

Long-term stability of clay minerals in the buffer and backfill

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Executive summary

Clay-based buffer and tunnel backfill materials are important engineered barriers in the KBS-3 repository concept for final disposal of spent nuclear fuel in Finland. One process relevant to buffer performance in a safety assessment context is that of clay mineral transformations and long-term stability with respect to the following:

- cementation due to precipitation of quartz and/or other minerals (including amorphous silica) in bentonite due to the effect of temperature;
- montmorillonite-groundwater interactions;
- cement-bentonite interaction (high pH waters); and
- iron-bentonite interaction.

The present study considers evidence for a number of related issues, namely:

- the applicability of thermodynamic concepts for evaluation of the long-term stability of bentonites;
- evidence for clay stability in Olkiluoto groundwaters; and
- clay stability in fluids from cementitious and silica-rich grouts.

Study results suggest that the thermodynamic approach is problematic for a number of reasons stemming from the compositional variability of the dominant smectitic clay minerals in bentonites. Taking into account additional limitations inherent in complementary experimental or analogue (natural/anthropogenic) methods suggests that uncertainties in predictions of the long-term stability of bentonite could be non-trivial and should be bounded to the extent possible.

The limitations in the thermodynamic approach can be addressed to some extent using simplifying assumptions and approximations. If these can be justified, the approach provides a basis for gaining insights concerning the long-term behaviour of buffer and backfill materials. The following observations were suggested by using the approach in the present study, for example.

- The common assumption that smectite stability can be defined in terms of a simple pH threshold (e.g., $\text{pH} < 11$) may not be valid and is inconsistent with thermodynamic principles governing phase stability. Such stability should instead be evaluated in terms of temperature, pressure and the activities of all aqueous species (and, if necessary and appropriate, components of clay mineral solid solutions) involved in corresponding hydrolysis reactions.
- Groundwaters from depth at Olkiluoto could be compatible with the long-term stability of montmorillonites, beidellites, and/or saponite clays in bentonite barriers at ambient temperatures. Reactions between these minerals and calcite may control cation ratios, pH and PCO_2 in the rock-groundwater system.

- A sequence of C-A-S-H type minerals and zeolites may form at interfaces between bentonites and cementitious repository materials. In fractured hard rock such as that at Olkiluoto, gradients in dissolved Al and Si may lead to the conversion of C-S-H gel in the cement/concrete to saponitic clays.
- The presence of silica-rich grouts in the rock-groundwater system may serve to help stabilise montmorillonite in bentonite by increasing the activity of dissolved silica in groundwater to that of amorphous silica solubility, which would tend to stabilise montmorillonite relative to other minerals such as illite.

ARTHUR Randy (Intera Inc.), SAVAGE David (Savage Earth Associates Limited). Savimineraalien pitkäaikaispysyvyys loppusijoituksen puskurissa ja tunnelintäytössä. STUK-TR 22. Helsinki 2016. 30 s.

Avainsanat: pitkäaikaispysyvyys, savimineraali, puskur, tunnelintäyttö, käytetty ydinpolttoaine, loppusijoitus, KBS-3-konsepti

Tiivistelmä

Savipohjainen puskur ja tunnelintäyttö ovat tärkeitä teknisiä vapautumisesteitä suomalaisen käytetyn ydinpolttoaineen loppusijoitukseen soveltuvassa KBS-3-konseptissa. Eräät puskurin toimintakyvyn, ja siten myös loppusijoituksen turvallisuuden, arvioimisen kannalta merkitykselliset prosessit liittyvät saven mineralogiseen muuntumiseen ja pitkäaikaispysyvyyteen:

- kvartsin ja/tai muiden bentoniitin sisältämien mineraalien (ml. amorfisen silikan) aiheuttama sementoituminen lämpötilan vaikutuksesta;
- montmorillonitiin ja pohjaveden vuorovaikutukset;
- sementin (korkeaemäksiset vesiliuokset) ja bentoniitin vuorovaikutus; ja
- raudan ja bentoniitin vuorovaikutus.

Tässä selvityksessä tarkastellaan myös seuraavia tutkimuskysymyksiä:

- termodynaamisten konseptien soveltuvuus bentoniittien pitkäaikaispysyvyyden arvioimiseen;
- saven pysyvyyden osoittaminen Olkiluodon pohjavesiolosuhteissa; ja
- saven pysyvyys sementtisistä ja runsassilikaisista injektointiaineista peräisin olevissa vesiliuoksissa.

Selvityksen tulokset viittaavat termodynaamisen lähestymistavan ongelmallisuuteen, johon syynä on bentoniittien valtaosin sisältämien paisuvahilaisten smektiittisavimineraalien koostumuksen vaihtelevuus. Ottamalla huomioon myös täydentäviin kokeellisiin menetelmiin ja analogioihin (luonnossa esiintyvät/ihmisperäiset) sisältyvät rajoitteet voidaan saada viitteitä siitä, että bentoniitin pitkäaikaispysyvyyden ennakoimiseen liittyvät epävarmuudet eivät suinkaan ole vähäpätöisiä; tästä syystä näiden epävarmuuksien suuruus tulisikin arvioida mahdollisuuksien mukaan.

Termodynaamisen lähestymistavan rajoitteita voidaan tarkastella yksinkertaistavien oletusten ja approksimaatioiden avulla. Näiden ollessa perusteltuja voidaan lähestymistavan avulla muodostaa käsitys puskur- ja tunnelintäyttömateriaalien pitkäaikaiskäyttämisenestä. Työssä käytetyllä lähestymistavalla havaittiin mm. seuraavaa:

- Varsin yleinen oletus, että smektiittisaven pysyvyys voidaan määritellä yksinkertaisen pH-kynnyksen (esim. $\text{pH} < 11$) avulla, ei välttämättä ole hyvin perusteltu ja voi olla ristiriidassa mineraalifaasien pysyvyyttä säätelevän termodynamiikan kanssa. Tätä pysyvyyttä tulisi sen sijaan arvioida lämpötilan, paineen ja kaikkien hydrolyysireaktioihin osallistuvien kemiallisten vesiosasläjien (ja tarvittaessa ja mikäli tarkoituksenmukaista, savimineraalin kiinteän liuoksen komponenttien) avulla.

- Olkiluodon syvien pohjavesien koostumus saattaa loppusijoituksen lämpötiloissa olla yhdenmukainen bentoniittipohjaisten vapautumisesteiden sisältämien montmorilloniittien, beidelliittien ja/tai saponiittisavien pitkäaikaispysyvyyden kanssa. Näiden mineraalien ja kalsiitin väliset reaktiot voivat säädellä kallio-pohjavesisysteemin kationisuhteita, pH:ta ja hiilidioksidin osapainetta.
- C-A-S-H-tyyppisten mineraalien ja zeoliittien on mahdollista muodostua bentoniitin ja sementtisten loppusijoitusmateriaalien rajapinnassa. Liukoisen alumiinin ja silikan gradientit voivat Olkiluodon rakoilleessa kallioperässä aiheuttaa sementin/betonin sisältämän C-S-H-geelin muuntumisen saponiittisiksi saviksi.
- Runsassilikaiset injektioaineet voivat tehdä bentoniitin sisältämän montmorilloniitin epästabiiliksi kallio-pohjavesisysteemissä kasvattamalla pohjaveteen liunneen silikan aktiivisuutta suhteessa amorfisen silikan liukoisuuteen. Tämä pyrkii stabiloimaan montmorilloniitin muihin mineraaleihin, kuten illiittiin, nähden.

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1 Introduction

Clay-based buffer and tunnel backfill materials are important barriers in the KBS-3 repository concept for final disposal of spent nuclear fuel in Sweden and Finland (Figure 1). A key issue in the use of these materials concerns their evolution from the initial state towards the defined target state. One process relevant for buffer performance from a safety assessment perspective is that of clay mineral transformations and long-term stability with respect to the following (Posiva, 2010, p363):

- cementation due to precipitation of quartz and/or other minerals (including amorphous silica) in bentonite due to the effect of temperature;
- montmorillonite-groundwater interactions;
- cement-bentonite interaction (high pH waters); and
- iron-bentonite interaction.

