

THE PERFORMANCE OF CLAY BARRIERS IN REPOSITORIES FOR HIGH-LEVEL RADIOACTIVE WASTE

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Received May 24, 2006

Highly radioactive waste is placed in metal canisters embedded in dense clay termed buffer. The radioactive decay is associated with heat production, which causes degradation of the buffer and thereby time-dependent loss of its waste-isolating potential. The buffer is prepared by compacting air-dry smectite clay powder and is initially not fully water saturated. The evolution of the buffer starts with slow wetting by uptake of water from the surrounding rock followed by a long period of exposure to heat, pressure from the rock and chemical reactants. It can be described by conceptual and theoretical models describing processes related to temperature (T), hydraulic (H), mechanical (M) and chemical performance (C). For temperatures below 90°C more than 75 % of the smectite will be preserved for 100 000 years but cementation may reduce the excellent performance of the buffer to a yet not known extension.

KEYWORDS : Bentonite, Clay, Radioactive Waste, Temperature, Chemistry

1. INTRODUCTION

The goal set by all states that make use of nuclear power is to eliminate the risk of contamination of the biosphere by radionuclides released from the waste. This is believed to be achieved by enclosing the waste in metal containers – canisters – that are surrounded by dense clay and placed in bored holes or tunnels Figure 1. In Sweden and Finland the waste consists of used fuel rods that have been kept under water for 40 years in an intermediate storage for reducing the heat release associated with the radioactive decay. The clay “buffer” offers a very good isolation of the canisters because of the following properties:

- Very low hydraulic conductivity
- Very low anion diffusion capacity and low transport capacity of positively charged radionuclides
- High swelling potential for self-sealing of gaps and openings in the buffer and its contacts with the rock and canisters
- Favourable rheological properties: sufficient bearing capacity to minimize settlement of the heavy canisters and sufficient softness to avoid transfer of high tectonically induced shear stresses to the canisters
- Sufficient thermal conductivity to transfer heat caused by the radioactive decay to the rock without being too hot
- Colloid filtering capacity
- Capacity to filter microbes

The most suitable clay types are those with a high content of smectite minerals because this gives the clay a particularly low hydraulic conductivity and high expandability. The optimum bulk density at fluid saturation is 1900 to 2100 kg/m³ for serving well with respect to the

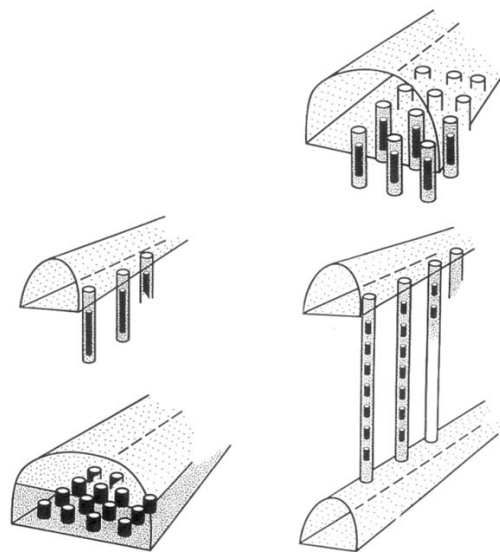


Fig. 1. Repository Concepts, Most of them Implying that Canisters with Highly Radioactive Waste are Surrounded by Dense Smetite Clay and Placed in Holes or Tunnels

criteria. Densities of this magnitude can not be achieved by compaction on-site but requires that air-dry clay powder is compacted in forms under very high pressures by which dense blocks are obtained. The clay blocks are water saturated by about 50 % and placed around the canisters they sorb water from the surrounding rock, expand and tightly embed the canisters while establishing tight contact with the rock. Figure 1 illustrates design principles for repositories.

A most important issue is the long-term performance of the clay. In some states the minimum period of effective isolation is set at some thousands of years, while it is 1 million years by Swedish authorities. This means that the buffer clay must not become significantly more conductive than originally or loose more than a small fraction of its expandability in the specified period of time.

