Research

Comment on the Long-Term Chemical and Mineralogical Stability of the Buffer

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SKi

SKI Perspective

Background

The chemical stability of bentonite, used as buffer material in the KBS-3 concept, needs to be thoroughly addressed in a safety assessment context. Chemical transformations of montmorillonite and other components may influence the physical properties of the buffer, which could affect its ability to protect the copper canister with the spent nuclear fuel. The safety significance would depend on the nature and extent of these transformations.

The Swedish Nuclear Waste Management Company (SKB) has during several decades conducted research connected to the chemical stability of bentonite. Models for illitisation, surface complexation, ion-exchange, and solid-solution behaviour of montmorillonite as well as trace component dissolution and precipitation (e.g. calcite and pyrite) have been developed based on laboratory experiments and natural analogues. A study to more thoroughly understand a possible alteration/cementation under elevated temperature has been announced.

Purpose of the project

This report provides an overview of relevant chemical processes that could be expected to occur within a bentonite buffer and the modelling approaches developed by SKB to handle these. The main purpose is to provide input for SKI's review of SKB's bentonite programme. The report does not in any detail address the safety assessment implications of the possible bentonite alterations.

Results

The authors' main conclusion is that changes imposed by possible ionic substitutions of octahedral and tetrahedral positions should be considered, which may involve further thermodynamic modelling of smectite clays.

Future Work

In a future review of the SR-Can safety assessment, the additional modelling work concerning buffer alteration during the thermal phase should be evaluated. Moreover, it needs to be assessed whether or not the SR-Can assumptions about long-term buffer performance are well supported by information from modelling, experiments and natural analogues. The possible consequences of the bentonite alterations, which can not be excluded, have to be evaluated in greater detail.

Project Information

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Summary

This report examines concepts and data that SKB *may* use to assess the long-term chemical and mineralogical evolution of bentonite barriers in a KBS-3 repository for spent nuclear fuel. Three interrelated topics are considered:

- mineral chemistry of the smectite clays;

- thermodynamic stability of the smectite clays; and

- bentonite-water interactions during the early thermal period of repository evolution.

Smectites are complex solid solutions having variable compositions resulting from ionic substitutions on exchange, octahedral and tetrahedral sites in the crystalline lattice. Although little is known about the mechanisms and rates of reactions involving the latter two sites, abundant observational evidence from natural systems suggests that such reactions could occur to an appreciable extent in the buffer over the million year time frame being considered for an intact canister. We are not aware of any efforts in SKB's current modeling strategy to account for such reactions, and therefore question whether the strategy is appropriate for modeling the long-term chemical evolution of the buffer and associated potential effects on the desirable physical and rheological properties of this barrier material.

The variable chemistry of smectites affects their thermodynamic stability. Models of smectite-water equilibria use either a fixed stoichiometric composition to approximate representative smectite varieties, or account for compositional variations using solid-solution models and ideal mixing relations among thermodynamic components. In either case the thermodynamic properties of a specific smectite composition or of individual solid-solution components must usually be estimated. Recent reports suggest that SKB will not account explicitly for the thermodynamic properties of smectite in its models of bentonite-water interactions. Rather, the models will assume that this clay mineral has a fixed, though unspecified, composition representing an ion-exchanger phase. This phase is assumed either to be stable or to alter to a less expandable mineral at an extremely slow, but predictable, rate. Unfortunately, this approach appears to have two inherent limitations: 1) it cannot be used to relate specific conditions of smectite stability/instability to evolving geochemical conditions in the near field, and 2) it may overemphasize the importance of accessory minerals and surface reactions in controlling the long-term chemical and mineralogical evolution of bentonite barriers.

Dissolution, transport and precipitation processes during the resaturation phase and transient thermal period of repository evolution could cause individual clay particles in the buffer to become cemented together. Cementation could adversely affect the physical and microstructural properties of this barrier. SKB's current approach for modeling bentonite-water interactions may not be an appropriate basis for evaluating the potential long-term effects of cementation on buffer performance, due to the basic limitations in this approach noted above.

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1   Introduction

SKI will evaluate within the next few years whether the bentonite buffer in a KBS-3 repository for spent nuclear fuel is likely to meet certain requirements that are needed to help protect the canister from excessive mechanical and chemical degradation. When fully water-saturated at high compaction densities, bentonite is a suitable buffer material due to its favorable physical, chemical and rheological properties under such conditions. These properties include:

- an extremely low hydraulic conductivity, which ensures that a diffusional transport barrier exists between the host rock and canister;

- a sufficiently low chemical activity of $H_2O(l)$ to prevent the survival and growth of microorganisms;

- a swelling pressure that is sufficiently high to establish and sustain good contact with the host rock and canister, but not so high as to deform the canister, or fracture the rock;

- a load-bearing capacity and rheological response sufficient to prevent the dense nuclear waste package from "sinking" through the lower density buffer and coming into direct contact with the host rock;

- a deformability that is high enough to absorb rock movements, but not so high as to cause the position of the canister to shift in its deposition hole or drift; and

- a thermal conductivity that is sufficiently high to ensure rapid dissipation of radiogenic heat.

In the event that a canister loses its containment function for any reason, the buffer may also provide:

- a favorable chemical environment promoting sorption and precipitation of any radionuclides released from the spent fuel;

- a permeability to gas flow that is high enough to allow any gases generated by corrosion of the canister's iron insert to pass through the buffer without forming permanent permeable channels or cavities; and

- a filtration capacity that effectively stops the migration of potential radionuclide-bearing colloids.

All these properties ultimately depend on the mineralogy and petrographic structure of bentonite. Bentonites contain smectite clays along with smaller amounts of quartz, feldspars, zeolites, carbonates, organics and sulfides. The clay minerals have a low interlayer charge, which results from isomorphous substitutions of various ions within their crystalline lattice. This allows the lattice to expand rapidly and reversibly as hydrated

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charge-balancing cations are forced to occupy interlayer positions at the lattice surface. The expandable nature of the smectite clays controls the swelling pressure of bentonite as a function of water content, water chemistry and compaction density. The swelling pressure, in turn, directly affects the hydraulic conductivity, gas permeability, deformability and filtration properties of this barrier material (*e.g.,* Pusch, 1996; 2001).

Given the importance of mineralogy in controlling the desirable barrier properties of the buffer, the question arises whether changes in bentonite mineralogy, especially changes in the chemistry and stability of the smectite clays, might result from evolving geochemical conditions in the near field (*e.g.,* during buffer resaturation) and far field (*e.g.,* by glaciation/deglaciation and associated changes in groundwater chemistry resulting from a rise or fall in sea level). The desirable barrier properties of the buffer should ideally persist over time scales that are at least as long as the containment period provided by intact canisters, which may be as long as 10^6 years. If this is not the case, allowance must be made for any degradation of buffer performance that cannot be convincingly excluded.

2   Objectives

This report evaluates concepts and data that may be used by SKB to assess the long-term performance of bentonite buffer materials in a KBS-3 repository for spent nuclear fuel. The views expressed in this report are intended to help provide a foundation for regulatory review of SKB's future license applications for the encapsulation plant and deep repository. Complementary reports addressing other aspects of the KBS-3 EBS include SKI (2002; 2003; 2004).