Smectites can be stable over geological time periods in some environments, but may also be destabilised by certain chemical conditions and by increased temperature. For example, the transformation to illite has been of considerable interest to waste disposal agencies for a number of years (e.g. Nagra, 1994). For this transformation process to occur, both an increase in layer charge and the availability of potassium are required (e.g., Karnland and Birgersson, 2006). Moreover, the activity of silica and a precipitation rate of SiO_2 affect illitisation. The reaction mechanism, which depends on many variables, is still under debate and a number of kinetic models exist (e.g. Meunier and Velde, 2004). At temperatures below 100°C , this reaction is slow and it has been suggested that for KBS-3-type conditions, only negligible amounts of montmorillonite can be

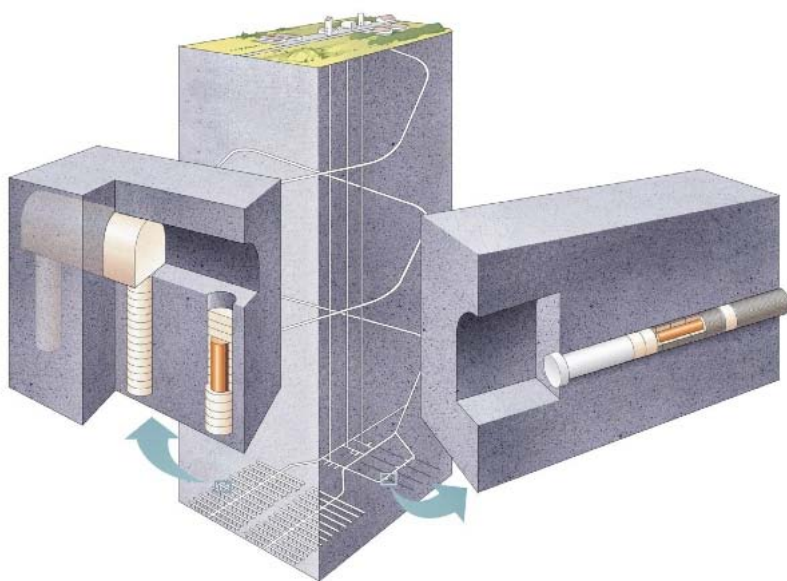


Figure 1 The KBS-3 concept for the geological disposal of spent fuel, highlighting the presence of clays in buffer and tunnel backfill (from SKB, 2011).

transformed (e.g. Karnland and Birgersson, 2006). However, in the case of Fe(III)-containing smectites, recent experimental evidence indicates that transformation rates can be accelerated significantly by the participation of microbes (e.g., Meleshyn, 2011; Dong, 2012).

Clay mineral stability will be affected by environmental variables. Groundwater chemistry may vary during the lifetime of the repository, for example, and understanding is needed on how changes in composition will affect the long-term stability of montmorillonite (Posiva, 2010, p. 370). Although alteration of a Na-type montmorillonite to a Ca-type montmorillonite via cation exchange may be important (e.g. Sena et al., 2011), there is potential also for conversion of montmorillonite to other smectites, illite, or to other non-swelling sheet silicates or zeolites.

Clay mineral stability may also be affected by other repository materials. The degradation of cement grouts and concretes, for example, may produce a highly alkaline leachate which can be reactive towards aluminosilicate minerals such as montmorillonite. The associated long-term safety concerns include a loss of bentonite swelling pressure, increased hydraulic conductivity, and possibly fracturing of the buffer due to cementation (Posiva, 2010, p371). Reactive transport model calculations carried out for the KBS-3V concept imply limited MX-80 bentonite alteration in a deposition hole intersected by a rock fracture that conducts a mixture of alkaline cementitious fluid and groundwater (Lehikoinen, 2009).

Approaches that could be used to evaluate the stability of clay-based buffer and backfill materials in relation to such changes in environmental conditions must account for time scales that are relevant to repository safety assessments (~100 ka or longer). Direct experimental approaches may not be feasible because the rates of key reactions tend to be too slow to have a detectable impact on system evolution over periods of time that are experimentally accessible (Savage et al., 2011). Attempts to accelerate the rates by increasing temperature or increasing

the reactive surface areas of solid reactants may inadvertently cause other reactions to occur that are not realistic for repository environments. Inferences drawn from observations of natural systems that may be analogous in certain respects to buffer materials that have evolved over many thousands of years may be complicated by uncertainties in initial and boundary conditions controlling the evolution of the natural systems. Interpretations based on observations of anthropogenic systems are subject to similar uncertainties, and relate to periods of time that are a small fraction of the total time over which the buffer and backfill are expected to fulfill their functional requirements.

For many of these reasons, an alternative, thermodynamic approach has been used in studies of natural systems, many of which also tend to evolve slowly even over geological time scales (e.g., Garrels and Christ, 1965). The approach is based on experimentally-determined standard thermodynamic properties for minerals, gases, aqueous species and reactions, and uses these properties together with phase-equilibrium constraints to construct phase diagrams depicting the stability (or metastability) fields of minerals and an aqueous phase in various chemical sub-systems at given pressures and temperatures. A distinct advantage of this approach is that mineral stabilities can be readily evaluated in relation to specific environmental conditions, such as the bulk compositions of groundwaters and bentonite pore waters.

This report considers the stability of buffer and backfill materials in a KBS-3 repository at Olkiluoto using equilibrium constraints as a guide to expected long-term behaviour. The report discusses evidence for a number of the issues noted above, namely:

- applicability of the thermodynamic approach to buffer and backfill materials (Section 2);
- evidence for clay stability in Olkiluoto groundwaters (Section 3); and
- clay stability in fluids from cementitious and silica-rich grouts (Section 4).

Some conclusions are drawn in Section 5.

2 Thermodynamic constraints on clay mineral stability

The buffer and backfill are chemical systems in a thermodynamic sense and, like all such systems, will tend to approach a state of equilibrium with the surrounding environment. An equilibrium state is one in which the chemical potentials of all system components are equal in all phases (e.g., Anderson and Crerar, 1993). Once achieved, a system at equilibrium will remain at equilibrium indefinitely, or until changes occur in pressure, temperature and/or component concentrations. Equilibrium concepts can be used to define the stable mineralogical composition of any chemical system, and could thus provide a useful framework for interpreting the long-term stability of the clay minerals in bentonite buffer and backfill materials.

Such a thermodynamic approach has long been used to identify environmental conditions favouring clay mineral stability in natural systems (e.g., Tardy et al., 1987). It has not been applied for a similar purpose to conditions that could exist in the near field of a KBS-3 repository in Scandinavia, however. Laine and Karttunen (2010) evaluated the long-term stability of bentonites in a KBS-3 repository at Olkiluoto in Finland based on a literature review of laboratory experiments and field-based investigations of bentonites in natural systems. Equilibrium constraints based on specifics concerning buffer and backfill mineralogical composition and the likely compositions of Olkiluoto groundwaters and bentonite porewaters were not considered, however.

This section considers whether such a thermodynamic approach could be used to help support evaluations of the long-term stability of the swelling clay minerals (i.e., smectites) in bentonite. Complications in applying equilibrium concepts to these minerals are summarized in Section 2.1. Section 2.2 considers how these complications can be addressed using simplifying assumptions, and includes discussion of an example illustrating how the long-term

stability of smectite in MX-80 bentonite can be interpreted using phase diagrams. This general approach is extended in Section 3 to an evaluation of smectite stability specifically in relation to representative groundwaters from Olkiluoto, and in Section 4 in relation to the chemistry of leachates from cementitious and siliceous grouting materials.

2.1 Complications in applying phase-equilibrium concepts to smectites

Phase diagrams provide a convenient visual basis for the consideration of complex stability relations among minerals and an aqueous phase in geochemical systems. Three simplifying assumptions must be valid in order to use such diagrams (Langmuir, 1997):

- all minerals are pure and fixed in composition;
- equilibrium can be attained among all phases; and
- accurate thermodynamic data are available for all relevant minerals, aqueous species and gases.

For reasons discussed below, the validity of all these assumptions for smectite-bearing systems is problematic.

2.1.1 Compositional variability

Smectites display a wide range of compositions in natural systems (e.g. Velde, 1992; Emmerich et al., 2009). Three groups of dioctahedral smectites have been classified based on their Al^{3+} and Fe^{3+} contents¹. Aluminous varieties include beidellites and montmorillonites. Nontronites contain relatively high concentrations of Fe^{3+} . A complete solid-solution

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

compositional range exists between the nontronites and beidellites, and a significant, but incomplete, compositional range exists between the montmorillonites and beidellites. Trioctahedral smectites, which are also swelling clays, include saponites and stevensites. Saponites are aluminous phases, whereas stevensites contain essentially no Al^{3+} .

The variable chemistry 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 2). Ionic substitutions in the octahedral and tetrahedral layers result in a net negative charge on the 2:1 framework (i.e., the layer charge), which is compensated by hydrated cations occupying interlayer positions (e.g., Grim, 1968). The layer 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). Layer charge in dioctahedral smectites can vary from about 0.2 to 0.6 equivalents per 2:1 unit of $\text{O}_{10}(\text{OH})_2$ anionic charge. Charge compensating cations occupying the interlayer sites typically include Na^+ , Ca^{2+} , Mg^{2+} and K^+ .

2.1.2 Attainment of equilibrium

Two models have been used to account for the effects of compositional variability on the thermodynamic stability of smectites. Both models are based on the assumption that equilibrium can be

attained between smectite, other minerals and an aqueous phase.

Stoichiometric models assume that smectites have a fixed and well defined composition, and that congruent dissolution results in the release of the mineral's elemental constituents in stoichiometric proportions (e.g., Garrels, 1984; Tardy et al., 1987; Aja et al., 1991a;b; Aja, 1995). Although this may be unrealistic for the reasons noted above, conventional phase diagrams can be used to assess the thermodynamic stability of a given, representative smectite composition relative to other clay and non-clay minerals. 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 closely associated minerals (e.g., zeolites).