2. BUFFER MATERIALS

The raw material – commonly bentonite – can occasionally be processed only by drying in the sun of the excavated material and subsequent grinding. However, in most cases drying must be made of the material by use of rotating kilns and also transformation of the clay from the initial Ca/Mg state to Na form, which gives the most suitable physico/chemical properties.

The processed clay is commonly stored in silos or in stock piles protected from rain and it is packed in 25-50 kg paper bags or 1000 kg big-bags for delivery. The preparation of buffer clay is made by compaction of dry clay powder to blocks with a high density and they are emplaced in the deposition holes to surround the canisters as illustrated by Figure 2 representing the Swedish KBS-3V concept. Full-size ring-shaped block of smectite-rich clay weighing 2 tons have been compacted by compressing air-dry clay powder under 150 MPa pressure for use in a Swedish KBS-3V repository.

3. EVOLUTION OF THE WASTE-EMBEDDING CLAY – THE BUFFER

The radioactive decay is associated with successively reduced heat production, which justifies specification of three major phases in the performance of the engineered buffer barrier; a first phase comprising application and evolution of the buffer including water uptake and swelling leading to maturation (0-100 years), a second phase with the matured buffer exposed to a thermal gradient (100-1000 years) and a third phase with tectonic or glacial impact under ambient or reduced temperature (1000-1000000 years). In the first phase complex physico/chemical processes take place in the maturing buffer, partly controlling its long-term performance. This phase can to some extent be investigated in field tests of 5-10 years duration and has therefore been in focus of most of the international work. One realizes that

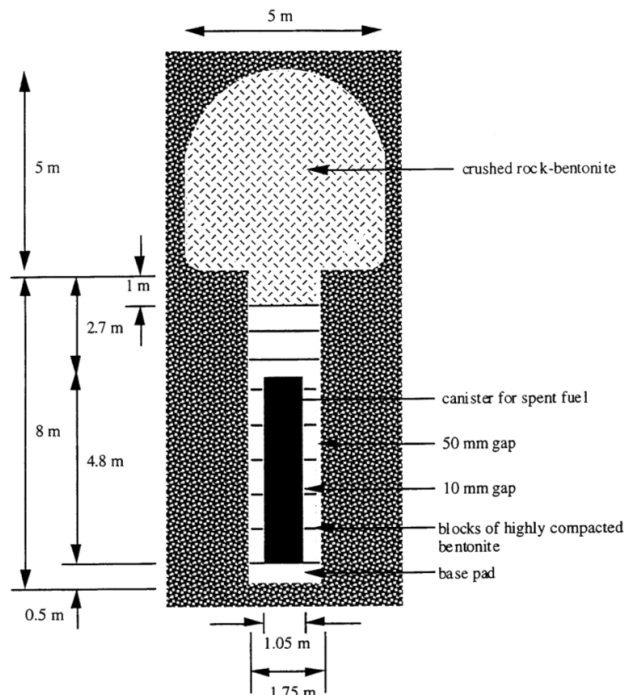


Fig. 2. Cross Section of a Deposition Tunnel and Hole for Disposal of 20 ton Canister of Copper and Steel Containing Used Reactor Fuel Rods. KBS-3 Concept

if the hydraulic conductivity and swelling pressure are not significantly changed in the early phases, the buffer may serve as an effective isolation of the waste also in a longer time perspective provided that significant mineral changes in the buffer will not take place. This makes prediction of the chemical stability of buffer minerals a major issue in planning repositories and also the matter of migration of radionuclides that may ultimately escape.

The first phase involves the following processes:

- Thermally induced redistribution of the initial porewater in the clay.
- Uptake of water from the rock and backfill leading to hydration of the buffer.
- Expansion of the buffer yielding displacement of the canisters and overlying backfill.
- Dissolution of buffer minerals and precipitation of chemical compounds in the buffer.

The evolution of the buffer can be described by conceptual and theoretical models describing processes related to temperature (T), hydraulic (H), mechanical (M) and chemical performance (C).

Thermally induced redistribution of the initial porewater and maturation of the pellet fill (TH)

The thermal gradient operating across the buffer clay

causes originally contained porewater to migrate in liquid and vapour form from the hot, canister-near part to the colder part of the buffer. This yields early saturation of the buffer close to the rock and desiccation close to the hot canister.