3   Discussion of results

Geochemical processes that could affect the ability of bentonite barriers to fulfill their performance requirements (Section 1) are considered below. The discussion is divided into three interrelated topics:

- mineral chemistry of the smectite clays;

- thermodynamic stability of the smectite clays; and

- bentonite-water interactions during the early thermal period of repository evolution.

For each of these topics we first consider how associated environmental conditions, processes and parameters have been conceptualized and quantified in numerical models, with special attention given to approaches used by SKB. Interactions between two or more processes are then evaluated, and uncertainties associated with these interactions are assessed. We then consider conditions that could affect the validity of the process models, and conclude with an assessment of how key processes may affect buffer performance.

The discussion is based on previous work carried out by and for SKI. These studies include a thorough review of the properties and uses of bentonite as a buffer material (Savage *et al.*, 1999) plus related reviews and supporting investigations (SKI, 1993; Apted, 1993; Arthur *et al.*, 1993; Arthur and Apted, 1996; SKI, 1999; Arthur and Zhou, 2000a, b; Stenhouse, 2000; Arthur and Wang, 2000; SKI 2001).

3.1   Mineral chemistry of the smectite clays

In this section we consider reactions that control the chemical composition of smectites. Compositional variations in these clay minerals could affect certain physical and rheological properties of the buffer (*e.g.,* Pusch, 1996), and may also influence the long-term geochemical evolution of the near field (Bruno *et al.,* 1999).

Smectites exhibit considerable compositional variability in natural systems (*e.g. Tardy et al., 1987)*. Three groups of dioctahedral smectites[1] are classified based on their Al and Fe^{3+} contents. Aluminous varieties include the beidellites and montmorillonites. Nontronites contain relatively high concentrations of Fe^{3+}. There is a complete solid-solution compositional range between the nontronites and beidellites, and a significant, but incomplete, compositional range between the montmorillonites and beidellites (Velde, 1992). Trioctahedral smectites, which are also swelling clays, include saponites and stevensites. Saponites are aluminous phases, whereas stevensites are essentially devoid of Al. Although there is some disagreement concerning representative compositions and compositional ranges for the dioctahedral and trioctahedral smectites, the data shown in

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[1] The term dioctahedral indicates that two thirds of cation sites in the octahedral layer of the clay's crystalline lattice (see below) are occupied; all of these sites are occupied in trioctahedral smectites.

Tables 3.1_1 and 3.1_2 are considered reliable because X-ray diffraction determinations were used to rule out the presence of mixed-layer or interlayer phases in samples selected for the chemical analyses (Velde, 1992).

The variable chemistry characteristic of smectites can be related to their crystalline structure. These clay minerals have a 2:1 lattice structure consisting of one octahedrally coordinated layer between two tetrahedrally coordinated sheets (Figure 3.1_1). Ionic substitutions in the octahedral and tetrahedral layers result in a net negative charge on the 2:1 framework, which is compensated by hydrated cations occupying interlayer positions (*e.g.,* Grim, 1968). Interlayer charge originates from ionic substitutions in the tetrahedral layer of beidellites (mainly Al^{3+} for Si^{4+}), and from ionic substitutions in the octahedral layer of montmorillonites and nontronites (divalent cations for Al^{3+} in montmorillonites and divalent cations, including Fe^{2+}, for Fe^{3+} in nontronites). Interlayer charge in dioctahedral smectites can vary widely between roughly 0.2 to 0.6 equivalents per 2:1 unit of $O_{10}(OH)_2$ anionic charge. These minerals may thus be stable over a considerable range of environmental conditions and associated ranges in porewater chemistry. Cations occupying the interlayer sites typically include Na^+, Ca^{2+}, Mg^{2+} and K^+.

3.1.1 Models, parameters and uncertainties

Ion exchange. Ion-exchange reactions involve rapid, reversible displacement of interlayer cations and replacement with cations in a coexisting aqueous phase (*e.g.,* Garrels and Christ, 1965). This process is assumed to occur without an appreciable compositional change in the basic 2:1 structural unit of the clay. Because the composition of this unit is fixed, it does not have to be treated explicitly with respect to mass-balance and charge-balance constraints imposed by a balanced chemical reaction.

Ion-exchange reactions considered by SKB for bentonite buffer materials include replacement of Na^+ in montmorillonite by Ca^{2+} or Mg^{2+} (Wanner *et al.,* 1992; Bruno *et al.,* 1999). The reactions are represented by:
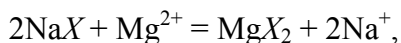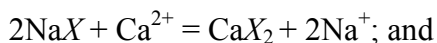
$$2NaX + Ca^{2+} = CaX_2 + 2Na^+; \text{ and}$$

$$2NaX + Mg^{2+} = MgX_2 + 2Na^+,$$

Table 3.1_1. Compositions of dioctahedral smectites[*] (Velde, 1992)

Beidellite			Montmorillonite			Nontronite		
	Typical	Range		Typical	Range		Typical	Range
Interlayer site[1]								
M^+	0.46	0.45-0.47	M^+	0.27	0.21-0.62	M^+	0.26	0.23-0.74
Octahedral site								
Al	1.96	1.39-1.99	Al	1.56	1.17-1.57	Al	0.60	0.02-0.75
Fe^{3+}	0.02	0.02-0.49	Fe^{3+}	0.15	0.01-0.22	Fe^{3+}	1.06	0.17-1.45
Mg	0.00	0.00-0.07	Mg	0.32	0.18-0.42	Mg	0.39	0.25-0.81
Fe^{2+}	0.00	0.00-0.01	Fe^{2+}	0.01		Fe^{2+}	0.00	0.02-0.06
Tetrahedral site								
Si	3.48	3.46-3.58	Si	3.93	3.80-4.00	Si	3.98	3.41-4.00
Al	0.52	0.41-0.54	Al	0.07	0.00-0.2	Al	0.02	0.00-0.59

[*] Cations per $O_{10}(OH)_2$; M^+ represents any monovalent cation.

Table 3.1_2. Compositions of trioctahedral smectites (Velde, 1992).*

	Saponite	Stevensite
Interlayer charge	0.42	0.16
Octahedral site		
Mg	2.86	2.89
Fe^{2+}	0.00	0.02
Al	0.08	0.00
Fe^{3+}	0.01	0.01
Tetrahedral site		
Si	3.75	4.00
Al	0.25	0.00

* Cations per $O_{10}(OH)_2$.

where X refers to the clay's 2:1 structural unit, or "layer surface site" (Wanner *et al.*, 1992)[2]. The equilibrium constant, K, for the first reaction (for example) is given by:

$$K = K_c \frac{\gamma_{Na^+}^2}{\gamma_{Ca^{2+}}}, \qquad (1)$$

where γ refers to an activity coefficient for the free aqueous species and K_c stands for a
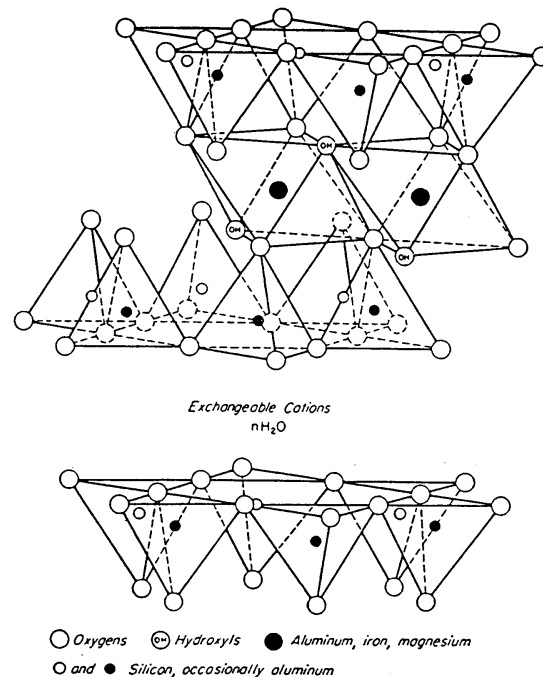

Figure 3.1_1. Schematic diagram showing the crystalline structure of the smectite montmorillonite (Grim, 1968).