Solid-solution models treat the compositional variability of smectites in terms of changes in the activities of model components. Two solid-solution models have been proposed. They differ depending on whether component activities are assumed to be controlled by ideal mixing of end-member components (Tardy and Fritz, 1981; Fritz, 1985; Bourcier, 1985; Tardy et al., 1987) or by ideal site mixing of individual atoms occupying the clay mineral's interlayer, octahedral and tetrahedral sites (Aagaard and Helgeson, 1983; Giggenbach, 1985). The latter models assume random mixing and equal interaction among the atoms occupying energetically equivalent sites and exchange of atoms between energetically distinct sites. Calculated component activities can then be used as descriptive

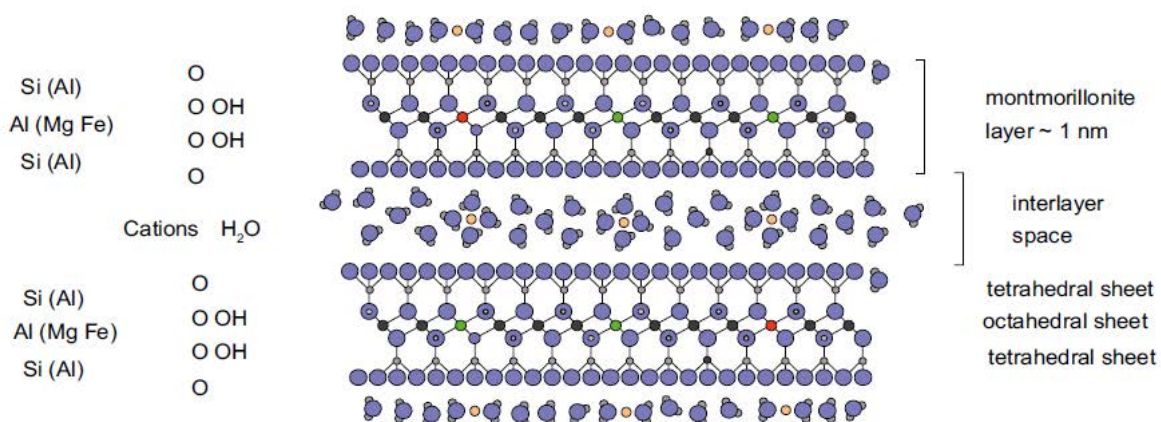


Figure 2 Schematic diagram showing the arrangement of tetrahedral and octahedral sheets in smectite (montmorillonite), and the distribution of interlayer cations and water molecules (Karnland, 2010).

variables enabling the stability fields of smectite solid solutions to be displayed on conventional phase diagrams (e.g., Aagaard and Helgeson, 1983; Arthur and Wang, 2000). Solid-solution models have not been widely used in studies of smectite-bearing systems because the thermodynamic properties of model components may not be known and because tests of the accuracy of model predictions may require detailed characterization of small changes in the compositions of individual smectite grains.

The underlying assumption in both these modelling approaches that smectites can attain equilibrium is controversial. Reversible solubilities have been determined experimentally at 25°C for fixed-composition clay minerals such as kaolinite, allophane and halloysite (e.g., May et al., 1986; Steefel and Van Cappellen, 1990). Lippmann (1979; 1982) and May et al. (1986), however, questioned whether similar equilibria can ever be demonstrated unequivocally for more complex variable-composition clay minerals such as smectites and illites. Aja et al. (1991a;b) and Aja and Rosenberg (1992) have since provided experimental evidence purporting to show that reversible solubility equilibria by smectite/illite mixed layers can be attained at low temperatures. The validity of this interpretation was questioned by Essene and Peacor (1995; 1997), however. These conflicting views suggest that the common occurrence of smectites in natural systems may be controlled by kinetic as well as thermodynamic factors (Langmuir, 1997). Tardy et al. (1987), for example, noted that because the rates of transformation from metastable to stable smectite compositions are apparently very slow at low temperatures suggests that differences in the corresponding Gibbs free energies of formation for these minerals are very small.

2.1.3 Thermodynamic data

Application of either the stoichiometric or solid-solution modelling approaches is complicated because the experimental data needed to retrieve fundamental thermodynamic properties for representative smectite compositions, or for end-member model components, are limited. These properties include, at the reference pressure (1 bar) and temperature (25°C), standard Gibbs free energies and enthalpies of formation (ΔG_f° and ΔH_f° , respectively), standard entropies (S°), and temperature-independent coefficients that can be used in an empirical expression

to calculate standard isobaric heat capacities as a function of temperature [$C_p^\circ(T)$]. These standard properties can be used to calculate the values of equilibrium constants (K) for any reaction as a function of temperature and pressure

Experimental techniques to determine these properties must contend with a number of potential difficulties. For example, solubility measurements, which can be used to retrieve ΔG_f° values, may be deficient because (May et al., 1986):

- attainment of equilibrium was not demonstrated due to inappropriate extrapolations of solution chemistry over time, or to a failure to approach equilibrium from both oversaturation and undersaturation;
- inappropriate analytical measures were used (e.g., to distinguish between aqueous and particulate forms of sparingly soluble elements such as Al or Fe);
- acidified solutions were used that may be incompatible with conditions of smectite stability;
- other possible phases that may have formed as a result of smectite dissolution were not accounted for; and/or
- the distribution of cations among exchange, octahedral; or tetrahedral sites was not accurately determined.

Also, although it may be assumed that the composition of a smectite does not vary during a solubility experiment, this is not necessarily true and is rarely confirmed by direct analysis both before and after an experiment (Tardy and Garrels, 1974). The use of calorimetric methods to determine $C_p^\circ(T)$ and S° is complicated by impurities that are difficult to remove completely from natural samples of clay minerals. Contributions from the impurities must be subtracted from measured heat capacities in order to determine C_p° values for natural smectites (Gailhanou et al., 2007). Interpretations of phase-equilibrium constraints on ΔG_f° that could be inferred from observations of natural clay-bearing systems are complicated by uncertainties in the compositions of the clay minerals and co-existing aqueous solutions, and by uncertainties concerning whether these phases attained equilibrium (Helgeson et al., 1978).

Given these experimental difficulties, various techniques have been developed and used to estimate the thermodynamic properties of smectites

and other clay minerals. All are based on the assumption that the thermodynamic properties of silicate minerals can be approximated in terms of the sum of the corresponding properties of oxide and/or hydroxide components of the constituent cations (Hazen, 1988).

The estimation techniques can be divided into two main groups. In one, ΔG_f° (and/or ΔH_f°) values are estimated by summing the contributions of each component as it exists in the silicate matrix. Linear regression techniques are used to quantify the free energy contribution of each component to the ΔG_f° of the mineral (e.g., Karpov and Kashik, 1968; Tardy and Garrels, 1974; Chermak and Rimstidt, 1989).

The other group of estimation techniques uses solid hydroxides (i.e., not in the silicate matrix) as model components (Nriagu, 1975; Chen, 1975; Matigod and Sposito, 1978; Sposito, 1986; Arthur et al., 2011; 2012). These approaches have the advantage of being based on a reliable set of calorimetric ΔG_f° values for model components, but a correction factor must be determined empirically using linear regression techniques to account for additional contributions to the ΔG_f° of a silicate due to the effects of changes in the coordination environment of exchangeable cations as they are conceptually transferred from a component to exchange sites in the mineral. These contributions may be parameterized in terms of the charge and/or crystallographic ionic radius of the exchangeable cations (e.g., Sposito, 1986).

The regression procedures used in both these types of estimation techniques are based on a calibration dataset of reliable, and preferably experimentally determined, ΔG_f° values. The available data are quite limited, however, due to the experimental difficulties discussed above. Standard errors in the regressions therefore tend to be strongly correlated and do not provide a reliable basis for quantifying the uncertainty in estimates for minerals outside the calibration dataset. A guide to the overall uncertainty may be suggested by the level of disagreement between predicted and experimentally determined ΔG_f° values for minerals not included in the calibration dataset.

2.2 Interpretations of clay mineral stability using phase diagrams

The potential complications in applying phase-equilibrium concepts to clay minerals can be addressed

to some extent using simplifying assumptions and approximations. The estimation techniques discussed above have been shown to be capable of providing reasonably accurate estimates of standard thermodynamic properties for clay minerals and closely associated phases (e.g., zeolites). These properties can be used to calculate corresponding values of equilibrium constants for hydrolysis reactions over a range of relevant temperatures and pressures. The equilibrium constants can be used to construct phase diagrams showing environmental conditions over which a given clay mineral would be stable. Computer programs, such as the Geochemist's Workbench (GWB; Bethke, 2008), can be used to quickly construct such diagrams for any stable, or metastable, configuration of a chemical system. This flexibility can be used to systematically evaluate the effects of alternative assumptions on mineral stability. An example illustrating how such an approach could be applied specifically to the clay minerals in MX-80 bentonite is discussed in the following section.

2.2.1 Example: Effect of pH < 11 grouts on the stability of MX-80 bentonite

This example considers whether the smectite in MX-80 bentonite would be stable if the buffer in a KBS-3 repository at Olkiluoto were to come into contact with leachates produced by the interaction of groundwater with low-pH grouts. Results can be used to evaluate the hypothesis that such materials would not affect the stability of clay minerals in bentonite as long as the leachate pH remains below a threshold value of 11 (e.g., Pusch and Ramqvist, 2007; SKB, 2011, p397).

