clays?

And finally, I think it is important eventually that we have to optimize what material we use as the backfill. Not going to pure end-members, but we are going to something which is economic and so on. So if we link those up with the answers that we've scribbled down to the questions, we can run some copies off. Whether we have answered the questions successfully or not, I do not know, but we have now got a piece of paper. They say a camel is a horse produced by a committee, so perhaps we've actually got a camel here, I do not know. At least it gives everybody something to take home to put in their trip reports. I will leave it here, I am not sure whether anybody has anything specific they want to say at this point. I will hand it back to Duwayne who can close this down.

Dr. Anderson:

Thank you Neal. That was a very good job that you have done for all of us. You may be surprised to learn that this workshop is not greatly different from the one held last year in Buffalo. We spent quite a lot of time in preliminaries. We did spend a little more time in reviewing papers and literature which we had spread around the table, because we wanted to deal with some factual matters. But in the end, we came at the problem pretty much the way, Neal has lead us through this today, by posing specific questions and asking for votes pro and con, and accepting only the items on which there was a consensus. And it is rather satisfying, I am sure to all of you, to see that there is a reasonably good consensus around this table on quite a number of things.

However, it is also quite clear, as it was to us earlier, that there are many open questions and when one takes into account the need to be site specific, as Marc has pointed out often is the case, then we are dealing with almost a wide open problem and it is almost impossible in a short period of time to come to any definitive conclusions. This would require specific tests, data and so forth.

I think, we should all thank our two chairmen, Jim and Neal, for bringing us to this successful conclusion. Before declaring the workshop to be at an end, I would like to give one further opportunity to each of you to make a statement, ask a question or say anything else that you would like to say, dealing with the topic of the workshop.

Dr. Altaner:

I think an additional possible area of study, instead of just considering the possibility of illite formation in terms of mineralogy, is to consider possible changes in hydration states of smectite at temperature/pressure and at a certain concentration of species in solution. It is possible to know the exact state of hydration. There is an apparatus at Illinois capable of high temperatures and high pressures, an x-ray cell where you can x-ray smectite clay.

Dr. Anderson:

Anything else? I have one additional question that I would like to put on the record and hear an answer to. Who around this table knows of additional occurrences in which we can be sure that a smectite has been transformed to illite? We have heard of one instance today or yesterday in Montana. There surely are others, I would like to have some indication as to how many field occurrences we know of in which we can demonstrate that smectite has been altered to illite a certain rate.

(No answer).

Thank you all. I hope you all have a safe journey home.

Meeting adjourned.

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.

1982
TR 82–28
The KBS Annual Report 1982.
KBS Technical Reports 82-01 – 82-27.

1983
TR 83–77
The KBS Annual Report 1983.
KBS Technical Reports 83-01–83-76
Summaries. Stockholm, June 1984.

1984
TR 84–01
Radionuclide transport in a single fissure
A laboratory study of Am, Np and Tc
Trygve E Eriksen
Royal Institute of Technology
Stockholm, Sweden 1984-01-20

TR 84-02
Radiolysis of concrete
Hilbert Christensen
Studsvik Energiteknik AB,
Nyköping, Sweden
Erling Bjergbakke
Risö National Laboratory,
Roskilde, Denmark 1984-03-16

TR 84-03
Effect of β-radiolysis on the products from α-radiolysis of ground water
Hilbert Christensen
Studsvik Energiteknik AB,
Nyköping, Sweden
Erling Bjergbakke
Risö National Laboratory
Roskilde, Denmark
1984-07-10

TR 84—04
Analysis of some laboratory tracer runs in natural fissures
Luis Moreno
Ivars Neretnieks
The Royal Institute of Technology
Department of Chemical Engineering
Trygve Eriksen
The Royal Institute of Technology
Department of Nuclear Chemistry
Stockholm, Sweden 1984-03-15

TR 84—05
Diffusion in clay—Experimental techniques and theoretical models
Trygve Eriksen
Royal Institute of Technology, Stockholm
Arvid Jacobsson
University of Luleå, Luleå
Sweden 1984-06-28

TR 84—06
Uranium series disequilibrium studies of drillcore Km3 from the Kamlunge test-site, northern Sweden
John AT Smellie
Swedish Geological
Luleå, Sweden 1984-03-30

TR 84—07
Study of strontium and cesium migration in fractured crystalline rock
Erik Gustafsson
Carl-Erik Klockars
Swedish Geological Co
Uppsala, Sweden 1984-09-28

TR 84—08
Fracture fillings in the gabbro massif of Taavinunnanen, northern Sweden
Sven Åke Larson
Geological Survey of Sweden
Eva-Lena Tullborg
Swedish Geological Company
Göteborg August 1984

TR 84—09
Comparative study of geological, hydrological and geophysical borehole investigations
Kurt-Åke Magnusson
Oscar Duran
Swedish Geological Company
Uppsala September 1984

TR 84—10

Geochemical simulation of the evolution of granitic rocks and clay minerals submitted to a temperature increase in the vicinity of a repository for spent nuclear fuel

Bertrand Fritz
Marie Kam
Yves Tardy
Université Louis Pasteur de Strasbourg
Institut de Géologie
Strasbourg, France July 1984