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[2] Wieland *et al.* (1994) propose similar reactions involving exchange of Na^+ by H^+ at interlayer sites on the "external surfaces" of montmorillonite (so-called "X" sites) as well as on "internal surfaces" of a montmorillonite "platelet" ("Y" sites). These reactions are not considered in further refinements of SKB's model (Bruno *et al.*, 1999) because they are unimportant relative to other surface reactions involving H^+ (see below).

conditional equilibrium constant. The conditional constant is valid only for a specific surface composition, ionic strength and temperature, and is given by:

$$K_c = \frac{[CaX_2][Na^+]^2}{[NaX]^2[Ca^{2+}]},$$ (2)

where the brackets denote concentration per unit volume of the aqueous solution. Equation (1) is derived assuming that activity coefficients for the sorbed cations equal unity. This may be a valid assumption, based on limited experimental data (see Wanner *et al*., 1992), provided changes in the concentrations of the surface species are not too large.

Wanner *et al.* (1992) used unpublished experimental data from SKB on the interaction of untreated MX-80 bentonite with distilled water or synthetic Swedish-type granite groundwater ("Allard water") at room temperature to estimate values of log K for the Na-Ca and Na-Mg exchange reactions[3]. Interpretation of these experimental results is not straightforward because dissolution of accessory minerals in the bentonite may have affected the aqueous concentrations of some important cations (notably Ca^{2+}) and anions (SO_4^{2-}), and because it is unclear whether equilibrium was attained for all relevant reactions, including the exchange reactions. The log K values estimated by Wanner *et al.* (1992) are nevertheless reasonably similar to those determined by Olin *et al.* (1995). The latter study retrieved exchange constants from experimental data obtained over a period of up to 9 months at 75°C in a system consisting of copper cylinders packed with MX-80 bentonite and reacted with Allard water or Allard water containing a 100-fold increase in K^+. The fair agreement between the exchange constants determined by Wanner *et al.* (1992) and Olin *et al.* (1995) is somewhat surprising given the significant differences in experiment design, time scale, and experimental conditions considered in these two studies.

Isomorphous substitutions. The variations in smectite compositions shown in Tables 3.1_1 and 3.1_2 indicate that ionic substitutions involving cations in octahedral and tetrahedral coordination also have an important influence on smectite chemistry. These reactions are referred to as isomorphous substitutions because they do not cause an appreciable change in the clay's crystalline structure. Little is known concerning the mechanisms and rates of these reactions, but they are likely to be much slower than ion-exchange reactions and thus may not be detectable over laboratory time scales. Conceptual models accounting for the effects of these reactions on clay-mineral stabilities are discussed in Section 3.2.2.

Surface complexation. In addition to the charge resulting from ionic substitutions within the crystalline lattice of smectite, ionization of surface OH groups can also generate a variable, pH-dependent charge. Deprotonated OH groups form surface complexes with metal ions, and thus have a minor influence on the overall composition of these clay minerals. More importantly, such surface-complexation reactions control the colloidal stability of smectites, as well as their sorption behavior with respect to trace concentrations of transition metals, actinides and fission products. Like ion-exchange models, surface-complexation models do not account explicitly for the composition of smectite's 2:1 layer framework.

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[3] The Na-K exchange reaction cannot be evaluated from these data because K^+ was not measured.

The following reactions are considered in SKB's surface-complexation model for the buffer (Wieland *et al.*, 1994):

$\equiv SOH_2^+ = \equiv SOH + H^+$, and

$\equiv SOH = \equiv SO^- + H^+$
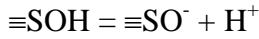
where $\equiv SOH_2^+$, $\equiv SOH$ and $\equiv SO^-$ represent positively charged, neutral and negatively charged surface hydroxyl groups, all of which are assumed to exist at edge faces of individual montmorillonite crystals. The corresponding mass-action expressions are given by:

$$K_{a1}^{int} = \frac{(\equiv SOH)(H^+)}{(\equiv SOH_2^+)} \exp(-\frac{F\Psi}{RT}), \text{and} \qquad (3)$$

$$K_{a2}^{int} = \frac{(\equiv SO^-)(H^+)}{(\equiv SOH)} \exp(-\frac{F\Psi}{RT}) \qquad (4)$$

where K_{a1}^{int} and K_{a2}^{int} represent intrinsic acidity constants, ( ) denotes activity of the indicated surface species, or of H^+ in bulk solution, Ψ stands for the electrical potential at the clay surface, and F, R and T refer to the Faraday constant, gas constant and temperature, respectively. Bruno *et al.* (1999) ignore contributions to K_{a1}^{int} and K_{a2}^{int} arising from electrostatic potentials near the clay surface, and thus effectively assume $\Psi = 0$ in the above equations.

Wieland *et al.* (1994) carried out acidimetric and alkalimetric titrations of Na-montmorillonite suspensions at room temperature. The starting montmorillonite was purified from MX-80 bentonite. Parameters in a model accounting for the surface complexation reactions discussed above were fit to the measured titration curves. Retrieved values at $\approx 25°C$ include log K_{a1}^{int} = -5.4±0.1 and log K_{a2}^{int} = -6.7±0.1. The total number of surface-complexation sites = $2.8x10^{-5}$ mol g^{-1}. Bruno *et al.* (1999) state that the titration data of Wieland *et al.* (1994) are the only experimental data available.

3.1.2 Interactions with other processes

Dissolution of accessory minerals in bentonite could affect the chemical composition of smectite if the accessory minerals contain cations that can be exchanged at interlayer positions. Such minerals in MX-80 bentonite, for example (see Bruno *et al.,* 1999), include carbonates [calcite ($CaCO_3$), and possibly also siderite ($FeCO_3$) and dolomite ($CaMg(CO_3)_2$)], plagioclase [albite ($NaAlSi_3O_8$) and possibly also anorthite ($CaAl_2Si_2O_8$)], anhydrite ($CaSO_4$), halite ($NaCl$) and illite [*e.g.,* $K_{0.8}Al_{2.4}Si_{3.5}O_{10}(OH)_2$]. A variety of Na-, Ca-, Mg- and K-bearing aluminosilicate minerals and carbonates will probably also exist in crushed-rock "ballast", which will be mixed with bentonite to make up the backfill.