Wetting of the buffer by uptake of water from the rock (THMC)

The buffer is initially not completely water saturated and the extreme hydrophilic nature of smectite clay means that it sucks water from the rock and backfill in a KBS-3V repository until it is totally saturated. If the rock gives off very little water to the buffer clay, it may remain dry near the canister for many decades or even centuries, which appears to have an impact on its hydrophilic nature. Where the rock gives off significant amounts of the buffer clay can be largely water saturated in some 5-10 years. Such richly water-bearing rock gives problems, however, in the backfilling and canister emplacement.

Slow wetting of the buffer clay has a C-effect since Ca^{2+} , Mg^{2+} , K^+ , SO_4^{2-} and Cl^- will be precipitated at the wetting front, which moves towards the canister. A rather large part of the buffer may hence contain such precipitates, which interact with the smectite minerals and the canisters. The temperature gradient has a C-effect since silicate minerals including the smectite component will dissolve to a larger extent close to the heater than at the rock, by which released silica migrates towards the rock and precipitates in the outer part of the bentonite. Silicification causes cementation and brittleness of the clay.

4. THEORETICAL MODELLING OF THE EVOLUTION OF BUFFER CLAY

The main evolution processes that are described by numerical formulations are [1]:

- Moisture migration takes place by flow and diffusion of liquid and vapour.
- Heat transfer includes conduction, convection and latent heat of vaporisation transfer in the vapour phase.
- The bulk flow of air in the maturing buffer is represented by the use of a generalised Darcy's Law. Henry's Law is employed to calculate the quantity of dissolved air and its flow is coupled to the flow of pore liquid.
- Deformation effects are included via either a non-linear elastic, state surface approach or an elasto-plastic formulation. In both cases deformation is taken to be dependent on suction, stress and temperature changes.
- Chemical solute transport for multi-chemical species includes diffusion dispersion and accumulation from reactions due to the sorption process.

Heat conduction and flow are expressed using classical physics but is generalized by including the velocities of liquid, vapour and air respectively. The rate of migration of pore liquid and pore air are calculated using a generalised

Darcy's law with special respect to the chemical solute concentration gradient and the conductivity of the air phase and the pore air pressure. Also, an osmotic flow term in the liquid velocity is included for representation of liquid flow behaviour found in highly compacted clays. Air in partly saturated soil is considered to exist in two forms: bulk air and dissolved air. The proportion of dry air in the pore liquid is defined using Henry's law.

For non-reactive chemical solutes the governing equation for chemical transfer can be expressed in terms of diffusion and dispersion, as derived in primary variable form and extended to a multi-chemical species form with a sink term introduced to account for mass accumulation from reactions due to the sorption process.

The total strain is assumed to consist of components due to suction, temperature, chemical and stress changes,

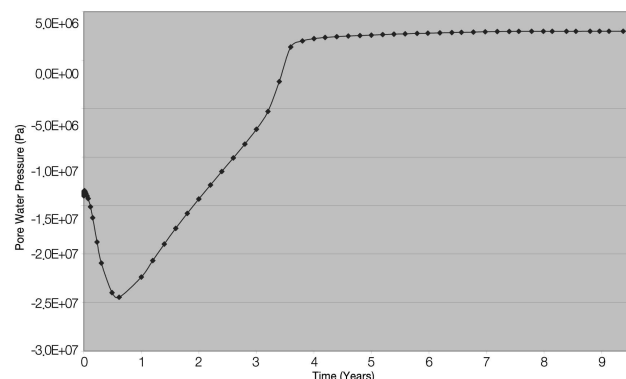


Fig. 3. Pore Water Pressure Plot at the Heater/buffer Interface at a Mid-height of the 5.5 m High Canister (Ongoing Modelling at Cardiff University for the EU-supported Project "Prototype Repository Project")