Thermodynamic database

The phase-equilibrium approach requires log K values for all relevant reactions. A thermodynamic database permitting calculation of such values was selected for use in this example (Arthur et al., 1999). The database is compatible with the SUPCRT model and software (Johnson et al., 1992). For minerals and gases, it includes standard Gibbs free energies and enthalpies of formation, standard entropies and volumes, and temperature-independent Maier-Kelley heat capacity coefficients at the reference temperature (25°C) and pressure (1 bar). For aqueous species, the database includes standard partial molal Gibbs free energies and

enthalpies of formation, standard partial molal entropies, and Helgeson, Kirkham and Flowers (HKF) equation-of-state coefficients at the reference pressure and temperature. The database includes these properties for 265 minerals, 1147 aqueous species and 16 gases.

Arthur et al. (2012) revised this database to include estimated or re-calculated standard properties for a range of representative compositions of zeolites, clay minerals, and cement hydrates. For clay minerals and zeolites, these properties were estimated using the so-called polymer model (Arthur et al., 2011). Adjustable model parameters were calibrated using experimental constraints on the ion-exchange properties of four montmorillonites. Additivity and structural analogue algorithms for 2:1 phyllosilicates were developed and used to estimate S° and $C_p^\circ(T)$ values for 26 smectites. The algorithms were constrained by $C_p^\circ(T)$ and S° values determined in a calorimetric investigation of an anhydrous smectite purified from MX-80 bentonite (Gailhanou et al., 2007). The estimated S° values for each of the 26 smectites were used with the Gibbs-Helmholtz relation and ΔG_f° estimates to calculate values of ΔH_f° at 25°C and 1 bar. The estimated ΔG_f° values averaged within $\pm 0.24\%$ of 18 experimental counterparts, all but one of which was retrieved from measured solubilities. The model also produced reasonably accurate estimates of ΔG_f° for illites based on a limited number of possible comparisons between experimental and estimated values.

Leachate data

Three leachates produced in an experimental study of low-pH grouting materials were considered (Vuorinen et al., 2005). The experiments were carried out at 25°C, which is slightly higher than temperatures expected in the near field at Olkiluoto after the effects of radiogenic heating have dissipated. The leachates were produced in experiments in which a low-pH mix, referred to as ‘w1’, was used. This mix included Egyptian white cement [similar to Ordinary Portland Cement (OPC)] and silica fume as binder materials. The leachates were produced using an equilibrium test method or a diffusion test method. In the equilibrium tests, a portion of the leach solution was extracted periodically and replaced with fresh leach solution. In the diffusion tests, the entire leachate volume was replaced

Table 1. Compositions of three low-pH cement leachates from the experiments of Vuorinen et al. (2005). Analytical data are in mg/l unless stated.

	Diffusion	Equilibrium dilute	Equilibrium saline
pH	10.86	11.21	10.14
Alkalinity		2.05	0.73
Na	35	54	4 800
K	5.5	19	52
Ca	8.1	24	4 300
Mg	0.06	< 0.1	2.0
Si	7.4	24	7.6
Al	< 1	< 2	< 10
S	4.0	7.7	9.6
SO ₄	16	24	29
Cl	66	56	13 300
Fe	< 0.05	< 0.1	< 0.1

at each exchange time. Two leach solutions were used in these experiments to represent dilute or saline groundwater. The total amount of leachate exchanged was 720 ml in a diffusion test with dilute leach solution (final pH = 10.9), and 78 ml in equilibrium tests involving both dilute and saline leach solutions (final pH = 11.2 and 10.1, respectively). The compositions of the three leachates are reproduced here as Table 1.

Results

Phase diagrams were constructed for the Na₂O-K₂O-CaO-MgO-FeO-Fe₂O₃-CO₂-HCl-H₂O system at 25°C and 1 bar pressure. The activity of SiO₂(aq) and the ratio of $a_{\text{Al(OH)}_4^-}$ to a_{OH^-} were adopted as diagram variables because Si and Al are the primary cationic constituents of all smectites. The aqueous speciation of the leachates analysed by Vuorinen et al. (2005) was initially calculated using the ‘SP8’ module in GWB and the thermodynamic database described above. The calculated activities of HCO₃⁻, Na⁺, K⁺, Ca²⁺, Mg²⁺ and Fe²⁺ were used with the ‘ACT’ module in GWB to construct the phase diagrams. Calculated values of $\log a_{\text{SiO}_2(\text{aq})}$ and $\log (a_{\text{Al(OH)}_4^-}/a_{\text{OH}^-})$ for each leachate were displayed on the diagrams by symbols. Equilibrium is indicated if a symbol plots within a mineral’s stability field, or along lines representing boundaries with other minerals. Minerals that were predicted to be stable, but which may not form at low temperatures for kinetic reasons, were excluded from consideration

(e.g., micas, feldspars). This assumption was also adopted for other diagrams considered elsewhere in this report.

The phase diagrams in Figure 3 show mineral stabilities for the cement leachate from the diffusion experiment (Table 1). The diagrams were drawn assuming MX-80 montmorillonite exists both metastably with respect to Na-, K-, Mg- and Ca-beidellites and illite (left-hand Figure) and also assuming that beidellites could form (right-hand Figure). The left-hand Figure shows that this montmorillonite would not be stable relative to scolecite (a zeolite) ± saponite in solutions leached from low-pH grouts. This suggests that pH values lower than a threshold value of about 11 may not be sufficient to stabilise the montmorillonite in MX-80 bentonite and prevent alteration of these swelling clay minerals to non-swelling zeolites.

The right-hand Figure of Figure 3 indicates that beidellites could replace MX-80 montmorillonite, but would still be unstable relative to scolecite. Beidellites would be stable in the saline leachates, however. Although beidellites are also swelling

clay minerals, their formation is a potential safety concern because they are believed to be more susceptible to illitization than montmorillonites (Pusch, 1999), and because illite is a non-swelling clay mineral whose formation could adversely impact buffer and backfill performance. Because beidellization of montmorillonite would involve primarily isomorphous substitution reactions on tetrahedral sites in these clay minerals, the rates of beidellization and illitization may be comparable.

Similar results are also seen for the results of the leachates from the equilibrium dilute test (Figure 4) and equilibrium saline test (Figure 5) carried out by Vuorinen et al. (2005).

These results suggest that MX-80 montmorillonite, and other smectites in general, may not be stable in the presence of leachates derived from low-pH grouts and could be altered to non-swelling phases such as zeolites. The assumption that smectite stability can be defined in terms of a simple pH threshold (e.g., $\text{pH} < 11$) may not be valid and is not compatible with thermodynamic constraints governing phase stability.

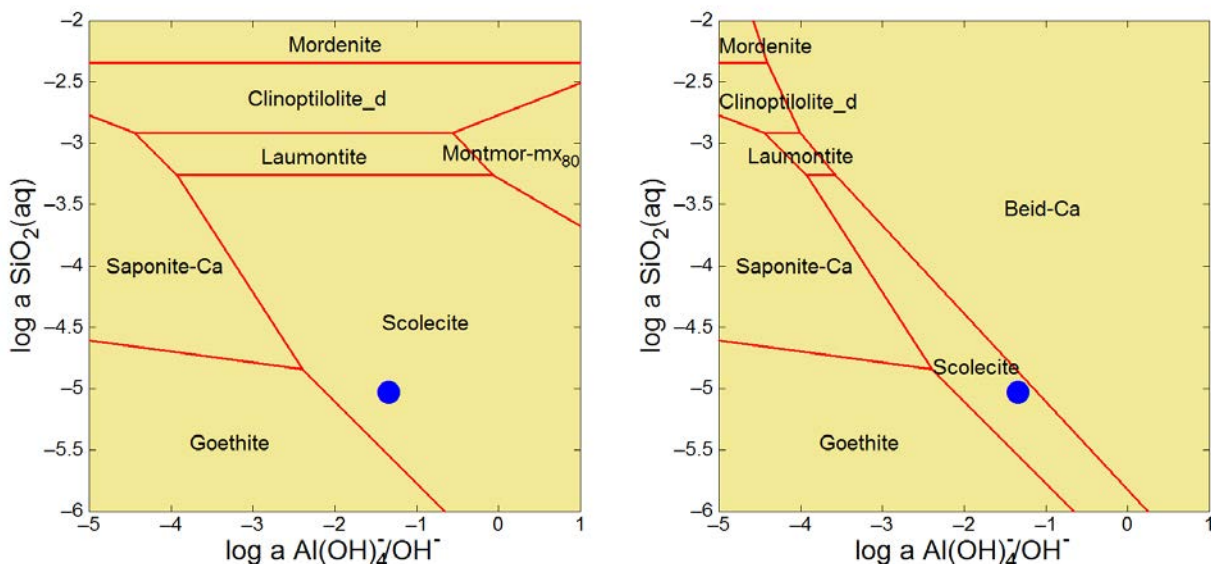


Figure 3 Phase diagrams for the cement leachate from the diffusion experiment of Vuorinen et al. (2005) at 25°C. Beidellites were assumed not to form in the left-hand Figure, but were included in the right-hand Figure. Filled symbols represent chemical conditions as defined by the leachate composition shown in Table 1. The descriptor ‘_d’ refers to a representative composition of clinoptilolite in low-temperature diagenetic systems (Chipera and Apps, 2001). A GWB-compatible database from Arthur et al. (2012) was used to construct the diagrams.