It is worthwhile noting that the accessory minerals in bentonite and ballast materials may each react at vastly different rates. Carbonate minerals, for example, tend to dissolve

sufficiently fast to equilibrate with an aqueous phase over laboratory time scales (days to months). Aluminosilicates, on the other hand, tend to react much more slowly and may not attain equilibrium with contacting groundwaters over many thousands of years. Such differences in dissolution rate are important because ion-exchange reactions are essentially instantaneous (*e.g.,* Stumm and Morgan, 1996). The dissolution reactions of different accessory minerals may thus affect smectite chemistry at different times and in different ways over the lifetime of a repository.

Isomorphous substitutions involving cations occupying octahedral and tetrahedral sites in smectite may also be affected by dissolution of accessory minerals. These reactions generally involve exchange of Mg, Fe, Al and Si, which suggests that dissolution of aluminosilicate accessory phases could affect the octahedral- and tetrahedral-site occupancies of smectites in the buffer. The rates of isomorphous substitution reactions may be extremely slow, however. This possibility is exemplified by the slow kinetics of the smectite illitization reaction (Section 3.2.1), which involves substitution of Al^{3+} for Si^{4+} in tetrahedral positions.

Corrosion of the canister's Cu shell and Fe insert may also affect smectite compositions. Karnland *et al.* (2000) measured an increase of up to 100 ppm Cu in a block of compacted MX-80 bentonite that was placed in contact with a heated Cu tube for one year in SKB's LOT (Long Term Test of Buffer Material) experiments at the Äspö HRL. Copper was dissolved from the tube and then apparently taken up by smectite, either at interlayer sites or within the octahedrally coordinated layer. Kamei *et al.* (1999) measured equilibrium constants for the exchange of Na^+ by Fe^{2+} at interlayer positions in a purified Na-smectite from Japan. Wilson *et al.* (2000) similarly found that an unidentified Fe(II) complex displaced Na^+ and other exchangeable cations from interlayer sites in a Na-montmorillonite. These authors noted that work was ongoing to assess whether Fe(II) was also incorporated into the smectite's octahedral layer. Marcos (2003) observes that there is no experimental evidence indicating that Fe(II) ions from a corroding canister insert can enter buffer porewaters and become incorporated into the 2:1 framework structure of smectite. Anantatmula *et al.* (1984) found that an iron-rich clay, possibly smectite, formed by the interaction of bentonite and Fe over a two week period at 150° and 250°C.

The chemistry of porewaters in the buffer will vary with changes in groundwater chemistry. Such changes could affect smectite compositions by inducing ion-exchange reactions or ionic substitutions at octahedral and tetrahedral positions.

3.1.3 Reliability of process models

SKB's ion-exchange and surface-complexation models for smectite refer to a specific, though unspecified, composition of the clay's negatively charged 2:1 framework. To apply such models it must be assumed that this lattice composition does not change over the time period of interest (Garrels and Christ, 1965; Stumm and Morgan, 1996).

This assumption may be unrealistic given the 10^6 year lifetimes now being considered for intact canisters. Although little is known about how quickly smectite's lattice chemistry can change as a result of ionic substitutions on all of its structural and exchange sites, the

widely variable compositions of these minerals in natural systems suggests that it is likely that significant changes in mineral chemistry, possibly including complete conversion of the initial montmorillonites to beidellites, saponites, *etc.,* could occur within 10^6 years. If so, SKB's current modeling approach does not appear to provide an adequate basis for evaluating these reactions and their effects on the long-term chemical evolution and isolation functions of the buffer.

The key question in this regard would seem to be whether changes in smectite's octahedral and tetrahedral site chemistry could significantly affect the ion-exchange and surface-complexation constants used in SKB's models. If not, then these constants could be used in a generic sense to represent smectite of any composition. We believe that some insight into this question might come from a broad-based literature review of experimentally determined constants covering as much as possible of the full range of dioctahedral and trioctahedral smectite compositions.

3.1.4 Potential impacts on buffer performance

The long-term chemical evolution of the buffer has been modeled by SKB (SKB, 1997; SKB, 2004) using the ion-exchange and surface-complexation models described by Bruno *et al.* (1999), Wieland *et al.* (1994) and Wanner *et al.* (1992). As noted in the previous section, these models do not, and cannot, account for possible changes in smectite mineral chemistry other than changes resulting from cation exchange. With the exception of illitization reactions (see below), the effects of other possible changes in smectite chemistry on the chemical evolution of the buffer have apparently not been considered by SKB. In our view, it is appropriate from a regulatory perspective to assume that favorable initial properties are not degraded to an unacceptable level only if all potential alteration processes have been thoroughly evaluated and either demonstrably discounted or accounted for with bounding assumptions.

The relative concentrations of interlayer cations in the smectite clays can strongly affect the physical and rheological properties of the buffer (*e.g.,* Pusch, 2001). The effects appear to decrease with increasing density, however, and may have little impact on buffer performance as long as the density at full water saturation remains above a threshold value of about 1900 kg m^{-3} (*e.g.,* SKB 2004). It is not clear whether a change in smectite chemistry from montmorillonitic to beidellitic, nontronitic or saponitic compositions could significantly alter this threshold density. Limited experimental evidence indicates that the swelling pressure and hydraulic conductivity of argillaceous materials containing nearly equivalent amounts of montmorillonite or saponite differ significantly even at a saturated density of 2000 kg m^{-3} (Pusch, 2001).

Marcos (2003) notes that the oxidation state of octahedral Fe in smectites can have a strong effect on the swelling pressure of bentonite. The swelling pressure is reduced nearly by half if octahedral Fe is in the ferrous rather than ferric state. Gates *et al.* (2000) point out that the oxidation state of Fe in smectites can profoundly alter their cation-exchange properties, particle size, surface acidity, swelling behavior and other properties. Wilson *et al.* (2000) suggest that precipitation of Fe oxyhydroxide phases on interlayer surfaces of smectite could result in a loss of cation-exchange capacity and (or) swelling capacity.

3.2 Thermodynamic stability of the smectite clays

This section considers conceptual models and data that can be used to interpret the thermodynamic stability of the smectite clays. These models are essential for assessing the long-term mineralogical evolution of buffer materials.

3.2.1 Models, parameters and uncertainties

Thermodynamic models for smectites are complicated by the extensive chemical variability characteristic of these clay minerals (Section 3.1). In the following discussion we distinguish between two basic modeling approaches that have been used to deal with these complications: 1) *stoichiometric models*, which adopt a fixed stoichiometric composition as being representative of smectites in general, or of specific smectite types (*i.e.,* montmorillonites, beidellites, *etc.*), and 2) *solid-solution models,* which explicitly account for compositional variations using solid-solution models and ideal mixing relations among thermodynamic components.