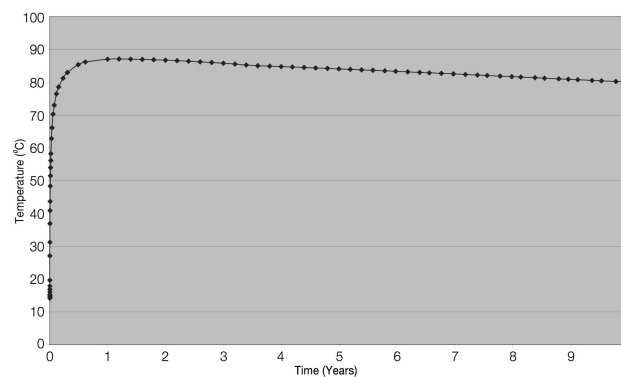


Fig. 4. Temperature Plot at the Heater/Buffer Interface at Mid-height of the 5.5 m High Canister (Ongoing modelling at Cardiff University for the EU-supported Project "Prototype Repository Project")

considering both elasticity and elastoplasticity formulations. For describing the contribution of the chemical solute to the stress-strain behaviour of the soil, an elastic state surface concept has been proposed. It describes the contribution of the chemical solute via an elastic relationship based on the osmotic potential.

Numerical solution of the governing differential equations is achieved by a combination of the finite element method using the Galerkin weighted residual method to formulate the finite element discretisation. For the flow and stress/strain equations shape functions are used to define approximation polynomials. A few examples of the outcome of predictive modelling made at Cardiff University of the

evolution of the “near-field” of the KBS-3V concept are shown in Figures 3, representing the porewater pressure in the buffer at the contact with the canister, and Figure 4 representing the temperature at the same contact. The predicted drying close to the hot canister being overwhelmed by inflow from the host rock and leading to eventual saturation is clearly demonstrated by the theoretical model and by full-scale experiments [2]. The peak in temperature evolution in Figure 4 represents the state when the buffer is at its driest. This demonstrates the effect of coupling between the hydraulic field and the temperature field, meaning that relevant numerical predictions should be based on coupled THMC models when possible.

Prediction of the hydraulic conductivity and swelling pressure agrees well with experimental data, which are exemplified by Tables 1 and 2.

Table 1. Hydraulic Conductivity in m/s of SKB-tested Potential Buffer Materials Saturated and Percolated with Distilled Water. Bulk Densities 1800 - 2100 kg/m³

Density, kg/m ³	1800	1900	2000	2100
MX-80	4E-13	2E-13	8E-14	3E-14
IBECO, Na	9E-13	-	4E-13	-
IBECO, Ca	2E-11	-	2E-13	-
RMN	-	4E-13	-	8E-12*
Kunigel	3E-12	-	E-12	-
Beidellite	5E-12	-	5E-13	-
Saponite	E-12	-	5E-13	-

* With 5 % graphite and 10 % quartz powder

5. LONG-TERM PHYSICAL PERFORMANCE OF THE BUFFER

Major issues related to the physical stability of the buffer clay are erodability, colloid transport and filtering, and microbiological filtering.

Colloid transport through buffers has not been examined in detail but some general conditions have been defined, as for minute smectite particles, which, through their ability to sorb positively charged radionuclides and other cations, can play a role in bringing contaminants to the biosphere. Such particles, like many other constituents of colloidal size, carry different electrical charges on different parts of their surfaces and hence form aggregates, gels and networks

Table 2. Swelling Pressure (p_s) in MPa of a Number of Tested Buffer Materials Saturated with Distilled Water

Density at saturation, kg/m ³	1300	1500	1700	1800	1900	2000	2100
MX-80	0.06	0.2	0.4	0.8-0.9	1.4	4-5	10-12
IBECO, Na	-	-	-	0.6-1	-	4-5	-
IBECO, Ca	-	-	-	0.2	-	5	-
RMN	-	-	0.45	1.9*	2.5**	3.9**	-
Beidellite	-	-	-	1.5	-	4.2	-
Saponite	-	-	-	2.5	-	8.8	-
Kunigel	-	-	-	0.2	-	0.9	-
Friedland	-	-	0.05	0.1	0.3	0.8-1	2-2.5

* Density at saturation 1850 kg/m³

** Mixture with 5 % graphite and 10 % quartz powder. Density at saturation 1950 kg/m³

that easily couple to the dense buffer clay [3]. Release of smectite aggregates can take place if the porewater flow is sufficiently high but this is estimated to be impossible under the regional hydraulic gradients that prevail in the rock after closing the repository.