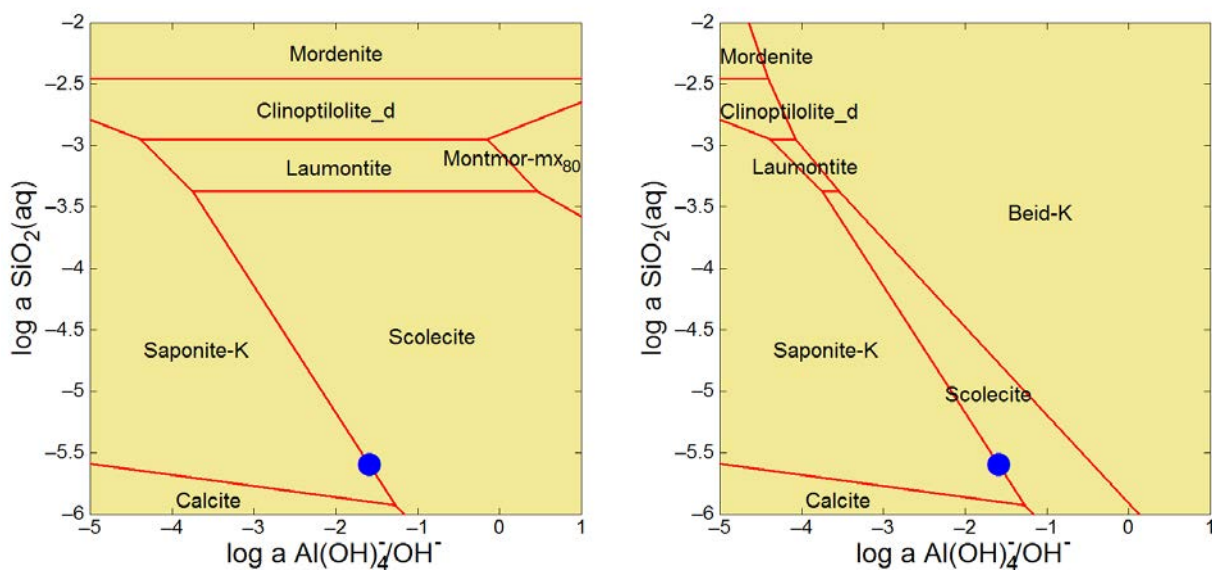


Figure 4 Phase diagrams for the cement leachate from the dilute equilibrium experiment of Vuorinen et al. (2005) at 25°C. Beidellites were assumed not to form in the left-hand Figure, but were included in the right-hand Figure. Filled symbols represent chemical conditions as defined by the leachate composition shown in Table 1. The descriptor 'd' refers to a representative composition of clinoptilolite in low-temperature diagenetic systems (Chiper and Apps, 2001). A GWB-compatible database from Arthur et al. (2012) was used to construct the diagrams.

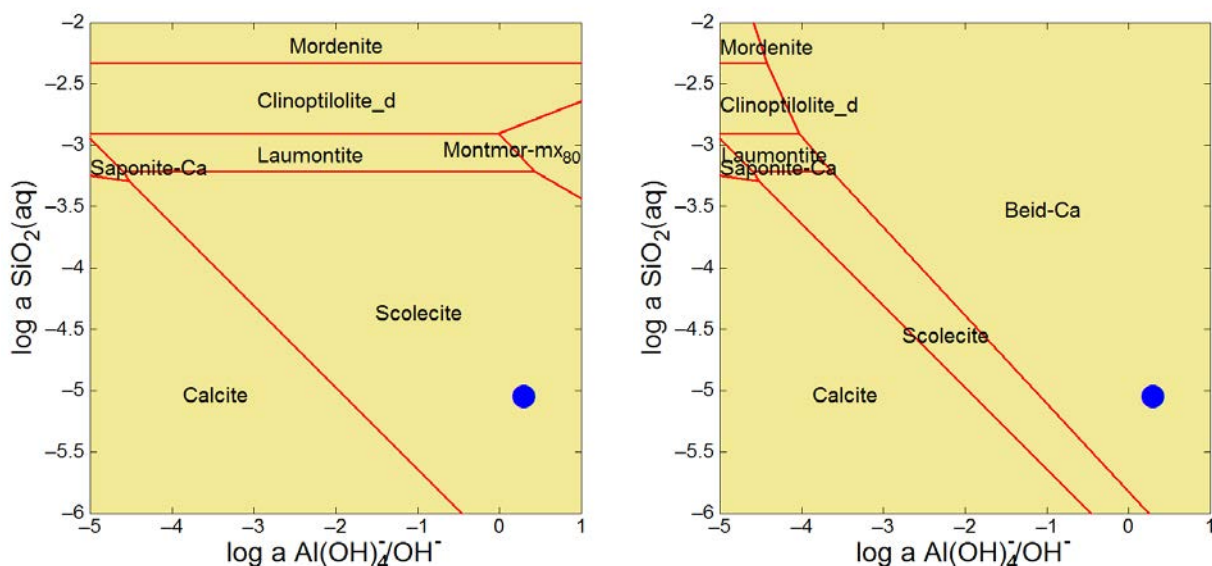


Figure 5 Phase diagrams for the cement leachate from the saline equilibrium experiment of Vuorinen et al. (2005) at 25°C. Beidellites were assumed not to form in the left-hand Figure, but were included in the right-hand Figure. Filled symbols represent chemical conditions as defined by the leachate composition shown in Table 1. The descriptor 'd' refers to a representative composition of clinoptilolite in low-temperature diagenetic systems (Chiper and Apps, 2001). A GWB-compatible database from Arthur et al. (2012) was used to construct the diagrams.

3 Clay stability in Olkiluoto groundwaters

Hellä (2010, Appendix 1; reproduced here as Table 2) has defined a number of reference groundwater compositions that may occur at Olkiluoto under different conditions and these will be used here to assess long-term clay mineral stability. Cation activity ratio plots are particularly useful in this regard in that they increase the number of variables which can be represented on a 2-D plot, and moreover avoid inclusion of H^+ (pH) which for groundwater can be prone to sampling/analytical errors due to CO_2 outgassing or absorption.

Figure 6 shows variations in $\log Ca/Mg$ activity ratio with $\log fCO_2(g)$ (equivalent to $\log PCO_2$). There are stability fields for beidellite, laumontite, saponite clays, montmorillonite and kaolinite. Bei-

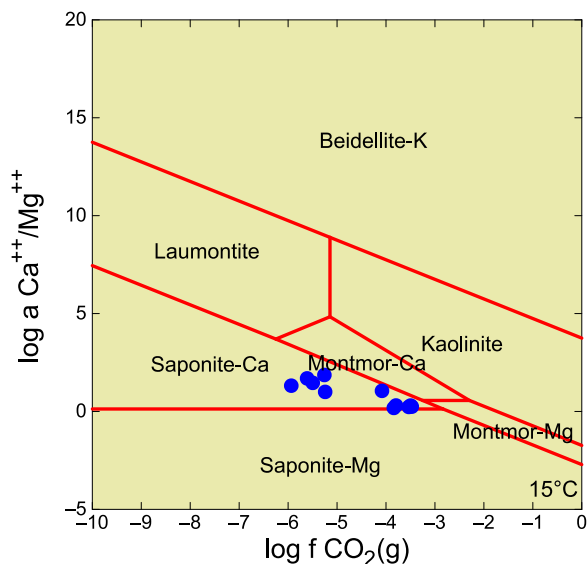


Figure 6. Mineral stabilities in the system $CaO-MgO-K_2O-Al_2O_3-SiO_2-H_2O-CO_2$ using Geochemists Workbench (Bethke, 2008) and LLNL database 'thermo.com.V8.R6.230' at 15°C. Ca^{2+} , Al^{3+} and $SiO_2(aq)$ activities are buffered by the solubilities of calcite, kaolinite and chalcedony, respectively. Blue dots represent compositions of groundwaters from Olkiluoto (from Hellä, 2010). Data suggest control of Ca/Mg , PCO_2 (and pH), by montmorillonite–saponite–calcite co-existence.

dellite, saponite and montmorillonite are all swelling clays (smectites), kaolinite is a non-swelling clay and laumontite is a calcium zeolite. Data for Olkiluoto groundwaters (blue dots) plot close to and parallel to the Ca-montmorillonite – Ca-saponite boundary suggests control of Ca/Mg ratios, pH and PCO_2 by the following reaction (conserving Mg^{2+} and Al^{3+}):

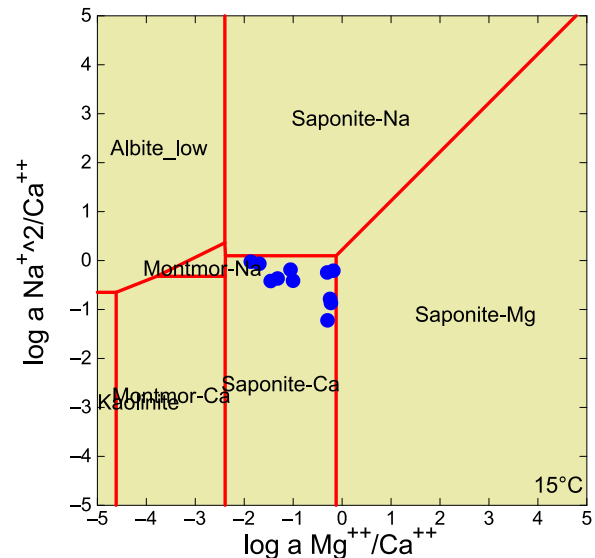
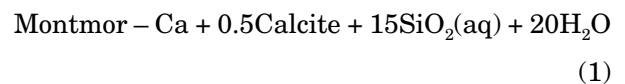
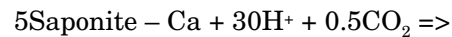


Figure 7. Mineral stabilities in the system $Na_2O-CaO-MgO-Al_2O_3-SiO_2-H_2O-CO_2$ using Geochemists Workbench (Bethke, 2008) and LLNL database 'thermo.com.V8.R6.230' at 15°C. Ca^{2+} , Al^{3+} , Mg^{2+} and $SiO_2(aq)$ activities are buffered by calcite, kaolinite, corrensite (Mg end-member) and chalcedony, respectively. $\log fCO_2(g) = -5$ bars (median value for Olkiluoto groundwaters). Thermodynamic data for corrensite from Morrison and Parry (Morrison and Parry, 1986) were employed. Blue dots represent compositions of groundwaters from repository depth at Olkiluoto (from Hellä, 2010). This suggests control of Na/Ca ratios either by various saponite compositions.