Stoichiometric models. These models are based on the assumption that smectites have a fixed stoichiometric composition (*e.g.,* Garrels, 1984; Tardy *et al.*, 1987; Aja *et al.*, 1991). This assumption, although generally unrealistic for smectites, enables conventional activity-activity diagrams to be used to assess the thermodynamic stability of a given, representative smectite composition relative to other clay and non-clay minerals (*e.g.,* Figure 3.2.1_1). The models can thus be used to establish approximate stability boundaries among the various dioctahedral and trioctahedral smectites, as well as between smectites and other minerals. The fact that clay minerals are metastable with respect to other silicate and oxide minerals (*e.g.,* May *et al.,* 1986), does not invalidate the approach because clays are globally observed to persist metastably in natural systems over geologic periods of time (*e.g.,* Giggenbach, 1981). Practical application of stoichiometric models to argillaceous systems is facilitated by advances in numerical techniques that allow reasonably accurate estimates to be made of the thermodynamic properties of any specific smectite composition as a function of temperature and pressure (Tardy and Garrels, 1974; 1976; Mattigod and Sposito, 1978; Hazen, 1985, 1988; Chermak and Rimstidt, 1989).

Solid-solution models. Solid-solution models treat compositional variations in terms of changes in the activities of thermodynamic components. Two solid-solution models have been proposed for smectites. They differ depending on whether component activities are assumed to be controlled by ideal mixing of end-member components or by ideal site-mixing of individual atoms occupying the clay's interlayer, octahedral and tetrahedral sites.

Ideal-mixing models are described by Tardy and Fritz (1981), Fritz (1985), Bourcier (1985) and Tardy *et al.* (1987). Smectite solutions are treated as simple "molecular mixtures", for which the saturation index, SI_{ss}, is calculated using (*e.g.,* Bourcier, 1985):

$$SI_{ss} = \sum_{i=1}^{n} X_i \log\left(\frac{Q_i}{K_i a_i}\right) \tag{5}$$
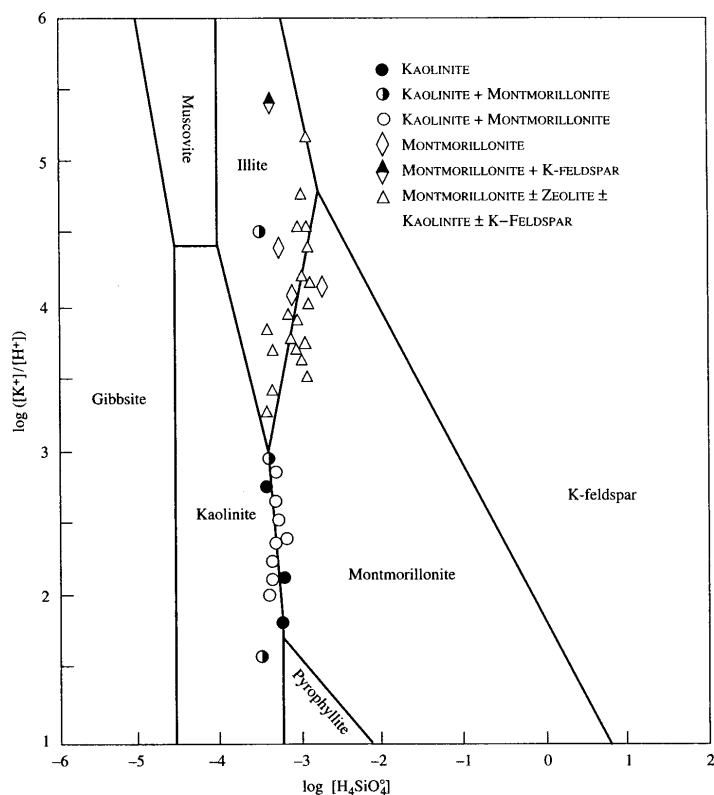
Figure 3.2.1_1. Activity-activity diagram for the K_2O-Al_2O_3-SiO_2-H_2O system at 25°C, 1 bar (Langmuir, 1997, after Garrels, 1984). The stability fields of montmorillonite and illite are drawn assuming fixed stoichiometry with $K_{0.3}Al_{1.9}Si_4O_{10}(OH)_2$ (montmorillonite) and $K_{0.8}Al_{2.4}Si_{3.5}O_{10}(OH)_2$ (illite). Symbols refer to chemical analyses of porewaters coexisting with clay minerals reported by Aagaard and Helgeson (1983). Trends in these data appear to indicate equilibrium between kaolinite and montmorillonite and montmorillonite and illite, and were used by Garrels (1984) to retrieve standard Gibbs free energies of formation for the selected montmorillonite and illite compositions.

where X stands for the mole fraction of the i-th component in an n-component solid, Q and K refer to the ion-activity product and equilibrium constant, respectively, for dissolution of the component in water, and a_i represents the component's activity in the solid. This equation can be rearranged to solve for the least soluble, and hence most stable, composition of smectite in contact with an aqueous solution of fixed composition. Assuming ideal mixing, *i.e.*, $a_i = X_i$, the result is given by:

$$X_i = \left(\frac{\dfrac{Q_i}{K_i}}{\displaystyle\sum_{i=1}^{n} \frac{Q_i}{K_i}} \right). \tag{6}$$

Smectite chemistry is thus controlled by the composition of the aqueous phase (*i.e.,* which controls Q_i) and equilibrium constants for dissolution reactions involving the end-member components. The solid-solution model developed by Tardy and Fritz (1981) and Fritz (1985) was used in two early studies for SKB (Fritz and Kam, 1985; Tardy *et al.,* 1987),

but it does not appear to be included in SKB's current strategy for modeling the long-term chemical and mineralogical evolution of the buffer (Bruno *et al.,* 1999). If not, an explanation of the rationale underlying this decision would be of considerable interest.

Ideal site-mixing models define the relation between smectite composition and component activities in terms of the mixing behavior of individual atoms on exchange, octahedral and tetrahedral sites (Aagaard and Helgeson, 1983; Giggenbach, 1985). Ideal mixing is assumed, which entails random mixing and equal interaction among the atoms occupying energetically equivalent sites and exchange of atoms between energetically distinct sites. Under such conditions, a component's activity in a smectite of given composition can be calculated using (Aagaard and Helgeson, 1983):

$$a_i^{sm} = k_i \prod_s \prod_j X_{j,s}^{v_{j,s,i}}, \tag{7}$$

where a_i^{sm} represents the activity of the *i*-th component in the solid solution, $X_{j,s}$ denotes the mole fraction of the *j*-th atom on the *s*-th site, $v_{j,s,i}$ stands for the stoichiometric number of the *j*-th atom on the *s*-th site in one mole of the *i*-th component and k_i refers to a dimensionless constant whose value depends only on the component's stoichiometry. Calculated component activities can be used as descriptive variables enabling the stability field of smectite solid solutions to be portrayed on conventional activity-activity diagrams. Cramer and Smellie (1994) and Arthur and Wang (2000) evaluate this approach using the chemistry of porewaters extracted from argillaceous rocks to assess the consistency of model predictions.