The buffer clay will tend to enter fractures in the rock and the front of fracture-penetrating clay may be very soft so that groundwater flowing in the fractures may tear off small aggregates and transport them if the flow rate exceeds a few millimeters per second. Experiments as well as experience demonstrate that their size may be up to 2-50 mm. Their surface charge makes them interact with and become fixed to the common fracture minerals chlorite and micas and it is therefore believed that the transport of smectite aggregates will be insignificant over long distances.

As to the role of bacteria, of which sulphate-reducing ones are of particular importance to engineered barriers of SKB-type, they may stay alive and develop in soft smectite clay. They usually carry a negative surface charge and can therefore move through clay like large organic molecules like humus colloids. However, there are limitations partly because of the hydration conditions and the very limited void space in dense buffer clay [4]. At higher density than 1800 kg/m³ of smectite-rich clay the small size of interconnected voids and the limited access to free water prevent bacteria from moving and staying alive. Only spores are therefore believed to be operative but the working hypothesis is that there will ultimately be eradication of all life forms in the buffer.

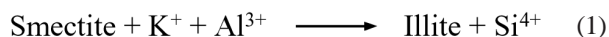
6. CHEMICAL STABILITY OF THE BUFFER

While gamma radiation is known to have a relatively small impact on the longevity of the buffer smectites [2], dissolution and conversion to non-expanding minerals is a threat. Their chemical integrity is determined by thermodynamically controlled reactions and mineral transformations take place that depend on the stability conditions of interacting minerals and porewater under the transient thermal conditions of which the temperature gradient appears to be of particular importance.

One can identify three major processes that take place in the water-saturated buffer:

- Dissolution/precipitation,
- Conversion of the smectite to non-expansive mineral forms,
- Cementation by neoformed precipitated complexes.

Dissolution of the smectite and other silicates in the buffer is negligible under normal pH conditions and ambient rock temperature, while it can be significant in hot repositories. Under temperature gradients released Si moves into colder parts, where precipitation takes place in the form of amorphous silica, cristobalite or quartz according to the generalized model expressed by Eq.1:



Conversion of smectite to non-expandable minerals ("illitization") is generally considered as the major threat to buffer smectites. It depends on the temperature and groundwater composition in a very complex way. Under commonly prevailing pH conditions the most probable mechanism causing alteration of smectite (S) is conversion to non-expanding hydrous mica, i.e. "illite" (I). Illite has a crystal structure that is similar to that of montmorillonite but with a higher lattice charge due to partial replacement of tetrahedral silica by aluminum, and with the interlamellar space collapsed through replacement of the hydrated cations by non-hydrated potassium. Such conversion is assumed to take place in two ways:

- replacement of tetrahedral silica by aluminum and uptake of external potassium, leading to mixed-layer (I/S) minerals with successively dominating I, and
- neoformation of hydrous mica in the voids of the smectite clay that supplies silica and aluminum or magnesium, while potassium enters from outside and triggers crystallization of hydrous mica.

The rate of conversion of smectite to illite is assumed to be controlled by the access to potassium irrespective of the conversion mechanism. Neoformation of illite is expected to take place at certain concentrations of silica (H₄SiO₄), aluminum and potassium, yielding crystal nuclei in the form of laths. When precipitation takes place the potassium concentration drops locally and the concentration gradient thus formed brings in more potassium by which the process continues. Geochemical codes tend to indicate that illite should be formed from smectites in a certain "window" of phase diagrams of silica, aluminum and potassium, but they do not seem to be able to indicate whether the conversion takes place via mixed-layer mineral stages or by dissolution/neoformation.