Table 2. Major element compositions of reference groundwaters for the Olkiluoto site. From Hellä (2010). Concentrations in mg/l unless stated.

	Fresh/brackish HCO ₃	Brackish SO ₄	Fresh/brackish HCO ₃	Fresh/brackish HCO ₃	Saline	Fresh/brackish HCO ₃
Sample	KR6_58_1	KR6_135_8	KR39_108_1	KR4_81_1	KR20_465_1	KR22_423_1
Depth, m	-42.53	-101.77	-88.18	-69.97	-360.71	-347.01
T, °C	10	10	10	10	10	10
pH	7.60	7.60	8.00	7.80	7.40	8.10
Eh, V		-0.24	-0.23	-0.26	-0.07	-0.24
Na	225	1760	267	302	2640	2320
K	7.90	19.00	7.70	9.70	11.00	10.00
Ca	86	650	54	54	1300	1700
Mg	26	180	19	18	62	91
Fe	1.24	0.32	0.49	0.45	0.13	0.12
SiO₂	11.50	11.00	13.40	12.00	10.00	6.80
Cl	369	4010	331	351	6400	6690
SO₄	126	460	100	92	20	
S²⁻	0.02	0.02		0.01	0.18	0.53
HCO₃⁻	170.00	111.00	379.00	279.00	40.10	14.20
	Saline	Saline	Saline	Brackish SO4	Saline	
Sample	KR27_503_1	KR4_861_1	KR8_556_1	KR4_T132_2	KR10_498_1	
Depth, m	-391.73	-818.75	-490.24	-119.58	-487.05	
T, °C	10	10	10	10	10	
pH	8.10	7.80	8.30	7.55	8.00	
Eh, V	-0.26		-0.15		-0.30	
Na	2540	9750	3780	1870	4830	
K	6.80	22.00	9.00	20.00	14.00	
Ca	2100	15700	4400	700	3570	
Mg	39	110	110	260	38	
Fe	0.02	2.00	0.04	0.37	0.11	
SiO₂	11.00	5.30	7.40	12.30	8.00	
Cl	7900	43000	13300	4500	13500	
SO₄	1.30			510.00	1.40	
S²⁻	0.04		0.05	0.03		
HCO₃⁻	8.20	12.20	6.00	92.10	6.70	

Moreover, it also suggests that the montmorillonite in bentonite could be altered to other smectites (saponites, beidellites) over the long-term but not be altered to non-swelling minerals such as laumontite or kaolinite.

Figure 7 shows variations in $\log(\text{Na}^+)/\text{Ca}^{2+}$ activity ratio with $\log \text{Mg}^{2+}/\text{Ca}^{2+}$ activity ratio. There are stability fields for albite, kaolinite, saponites, and montmorillonites. Albite is a sodium aluminosilicate framework mineral (plagioclase

feldspar) common in granitic (*sensu lato*) rock types. It can be seen from this diagram that the Olkiluoto groundwater data either plot adjacent to the Na-montmorillonite stability field along the boundaries between Na-, Ca- and Mg-saponite, providing additional evidence for the relevance of equation (1) above in controlling not only $\text{Mg}^{2+}/\text{Ca}^{2+}$ activity ratios, but also $(\text{Na}^+)/\text{Ca}^{2+}$ activity ratios in Olkiluoto groundwater compositions.

Figure 8 shows variations in log activity K^+/Mg^{2+} ratio versus activity of $SiO_2(aq)$. There are stability fields for muscovite (K-mica), laumontite, illite, and

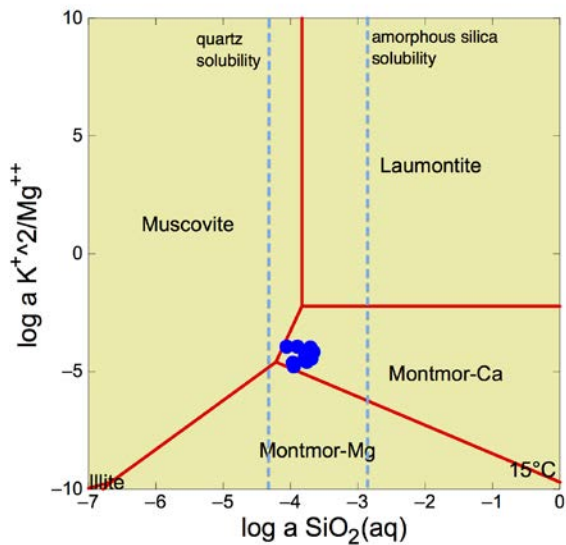


Figure 8. Mineral stabilities in the system K_2O - CaO - MgO - Al_2O_3 - SiO_2 - H_2O - CO_2 using Geochemists Workbench (Bethke, 2008) and LLNL database 'thermo.com.V8.R6.230' at 15°C. K^+ , Ca^{2+} and Al^{3+} activities are buffered by K-feldspar, calcite and boehmite, respectively. $\log fCO_2(g) = -5$ bars (median value for Olkiluoto groundwaters). Blue dots represent compositions of groundwaters from Olkiluoto (from Hellä, 2010). Solubilities of quartz and chalcedony are indicated by dashed lines. The distribution of the groundwater data suggests control of $SiO_2(aq)$ by montmorillonite-muscovite coexistence.

montmorillonites. Solubility limits for quartz and chalcedony are also shown. It may be seen from this figure that $SiO_2(aq)$ activities are in excess of that for quartz solubility at 15°C. Again, montmorillonites appear important in controlling K/Mg ratios.

The potential importance of clays and calcite in controlling water chemistry is supported by mineralogical evidence from fracture fillings at Olkiluoto (Figure 9). Posiva report that the major fracture-filling minerals (as percentage of fractures containing a filling mineral) in drill-holes KR1-40 at Olkiluoto are clay minerals (49%), calcite (35%) and sulphides (31%) (Posiva, 2009, p395). Fracture fillings are composed of different combinations of the major filling minerals so that fractures containing only clay minerals are the most common. Other major filling mineral combinations are clay + sulphide, calcite, and clay + calcite. Analysis of 'gouge fillings' at ONKALO showed that the main minerals were quartz, chlorite, illite, kaolinite, montmorillonite, calcite and feldspars which also suggest the importance of clays and calcite as products of water-rock interaction (Gehör, 2007).

This analysis suggests that groundwaters are compatible with the stability of montmorillonite, saponite and calcite as fracture fillings at Olkiluoto and, moreover, with the potential long-term stability of smectites in the engineered barrier system of a deep geological repository sited there.



Figure 9. Typical clay filled fracture with a calcite coating that is partly covered by pyrite (from the core of OL-KR20 at 97.75 m depth). From Posiva (2009, p396).

4 Clay stability in cementitious and silica-rich grouts

As well as being demonstrably stable in fluids from the natural barrier system (groundwaters), it is desirable that clays have predictable behaviour in fluids derived from engineered barrier components such as cementitious and silica-rich grouts.

4.1 Stability in cementitious grouts

4.1.1 Background

Cement and other construction materials will be used in the construction of a spent fuel disposal facility (KBS-3V or KBS-3H). The purposes of such materials are to limit the groundwater inflow (grouting), to stabilise the rock (shotcrete, castings of rock bolts), to construct plugs and seals (e.g., drift end plugs, compartment plugs), to fill, for example, anchoring holes and for operational safety purposes (floors, supporting walls etc.) (Gribi et al., 2008). Concrete will also be used for temporary construction elements (walls, intermediate floors, doors). Most of the cementitious materials will be removed before the final closure of the repository but, according to the estimates of residual materials in the KBS-3H repository, between 1.2 and 1.8 million kg of cement will be left in the entire repository. Of these, an average of 2,600 to 3,900 kg of cement will be located in each drift (Hagros, 2007).

Three grouting materials are considered for both KBS-3H and KBS-3V in various parts of the repository:

- ordinary (Portland) cement;
- low-pH cement; and
- colloidal silica.

Shotcreting will not be needed in the deposition drifts because the quality of the rock and inflow rate should be adequate for drift constructability by design (Gribi et al., 2008). However other parts of the repository may require supporting by shotcreting.