The thermodynamic properties of solid-solution components are not generally well known and must therefore be estimated or approximated. The ideal-mixing model described by Bourcier (1985), for example, uses components that were originally evaluated by Wolery (1978). Wolery (1978) adopted the idealized formula $(Mg_{0.33}Al_{1.67})Si_4O_{10}(OH)_2$[4] to represent the basic montmorillonite structure, and then estimated standard molal thermodynamic properties (including temperature-dependent heat capacities) for pure Na-, K-, Ca- and Mg- end members using techniques described by Tardy and Garrels (1974) and Helgeson *et al.* (1978). The thermodynamic properties of analogous end-members were similarly estimated for beidellites $[(Al_2)Al_{0.33}Si_{3.67}O_{10}(OH)_2]$ and nontronites $[(Fe_2)Al_{0.33}Si_{3.67}O_{10}(OH)_2]$. These component properties are used in the solid-solution model for dioctahedral smectites that is included in the EQ3/6 geochemical software package (Wolery, 1992). Tardy and Fritz (1981) and Fritz (1985) use a similar approach to develop an ideal solid-solution model for smectites that is supported by temperature-dependent thermodynamic properties for 27 end-member components. The ideal site-mixing models of Aagaard and Helgeson (1983) and Giggenbach (1985) are defined in terms of thermodynamic components that are stoichiometrically equivalent to the minerals pyrophyllite and muscovite. The thermodynamic properties of these minerals are well characterized and can be used for the corresponding components if a standard state calling for unit activity for the pure component is adopted in the model. Aja *et al.* (1991) point out that this approach may not be appropriate because the thermodynamic properties of the components are based on those of non-clay minerals.

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[4] Octahedral cations enclosed by parentheses.

Illitization. The thermodynamic stability of the smectite clays is often considered in terms of reactions involving the transformation of smectite to illite. Illite is a non-expandable mineral, and its formation could therefore have a detrimental affect on the buffer's isolation functions (Section 1). Illitization reactions have been studied in considerable detail by SKB and others, and are discussed separately here. Pusch (1993) and Karnland *et al.* (1995) provide useful reviews of these studies.

The mechanism by which montmorillonite is transformed into illite is not well understood, but the overall process can be represented by the following schematic reaction:

$$montmorillonite + Al^{3+} + K^+ \rightarrow illite + Si^{4+} + Ca^{2+}/Na^+ + Fe^{2+}/Mg^{2+},$$
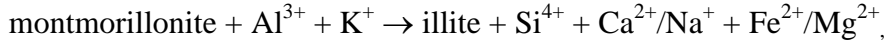
where the right-facing arrow emphasizes the possibility that the transformation rate is extremely slow. Whether the reaction involves a solid-state, layer-by-layer replacement of smectite by illite, or complete dissolution of smectite followed by precipitation of neoformed illite, is still an open question. In general, however, the reaction results in an increase in layer charge due to replacement of Si^{4+} by Al^{3+} at tetrahedral positions, a decrease in the Fe^{2+} and Mg^{2+} content of octahedral sites and an increase in interlayer K^+ at the expense of other interlayer cations, including Na^+ and Ca^{2+}.

The rate of the smectite-to-illite reaction has been investigated in a few experimental studies. Karnland *et al.* (1995) recommend the kinetic model proposed by Huang *et al.* (1993) for use in evaluating the rate of smectite transformation under environmental conditions that could exist in the near field of a KBS-3 repository. Karnland *et al.* (1995) prefer this model because it is based on data obtained in hydrothermal experiments and because it has been successfully used to explain depth distributions of smectite and illite in natural systems. An alternative model proposed by Pytte (1982) has also been used in several SKB studies (*e.g.*, Pusch and Madsen, 1995).

In the model proposed by Huang *et al.* (1993), the rate of smectite alteration is given by:

$$-\frac{dS}{dt} = A \exp\left(\frac{-E_a}{RT}\right)(K^+)S^2, \tag{8}$$

where S stands for the fraction of smectite relative to smectite + illite, t represents time in seconds, A denotes a frequency factor = 8.08×10^4 liter mol^{-1} sec^{-1}, E_a refers to an activation energy = 28 kcal mol^{-1}, (K^+) indicates molar concentration, and R and T stand for the gas constant and temperature (°K), respectively. Integration of this rate expression at constant temperature results in (Huang *et al.,* 1993):

$$S = \frac{S_0}{\left(1 + S_0(K^+)A\exp\left(\frac{-E_a}{RT}\right)t\right)}, \tag{9}$$

where S_0 stands for the initial smectite fraction at time zero. Thus, for a given temperature and time the availability of K^+ is rate limiting.

Karnland *et al.* (1995) use this model with reasonable K^+ concentrations in typical granite groundwaters and expected temperatures in the KBS-3 near field to show that almost all of the smectite in the buffer would not be converted to illite even after 1 million years of repository evolution. These authors also point out, however, that the model considers changes only in K^+ concentration, whereas other cations are known to be involved in the transformation reaction and may have an accelerating or inhibiting effect on the reaction rate, and that there is some uncertainty in the Arrhenius parameters A and E_a, which may strongly affect the calculated reaction rate.

Chloritization. Smectite is altered to chlorite by incorporation of an additional octahedrally coordinated layer of cations (Mg, Fe) and OH anionic units to the smectite 2:1 framework (Velde, 1992). Chloritization often occurs concomitantly with illite formation, and may thus be a slow process at repository temperatures. Marcos (2003) states that chlorite can replace nontronite or saponite only at temperatures greater than 85°C, and montmorillonite only at temperatures in excess of 300°C. Chlorites, like smectites, have variable compositions, which complicates interpretations of their mutual stability relations.

Properties of H₂O(l) in bentonite porewaters. Liquid water is an important reactant in all the models discussed above, and it is therefore of interest to consider whether its thermodynamic properties are significantly affected by the electrical double layer existing adjacent to smectite surfaces in highly compacted bentonites. The chemical activity of water under such conditions differs only slightly from its activity in bulk solution (*e.g.,* Pedersen, 2000), which suggests that these effects will be relatively small and can probably be ignored. Curti and Wersin (2003) demonstrate that "simple" geochemical models, *i.e.,* those that neglect these effects, can adequately explain trends in the chemistry of clay porewaters over a wide range of solid-liquid ratios.

3.2.2 Interactions with other processes

The thermodynamic stability of smectite depends mainly on temperature, mineral chemistry and porewater chemistry (total pressure, including swelling pressure, will probably have only a minor effect on stability). Thus any process potentially affecting these parameters could influence the mineralogical evolution of the buffer. Such processes include:

- conduction of radiogenic heat through the buffer;

- vaporization of porewater and concentration of solutes in residual liquids during buffer resaturation;

- interaction of smectite with heated water vapor [*e.g.,* so-called "Couture effect" (Couture, 1985; Pusch, 2000);

- contact of the buffer with hyperalkaline pore fluids emanating from concretes and shotcretes that could be used in the repository as grouting materials and plugs;

- dissolution of accessory minerals in bentonite [and ballast minerals in the backfill, which could affect the availability of K^+ in porewaters and thus the illitization rate, (Karnland *et al.,* 1995)];

- changes in the salinity and composition of groundwaters coming into contact with the buffer (*e.g.,* driven by periods of glaciation/deglaciation); and

- diffusion into buffer porewaters of corrosion products from the canister's shell and insert.

Several of these processes are rate-controlled and may be strongly coupled (*e.g.,* heat conduction, ionic diffusion, and mineral dissolution/precipitation).