Natural analogs provide examples of the extent and rate of conversion from smectite to non-expandable minerals. Detailed descriptions of the Swedish Ordovician Kinnekulle bentonite, which still contains about 25 % smectite after a heating sequence much like the one expected in a KBS-3 repository, and of the Silurian Hamra bentonite with about the same smectite content after 10 million years exposure to somewhat more than 100°C [2], seem to validate the working model that is presently used in the Swedish R&D work on smectite conversion. It is based on the hypothesis that smectite alteration can take place either by successive transformation to mixed smectite/illite and further to pure illite, or by dissolution of smectite and neoformation of illite. Both require sufficient energy and access to potassium. The model is based on Pytte's theory [5] and has the following basic mathematical form:

$$-dS/dt = [Ae^{-U/RT(t)}] [(K^+/Na^+)mS^n] \quad (2)$$

where:

S = Mole fraction of smectite in I/S assemblages

R = Universal gas constant

T = Absolute temperature

t = Time

m, n = coefficients

The problem with this and similar theories is that the activation energy is not known with great certainty. It is assumed to be in the range of 26 to 28 kcal/mole for which calculations give reasonable agreement with natural analogs. The potassium content is the most important parameter for any temperature. Figure 5 shows the temperature dependence of illitization for an activation energy of 27 kcal/mole and a potassium concentration of 0.01 moles/liter in the water, which is high. It implies that 90 % of the smectite would remain after 1000 years at 100° C temperature and 50 % would still be intact after 10000 years. Since the

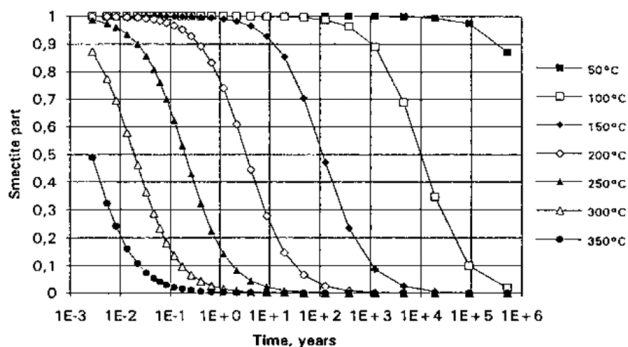


Fig. 5. Rate of Conversion of Smectite to Illite According to the Pytte-based Model for 27 kcal/moles Activation Energy and a Potassium Concentration of 0.01 moles per liter [6]. The Initial Smectite Content (smectite part) that is Taken as 100 % (unity) Drops Successively with Time

temperature will be down to ambient already after a few thousand years the large majority of the smectite minerals in the buffer will be preserved for hundreds of thousand of years provided that the temperature does not exceed 100-150° C in any of the buffer evolution phases.

Cementation by precipitation of neoformed substances can take place by release of silica in the hottest part of the buffer and migration of silicons in hydrated form towards the colder part, where precipitation and cementation of stacks of smectite lamellae can take place [6]. It has been demonstrated by applying solid state conversion models of smectite using the activation energies 28 and 24 kcal/mole, and applying chemical codes described in the reference, that the amount of dissolved smectite and thereby released silica that can have been precipitated in the Kinnekulle case are small. In principal agreement with these results, shear tests indicate that silicification has only led to slight cementation, yielding a slightly brittle behaviour and a shear strength that is somewhat higher than the overburden pressure would produce.

REFERENCES

- [1] Pusch, R., Yong, R., 2006. Microstructure of Smectite Clays and Engineering Performance. Taylor & Francis, London and New York. (ISBN10:0-415-36863-4).
- [2] Pusch, R., 1994. Waste Disposal in Rock, Developments in Geotechnical Engineering, 76. Elsevier Publ. Co. (ISBN: 0-444-89449-7).
- [3] Pusch, R., 1999. Clay colloid formation and release from MX-80 buffer. SKB Technical Report TR 99-31. SKB, Stockholm.
- [4] Pedersen, K., Investigations of subterranean microorganisms and their importance for performance assessment of radioactive waste disposal. SKB Technical Report TR 97-22. SKB, Stockholm.
- [5] Pytte, A.M., 1982. The kinetics of the smectite to illite reaction in contact metamorphic shales. M.A. Thesis, Dartmouth College, Hanover, N.H.
- [6] Pusch, R., 1998. Chemical processes causing cementation in heat-affected smectite – the Kinnekulle bentonite. SKB Technical Report TR 98-25. SKB, Stockholm.