For both KBS-3V and -3H, ordinary and low-pH cement are both considered as shotcreting materials. Shotcrete will be removed to the maximum extent practical before closure (Gribi et al., 2008).

4.1.2 Thermodynamic stability

OPC-type cements

At the low water/clay ratios typical of compacted bentonite barriers, the compositions of migrating cement pore fluids may evolve rapidly through reaction with clay, leading to a lowering of pH, removal of calcium in rapidly forming C-(A)-S-H gel, and an increase in silicon and aluminium pore fluid concentrations through dissolution of aluminosilicate minerals in the clay (e.g. Figure 10).

Although there are many uncertainties concerning the thermodynamic stability of clays and their potential hyperalkaline alteration products (e.g. see Section 2 and discussion in Savage et al., 2007), a potential reaction path for cement in contact with clay is illustrated in an $\text{Al}^{3+}/\text{H}^+$ versus $\text{SiO}_2(\text{aq})$ activity diagram [e.g. as developed for examination of alteration in natural hydrothermal systems (Giggenbach, 1984)] for the system $\text{CaO-K}_2\text{O-Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$.

Figure 11 shows the reaction-path of an hypothetical OPC-type cement pore fluid (here represented by the portlandite stability field) with bentonite (here shown by the Ca-beidellite stability field), progressing through a stability field of C-S-H (tobermorite), then low Si/Al Ca-zeolites, such as gismondine or scolecite, to high Si/Al zeolites such as stilbite or mordenite before equilibration with clay minerals (beidellite in this figure). A stability field for a C-A-S-H solid(s) would be expected to exist between that for C-S-H and the zeolite stability fields, but currently, no thermodynamic data are available for this suite of solids (Savage et al., 2007).

This diagram and reaction path are informative, but in real systems the presence of magnesium and dissolved CO₂ in groundwater must also be considered. In fractured hard rocks, Mg-bearing aluminosilicates rather than dolomite, may control Mg solubility (Coudrain-Ribstein et al., 1998). Regarding CO₂, Coudrain-Ribstein et al. (1998) have shown that two distinct natural systems exist: sedimentary basins, where partial pressures of carbon dioxide range from 0.002 to 130 bar at 10 to 200°C; and fractured hard rocks, where P_{CO₂} is much lower, ranging from 10⁻⁶ to 50 bar across the same temperature range. P_{CO₂} in groundwaters from Olkiluoto ranges from 10⁻⁶ to 10^{-3.5} bars at 15°C (Figure 6). Mg and CO₂ are introduced to the cement-clay system in Figure 12.

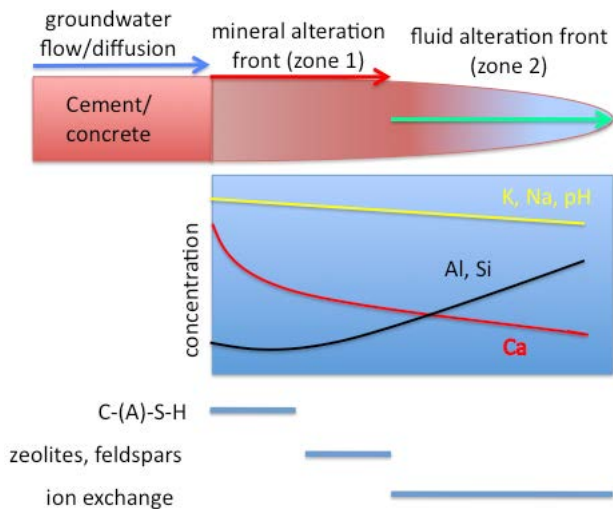


Figure 10. Schematic diagram of the migration and reaction of hyperalkaline fluids with rocks or clay barriers, showing possible variations in fluid composition and alteration mineralogy (after Savage, 1998). A zone of perturbed fluid composition (elevated pH, Na, K, Al and Si) where ion exchange reactions dominate ('Zone 2'), migrates ahead of a zone of mineral dissolution and growth ('Zone 1'). Calcium concentrations in the migrating cement pore fluid decrease relatively close to the cement/concrete due to precipitation in C-(A)-S-H solids through reaction with the host rock/clay barrier. Similarly, Al and Si concentrations in the migrating fluid increase with distance due to dissolution of host rock/buffer minerals. Secondary minerals which form as a result of these interactions reflect the composition of the fluid, such that calcium silicate hydrates (C-(A)-S-H) form nearest the cement, whilst zeolites and feldspars form further away. With time, this mineral sequence evolves as the fluid migrates. From Savage (2011).

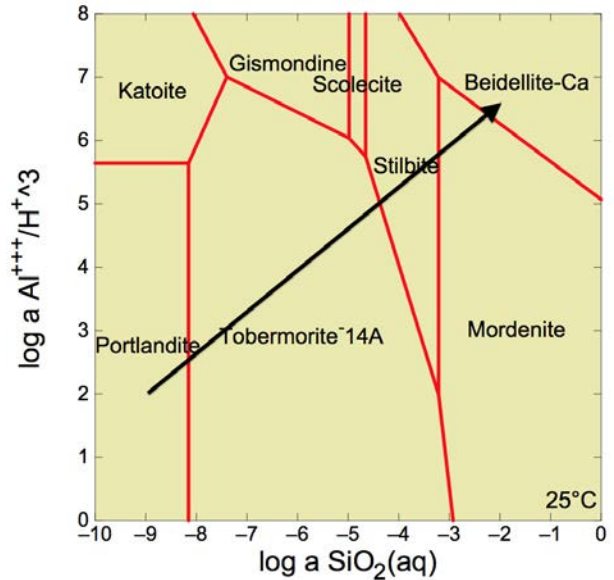


Figure 11. Mineral stability relationships in the system CaO-K₂O-Na₂O-Al₂O₃-SiO₂-H₂O, plotted as the activity of Al³⁺/(H⁺)³ versus activity of SiO₂(aq) using Geochemists Workbench (Bethke, 2008) and LLNL database 'thermo.com.V8.R6.230' at 25°C. K, Na and Ca solubilities are defined by K-feldspar, analcime, and portlandite respectively. The arrow shows a hypothetical reaction path between cement (represented by portlandite, lower left) and bentonite (represented by Ca-beidellite, upper right).

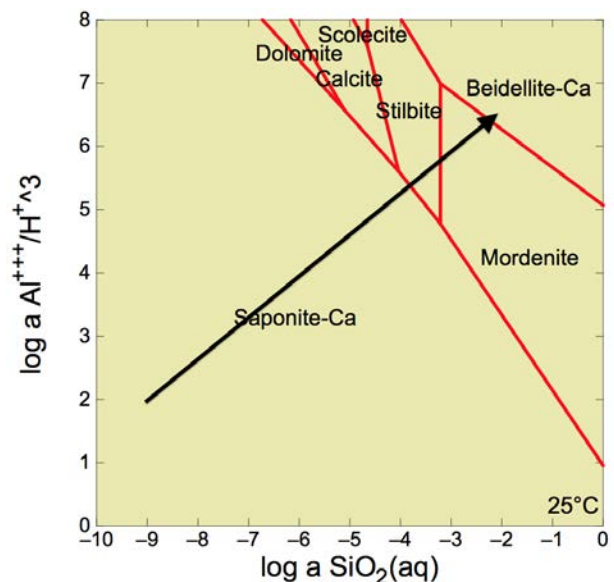


Figure 12. Mineral stability relationships as per Figure 11, but including CO₂ and Mg. Log *f* CO₂(g) = -5 bar; Mg solubility is defined by corrensite (with thermodynamic data for corrensite from Morrison and Parry, 1986). The arrow shows a hypothetical reaction path between cement (lower left) and clay (upper right).

The chemical conditions of Figure 12 are relevant to the use of cement and clay engineered barriers (e.g. compacted bentonite) in a fractured hard rock environment, such as Olkiluoto. In this case, PCO_2 is significantly lower than that in sedimentary basins (10^{-5} bar) and the mineral controlling Mg solubility is assumed to be corrensite, a mixed-layer smectite-chlorite sheet silicate which is commonly associated with groundwater-bearing fractures in granitic rocks (e.g. Sugimori et al., 2008). Under these conditions, the stability fields of portlandite and C-S-H (tobermorite) shown in Figure 11 are replaced by the clay Ca-saponite, reflecting the chemical gradients in Al and Si at clay-cement interfaces. The stability field of calcite is minor, occupying space at high Al^{3+}/H^+ and intermediate $SiO_2(aq)$ activities only. Analysis of alternative systems with different solubility-limiting minerals for Mg, such as sepiolite, shows that stability fields for calcite and dolomite may disappear altogether for this type of environment.

Low-pH cements

The principal solid phase in low-pH cement is a low Ca/Si (< 1.0) CSH gel. Reaction with pozzolans also tends to increase the Al/Ca ratio of the C-S-H. With microsilica as the additive, the mean Ca/Si ratio remains at about 1.5 for as long as any portlandite remains. If all the $Ca(OH)_2$ is consumed, then the Ca/Si ratio decreases to around 1.0 (Savage and Benbow, 2007).