3.2.3 Reliability of process models

SKB's current modeling strategy for the long-term chemical and mineralogical evolution of the buffer does not seem to explicitly account for the thermodynamic stability of the smectite clays (Bruno *et al.,* 1999). Rather, these minerals are assumed to be stable and to have a fixed, unspecified composition represented by an ion-exchanger phase. The validity of this assumption has been evaluated to some extent in numerous studies carried out by SKB and others examining the effects of heat, accessory minerals and water chemistry on bentonite behavior. Of these, by far the most emphasis has been placed on the rate of smectite illitization.

Process models based on a thermodynamic interpretation of the stability of the smectite clays were developed in early SKB studies by Fritz *et al.* (1984), Fritz and Kam (1985) and Tardy *et al.,* (1987). There seems to have been little application or refinement of these or alternative models in recent years, however. We are unaware of any current or planned work by SKB to develop a robust theoretical basis for assessing the thermodynamic stability of these clay minerals quantitatively and in relation to the range of temperatures and aqueous chemical conditions that could exist in the near field. Such basis would complement SKB's ongoing experimental and natural analogue studies addressing the behavior of bentonite buffer materials over time scales as long as 10^6 years.

3.2.4 Potential impacts on buffer performance

A substantial loss of montmorillonite from buffer materials could adversely affect repository performance because the functional requirements of these barriers are largely determined by their smectite content. Other minerals produced by smectite alteration would almost certainly have inferior physical and rheological properties, but these properties may still allow altered buffer materials to fulfill some functional requirements (*e.g.,* Pusch and Karnland, 1988).

3.3 Bentonite-water interactions during the thermal period

The long-term chemical and mineralogical stability of the buffer could be influenced by a number of processes that are expected to occur during the early resaturation and thermal periods of repository evolution. Radiogenic heat may cause portions of the buffer nearest the canister to partially dry out prior to resaturation with groundwater imbibed from the host rock. Portions of the buffer may thus be exposed to water vapor at relatively high temperatures for an indefinite period of time. Vaporization of water near the wetting front may concentrate solutes in residual liquids and precipitate a variety of minerals and salts. Coupled reactive-transport processes driven by the temperature gradient across the buffer before and after resaturation could result in: 1) mineral dissolution at the hot/cold end of the buffer, 2) solute migration down/up the temperature gradient, and 3) mineral precipitation at the cold/hot end of the buffer.

Key results of selected studies that have been carried out to investigate these processes are briefly summarized below. This is followed by an assessment of implications regarding models of the long-term chemical and mineralogical evolution of the buffer.

3.3.1 Experiments and natural analogues

Pusch *et al.* (1992a, b) carried out field experiments to determine the effects of heating on the physical, chemical and mineralogical properties of buffer materials. Prefabricated blocks containing the French Fo-Ca 7 clay surrounding electrically heated steel tubes were installed in vertical boreholes in the Stripa mine. The heaters were used to maintain a constant temperature at the steel-buffer interface of about 170°C. The temperature at the buffer-host rock interface was about 80°C. The thickness of the buffer was 7.5 cm. The experiments were carried out in two separate boreholes: one for a period of 8 months, the other for about 4 years.

Results from the 4-year test revealed that anhydrite precipitated at the hot end of the buffer, and that this was accompanied by significant dissolution of quartz, feldspar and kaolinite. Bulk chemical analyses of buffer samples also indicated that silica and aluminum increased significantly at the cold end of the buffer. These results were interpreted as follows:

- dissolution of quartz, feldspar and kaolinite at the hot end of the buffer locally increased the concentrations of dissolved silica and aluminum in pore solutions, which caused these solutes to diffuse down the resulting concentration (and temperature) gradient toward the cold end, where amorphous silica and aluminum compounds precipitated onto surfaces of the clays, and

- dissolution of gypsum and feldspars at the cold end of the buffer, and release of Mg from interlayer positions in smectite, locally increased the concentrations of Ca, Mg and sulfate in pore solutions, which caused these solutes to diffuse up the resulting concentration (and temperature) gradient toward the hot end, where anhydrite and possibly hexahydrate precipitated.

A region about 6 to 8 mm thick extending into the buffer from the steel-buffer boundary had been dehydrated as a result of porewater evaporation/condensation and possibly also due to formation of $H_2(g)$ by corrosion of the steel. The ductility and swelling capacity of the clay in this zone were completely lost. The hydraulic conductivity of the zone was also increased by three orders of magnitude relative to the unaltered clay. The entire thickness of the buffer had been cemented by precipitation of silica compounds, and this strongly affected the rheological behavior of the clay. Recent, elemental analyses of the altered buffer show that Al and Fe were preferentially enriched in alteration minerals precipitated at the cold boundary with the host rock, whereas Ca and Mg were enriched in precipitated minerals at the hot end (Pozo *et al.,* 1998).

Cuevas *et al.* (1997) investigated the effects of simultaneous heating and hydration of a natural montmorillonite clay from Almeria, Spain. The clay was uniaxially compacted inside a cylindrical stainless steel cell (diameter = 15 cm; height = 14.6 cm) with an initial dry density of 1.62 g cm^{-3} and initial water content of 11.2%. The cell was equipped with an extraction piston enabling a constant pressure of 60 MPa to be continuously imposed on the clay sample. Deionized water was injected at a pressure of 1 MPa into the sample through 2 hydration ports located in the bottom of the cell. A flat heater was positioned at the top of the cell, where the temperature was fixed at 100°C. A thermal steady state was achieved within 15 hours after heating commenced. Temperatures varied from 100°C at the top of the cell to 65°C at the bottom, corresponding to a linear temperature gradient of 2.8°C/cm. The test lasted for 2619 hours. Key results are: 1) trace amounts of salt impurities were rapidly solubilized and diffused up the temperature gradient, and 2) the distribution of exchangeable cations in the clay was altered with increasing temperature in favor of Mg^{2+} at the expense of Na^+. No discernible changes in the bulk mineralogy of the clay were detected visually and by XRD.

Poinssot *et al.* (1998a) [see also Poinssot *et al.* (1996a,b)] enclosed powdered nuclear waste glass between two layers of argillaceous buffer materials in a sealed gold tube filled with distilled water. The tube was placed in a cold-seal vessel and subjected to a thermal gradient at high temperatures (300-200°C at the hot end, room temperature at the cold end) at 14 MPa for 100 days. The relevance of the results to the present study is difficult to assess due to the presence of glass in the experimental system, but Poinssot *et al.* (1998b) note that trends in elemental mass transfers are similar to those observed in field experiments at Stripa (Pusch *et al.,* 1992a, b; see above). Calcium, S and Mg were taken up in solid phases at the hot end of the system, whereas Fe and Al were concentrated in solids at the cold end.

Karnland *et al.* (2000) examined changes in the chemistry and mineralogy of MX-80 bentonite exposed to relatively high temperatures, moderate temperature gradients and aqueous solutions containing relatively high concentrations of OH$^-$ and K$^+$. Two pilot parcels were evaluated in these experiments. Each parcel consisted of a central heater surrounded by a copper tube, which in turn was surrounded by 40 cylindrical rings of highly compacted bentonite (calculated water-saturated density of 2000 kg m^{-3}). The parcels were placed in vertical boreholes located 450 m below ground level in the Äspö HRL. The lower half of both parcels was equipped with a heater. In one parcel the temperature at the surface of the Cu tube was maintained at 90°C, and the temperature at

the rock surface was 50°C. The corresponding temperatures in the other parcel were fixed at 130° and 80°C. The experiments were terminated after one year, and the parcels were recovered. Examination of the parcels revealed no degradation of the bentonite rings with respect to buffer performance as a result of heating and water saturation. Precipitation of mainly gypsum and uptake of Cu by montmorillonite were observed in portions of the rings exposed to the highest temperatures.