Experimental work by Harris et al. (2002) shows that to achieve a pH less than 11, then the C-S-H gel must have a Ca/Si ratio less than 0.81. Unlike gels with a greater Ca/Si ratio, gels of $Ca/Si \leq 0.81$ do not show dramatic incongruent dissolution behaviour. In other words, leaching of these gels produces a fluid with a broadly constant Ca/Si ratio with time/volume throughput. Unlike the higher Ca/Si ratio gels, those with $Ca/Si \leq 0.81$ show a Ca/Si ratio increasing towards unity as leaching proceeds. This implies preferential leaching of silica from the gel, which contrasts with gels of higher Ca/Si ratio which show the preferential removal of Ca.

Low-pH cement grouts produce pore fluids relatively rich in Si, compared with natural groundwa-

ters. The concentrations of Si measured by Harris et al. (2002) in C-S-H gel leaching experiments were up to 2.2 mmol/l ($\log a_{SiO_2(aq)} = -4.11$ in Figure 12), which is equivalent to the solubility of amorphous silica at neutral pH at 25°C. Most natural groundwaters contain Si contents equivalent to that of chalcedony (0.2 mmol/l at 25°C) or quartz (0.1 mmol/l). The higher Si concentrations associated with low-pH grout pore fluids will help to stabilise montmorillonite (see below).

Reaction paths between low-pH cements and bentonite are most likely to occur along the same vector shown in Figure 11 and Figure 12, albeit shortened to lie between tobermorite (a proxy for C-S-H gel) and Ca-beidellite.

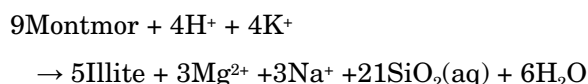
4.2 Stability in silica-rich grouts

Silica-rich grouts will be used to seal fine fractures adjacent to disposal drifts in the KBS-3 concept. Grouting protects the buffer and backfill from high, transient water flows prior to repository saturation, and prevents drawdown of surficial waters or up-coning of saline water, thus supporting the safety functions of the host rock (Posiva, 2010, p. 290). In designing all engineered components, it is required that their presence should not significantly impair the safety functions of other components (engineered or natural).

The presence of such grouts may lead to the development of pore fluids (groundwater) saturated with respect to amorphous silica in and around deposition holes. This could have two potential effects:

- re-distribution of silica during the thermal period, potentially leading to cementation of clay grains within the bentonite, and/or
- impacts upon clay stability.

Regarding the latter effect, montmorillonite is known to be stabilised relative to illite by silica concentrations controlled by amorphous silica solubility (e.g. SKB, 2010, p147; Abercrombie et al., 1994):



In other words, higher silica concentrations drive the above reaction to the left, in favour of the stability of montmorillonite.

Since potassium concentrations in Olkiluoto groundwater may be quite low (< 20 mg/l – Hellä, 2010), it seems reasonable to expect that long-term transformation of montmorillonite to minerals other than illite may be more relevant. This idea is investigated in Figure 13 which is constructed in a similar way to Figure 11 and Figure 12 but with the assumption that calcite solubility determines the activity of Ca^{2+} in the system, rather than portlandite. From this figure it can be seen that at silica activities buffered by quartz solubility, mineral stability fields are saponite at relatively low activities of $\text{SiO}_2(\text{aq})$ and $\text{Al}^{3+}/\text{H}^+$ and albite at high $\text{Al}^{3+}/\text{H}^+$. Montmorillonite and beidellite are stabilised at dissolved silica activities equivalent to the solubility of amorphous silica or greater, although zeolites such as clinoptilolite at intermediate $\text{SiO}_2(\text{aq})$ and $\text{Al}^{3+}/\text{H}^+$ may be important. Consequently, this diagram suggests that the higher silica activities in pore fluids associated with silica-rich grouts may help to stabilise smectite clays relative to feldspars, zeolites or illite.

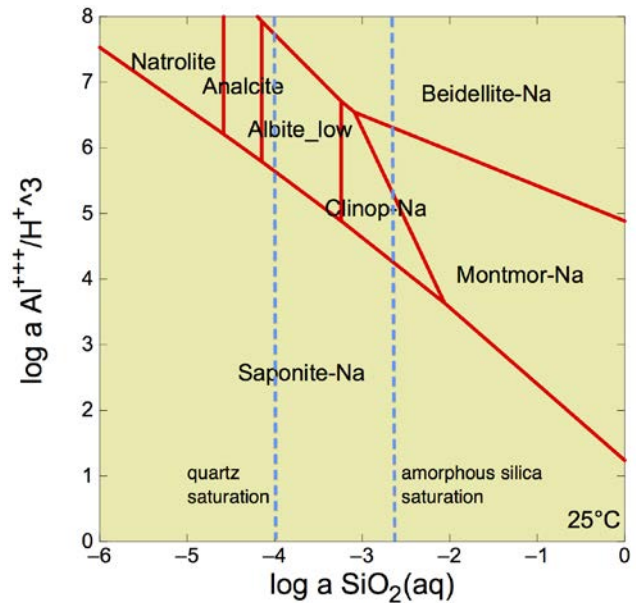


Figure 13. Mineral stability relationships in the system $\text{CaO-K}_2\text{O-Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2\text{-CO}_2\text{-H}_2\text{O}$, plotted as the activity of $\text{Al}^{3+}/(\text{H}^+)^3$ versus activity of $\text{SiO}_2(\text{aq})$ using Geochemists Workbench (Bethke, 2008) and LLNL database 'thermo.com.V8.R6.230' at 25°C. K, Na, Ca and Mg solubilities are defined by K-feldspar, Na-montmorillonite, calcite and corrensite respectively. $\log f \text{CO}_2(\text{g}) = -5$ bars. The dotted blue lines show activity of $\text{SiO}_2(\text{aq})$ as defined by quartz and amorphous silica solubilities, respectively.

5 Conclusions

Evaluations of the mineralogical stability of clay-based buffer and backfill materials must account for evolving environmental conditions in the near field over time scales that are relevant to repository safety assessments. Conventional experimental methods can support such evaluations, but the methods are fundamentally limited to impacts on mineral stability that occur within accessible experimental time scales. Qualitative inferences drawn from observations of analogous natural or anthropogenic systems are also useful, but quantitative interpretations may be complicated by large and irreducible uncertainties in initial and boundary conditions controlling system evolution.

The application of thermodynamic concepts to evaluations of clay mineral stability is also problematic for several reasons:

- the available experimental evidence purporting to show that these minerals can attain equilibrium in aqueous systems at low temperatures is inconclusive;
- interpretations of phase stability are complicated by the variable nature of smectite compositions;
- stoichiometric and solid-solution models can deal with this compositional variability in an approximate manner, but verification of the accuracy of model predictions is difficult; and
- the models must be supported by reliable thermodynamic properties for specific and well-defined smectite compositions, or for solid-solution components, but solubility, calorimetric, and phase-equilibrium constraints on these properties are generally lacking.

These limitations in understanding suggest that uncertainties in predictions of the long-term stability of clay minerals in bentonite buffer/backfill materials could be non-trivial and should be bounded to the extent possible.

Limitations in the thermodynamic approach can be addressed to some extent through the judicious use of simplifying assumptions and approximations. Models and algorithms are currently available for estimating standard thermodynamic properties for dioctahedral and trioctahedral smectites of any specified composition, or for the components of solid-solution models. These properties can be used to calculate the values of equilibrium constants for corresponding hydrolysis reactions over a range of relevant temperatures and pressures. The equilibrium constants can be used to construct phase diagrams, which provide a concise visual basis for quantitative evaluations of complex equilibrium relations among clay minerals, other minerals, and an aqueous phase. Computer programs can be used to quickly construct such diagrams for any stable, or metastable, configuration of a chemical system. This flexibility can be used to systematically evaluate the effects of alternative assumptions and parameter values on clay mineral stability.

Assuming such assumptions and approximations can be justified, the thermodynamic approach provides a basis for gaining insights concerning the long-term behaviour of buffer and backfill materials. An example considered in the present study suggests that the montmorillonite in MX-80 bentonite may be unstable in the presence of leachates from low-pH grouts and could be altered to beidellites or non-swelling zeolites. The common assumption that smectite stability can be defined in terms of a simple pH threshold may not be valid and is not consistent with thermodynamic principles governing phase stability. Such stability should instead be evaluated in terms of temperature, pressure and the activities of all aqueous species (and components of clay mineral solid solutions) involved in corresponding hydrolysis reactions.

Application of such an approach using currently-

available thermodynamic data for clays and associated minerals suggests that groundwaters from depth at Olkiluoto could be compatible with the long-term stability of dioctahedral smectites (including montmorillonites) and saponites in bentonite barriers at ambient temperatures and that reactions between these minerals and calcite may control cation ratios, pH and PCO_2 in the rock-groundwater system.

A similar evaluation of potential reactions between bentonite and OPC pore fluids suggests that

a sequence of C-A-S-H type minerals and zeolites may form at interfaces between the two materials. In fractured hard rock such as that at Olkiluoto, gradients in dissolved Al and Si may lead to the conversion of C-S-H gel in the cement/concrete to saponitic clays. The presence of silica-rich grouts in the rock-groundwater system may serve to help stabilise montmorillonite in bentonite by increasing the activity of dissolved silica in groundwater to that of amorphous silica solubility, thus stabilising montmorillonite relative to illite.

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