Igneous intrusions in argillaceous rocks provide an additional basis for understanding possible effects of transient heating on the chemical, mineralogical, hydraulic and mechanical properties of buffer materials (*e.g.,* Pusch and Karnland, 1988; Pusch and Madsen, 1995; Gera *et al.,* 1996; Metcalfe and Moore, 1998; Pellegrini *et al.,* 1999). A key result is the observation that the impacts of past heating events are preserved in the rock for long periods of time. Although intrusion-emplacement temperatures are high, cooler zones that are more representative of near-field temperatures can be identified in portions of the preserved alteration halo. At temperatures less than 100°C, changes in the chemical and mineralogical properties of the host rock are minor. More pronounced changes are observed in the mechanical properties of the rock, including its strength, stiffness and plasticity. Increases in the permeability of the rock are also commonly observed, and may result from microcracking or some other subtle change to the rock's microstructure. These changes depend on heating rates, the availability of water and extent of mass transfer between the intrusion and host rock.

3.3.2 Assessment of current understanding

The experimental and natural-analogue studies discussed above suggest that mineralogical changes occurring in the buffer during the thermal period could be important because they may affect key physical properties of this barrier. These changes do not appear to be reversible (*i.e.,* as a result of cooling after the thermal period) over laboratory or geologic time scales, but this possibility cannot be ruled out completely at the present time.

The relevance of some of these studies to the KBS-3 concept may be questionable, however. Most of the studies consider temperatures and temperature gradients that are significantly greater than those likely to exist in the buffer. The spacing between waste packages in a KBS-3 repository is designed specifically to minimize the temperature at the canister-buffer interface such that a maximum of about 85°C is reached about 40 years after deposition, at which time the temperature at the rock-buffer interface is about 55°C (*e.g.,* Karnland *et al.,* 2000). Model calculations also suggest that the thermal gradient across the buffer will dissipate quickly. For example, Karnland *et al.* (2000) estimates that after 100 years the temperature at the canister-buffer interface will be 60°C and the temperature at the rock-buffer interface will be 50°C. The corresponding thermal gradients at 40 years and 100 years, assuming a buffer thickness of 35 cm as in KBS-3, are 0.9°C/cm and 0.3°C/cm, respectively. In contrast, the thermal gradient evaluated in the field experiments of Pusch *et al.*, (1992a,b) was 13°C/cm (for 4 years). The gradient in the experiments described by Cuevas *et al.* (1997) was roughly 3°C/cm (for 0.3 years), with temperatures at the hot and cold ends of their experimental cell near 100° and 65°C. Poinssot *et al.* (1998a) evaluated temperature differences between the hot and cold ends of their experimental apparatus between 300° to 200°C and room temperature. An additional limitation in the experimental

investigations is the limited time over which it is practical to carry out such investigations compared to resaturation times and the duration of the thermal period. Thus the fact that observed changes in mineralogy are small in experiments carried out for one year may not be particularly relevant if the buffer resaturates over a period of hundreds of years. The available experimental data do not permit any definitive conclusions to be drawn concerning the rates and mechanisms of the controlling mineral dissolution/precipitation reactions.

Models capable of simulating the processes involved in buffer cementation under repository relevant time-temperature conditions could help overcome some of these limitations. The authors are aware of only two SKB studies that are peripherally related to this subject, however (Pusch *et al.,* 1998; Arcos *et al.*, 2000).

4 Conclusions

SKB's model of the chemical and mineralogical evolution of the KBS-3 buffer apparently includes the following processes (SKB 2004):

- diffusive transport in the buffer

- diffusive and advective transport in the backfill

- diffusive and advective transport in the host rock,

- precipitation-dissolution of accessory minerals in bentonite and host rock,

- precipitation-dissolution of secondary minerals in bentonite and host rock,

- cation exchange in bentonite

- surface acidity of smectite

- corrosion of the canister's iron insert, and

- thermal gradient.

The model at present apparently assumes that all chemical and thermodynamic properties of smectite (*i.e.,* montmorillonite) need not be considered explicitly. Rather, ion-exchange and surface-complexation reactions involving this mineral will be modeled using the approaches described by Bruno *et al.* (1999), Wieland *et al.* (1994) and Wanner *et al.* (1992). Transformation of smectite to less-expandable minerals will be modeled using a kinetic expression and a transport model for dissolved silica.

The following comments are based on the assumption that long-term mineralogical changes in the buffer could adversely affect the assigned isolation functions and properties of this barrier noted in Section 1. These perspectives are based, to a significant degree, on the quantitative relationships between these properties and the mineralogy of bentonite barriers as described by Pusch (1996). Based on the detailed discussions in Section 3, we believe SKB's current approach may have three issues requiring re-evaluation for their successful resolution:

1. SKB's ion-exchange and surface-complexation models do not account for possible changes in the composition of smectite resulting from ionic substitutions on octahedral and tetrahedral sites in the crystalline lattice. There is abundant evidence from natural geological systems that such reactions do occur over time scales that are relevant to the assessment period for a KBS-3 repository ($\approx 10^6$ years). The mechanisms and rates of these reactions are not well studied, nor are associated impacts on the buffer's physical and rheological properties well known. The absence of, and difficulty in collecting, such information is not a valid or adequate reason for excluding the possibility that such reactions could occur, however. In

view of the observations and analyses presented here, we believe there is a need for SKB to more fully defend and document its approach as being (1) comprehensive, realistic and testable, or (2) credibly bounding with respect to providing assurance that assigned isolation functions and properties of the buffer will be maintained over repository-relevant time scales. Any plans by SKB to evaluate and/or implement additional models accounting for long-term substitution reactions in smectites should also be identified.

2. SKB apparently believe that the thermodynamic behavior of the smectite clays can be handled with the bounding assumption that either smectite is stable, or, if not, that it alters to a less expandable mineral at a predictable rate. This assumption is an oversimplification from a purely scientific point of view because it obviates the need for *understanding* the specific conditions of smectite stability/instability in relation to evolving geochemical conditions in the near field and far field. Furthermore, the current SKB approach may overemphasize the importance of accessory minerals and surface reactions in controlling the long-term chemical evolution of these barriers. Early SKB studies focused on the equilibrium thermodynamics of smectite solid-solutions, but this work now seems to have been abandoned. An explanation and defense of this change is needed.

3. The current SKB approach may be overly simplistic for application to the thermal period of repository evolution because it ignores potentially important and irreversible changes in the chemistry and thermodynamic stability of the smectite clays. Thermal effects on dissolution-transport-precipitation processes apparently will be considered for a few mineral "impurities" in the buffer, but it is unclear whether confirmatory analyses will be carried out to demonstrate the defensibility, or bounding nature, of this approach.

Recommendations that we believe could be used to help address these potential areas of concern have been discussed in this report. These recommendations may provide a starting point for the further exchange of views and information between SKI and SKB.

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