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Application of the general microstructural model to erosion phenomena — mechanisms for the chemical–hydrodynamic conversion of bentonite to a pumpable slurry in conjunction with retrieval

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Abstract

One of the requirements of a system for disposal of spent nuclear fuel is that it should be possible and feasible to retrieve the canisters even after they have been put in place and the surrounding bentonite has absorbed water and developed a swelling pressure. This 'gripping' of the canister must be released before the canister can be retracted from the deposition hole.

One way to achieve this is to convert the bentonite into a slurry by exposing it to a flow of water containing dissolved salts such as sodium or calcium chloride. The potential efficiency of such a process is remarkable in view of the well-known tardiness of the saturation of compacted bentonite with pure water. The present study of the mechanisms involved was prompted by the need to understand the prerequisites and limitations of such a conversion process.

Thus, the literature on the molecular structure of montmorillonite (the major constituent of bentonite) was reviewed as well as the literature on the microstructure of montmorillonite–water systems. A review was also made of some chemical literature which led to identification of two rate-limiting factors for montmorillonite microstructure conversion: diffusion over large distances and association–dissociation of primary montmorillonite particles.

The knowledge compiled was then used in analyses of the kinetics involved and the following conclusions were made: (1) Exposure of the compacted bentonite with fresh water causes it to swell and to produce free particles by exfoliation. They form gels which cause closure of the pores so that further uptake of water becomes limited by diffusion. (2) Exposure of the compacted bentonite with water containing dissolved salt causes the exfoliated material in the microstructure to shrink (or at least swell less than in the fresh water case). Thus more water can penetrate into the pores and cause differential expansion in the aggregate residues which, in turn, leads to further widening of the pores. (3) The gel formed in the above described process may be removed by the flow of the water thus exposing fresh bentonite surface to continued attack.

The paper is based on the general microstructural model but goes beyond it by including also dilute systems.

It is concluded that the chemical–hydrodynamical method for removing bentonite from around a deposited canister might be shown to be a robust and efficient one provided that differential expansion of the individual grains in the microstructure is accomplished, that flocculated conditions can be avoided and that the chemically modified material can be removed by flushing. © 1999 Published by Elsevier Science B.V. All rights reserved.

Keywords: Bentonite; Erosion; Microstructure; Salt; Slurry; Smectite

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1. Introduction

The Swedish Nuclear Fuel and Waste Management Company, SKB, is developing a system (SKB 1998a,b) for the management of spent nuclear fuel and other radioactive waste from nuclear power operation and other activities. In the reference system, KBS-3, there is a clay buffer between the canister containing the spent fuel and the crystalline bedrock.

One of the requirements of the disposal system is that it should be possible and feasible to retrieve the canisters even after they have been deposited and the surrounding bentonite has absorbed water to saturation point and developed the corresponding swelling pressure (SKB 1998a,b). This pressure and the associated 'gripping' of the canisters must be considered in a retrieval process since in cannot be assumed that the canisters can be removed solely by force without becoming damaged.

A number of methods have been investigated (Kalbantner and Sjöblom 1998) and preliminary ranking has been performed (Kalbantner and Sjöblom 1998). In one of the most promising alternatives, the bentonite is flushed with salt solution (containing, for instance, a few percents of sodium chloride) whereby the bentonite rapidly converts into a slurry.

The main principles of operation according to this method are as follows[1]: water containing between 5 and 10 wt% of calcium chloride or sodium chloride is flushed over the surface of the bentonite to be removed. This bentonite has a density which corresponds to a saturation density in a repository of ca 2.0 tons per cubic meter. The flushing is carried out under water using nozzles connected to a circulation pump which provides a pressure on the order of a few bars. In the process, the originally stiff bentonite becomes soft and readily removable by the relatively weak water jet. The removal of the softened bentonite uncovers previously relatively unaffected bentonite and exposes it to chemical attack. Thus, the process is based on a combination of chemical and low pressure hydrodynamical interactions.

The rate of removal may be on the order of half a meter per hour, at least for relatively dry bentonite. The potential capacity of this process is remarkable in view of the well-known sluggishness of the saturation of compacted bentonite with pure water[2].

The rapid rate of removal of compacted bentonite by means of flushing with salt solution mentioned above implies that a good potential exists for an efficient process. Ongoing work on developing such a process includes testing the rate of attack under diverse conditions with the intent to determine the sensibility of the process with respect to a number of relevant parameters such as the following:

- water content of the bentonite;
- type of salt in the salt solution;
- concentration of salt in the salt solution;
- density of the bentonite;
- composition of the water with which the bentonite has been contacted or saturated;
- concentration of the salt in the water with which the bentonite has been contacted or saturated; and
- modes of flushing of the water.

The results obtained to date (Bjurström 1997, Kalbantner et al., 1998; Kalbantner and Sjöblom 1998) indicate the following:

- the process is efficient under all reasonable repository conditions
- the rate of attack increases with decreasing water content of the bentonite;
- the concentration of salt in the solution must exceed a minimum value — for sodium and calcium chloride this value is in the range[3] 2–8 wt%;
- an increase in salt concentration above this value leads to a moderate increase in the rate of attack;
- a decrease in salt concentration below this value

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[1] It should be recognized that this method is under development and that the eventual process may differ from the one described here.

[2] It takes about a couple of months for water to fully saturate a specimen having a thickness of a few centimetres. The example relates to Wyoming bentonite (MX-80) kept at constant volume and having a density at full saturation of ca 2.0 g cm^{-3}.

[3] The appropriate value depends somewhat on the conditions.

leads to a very rapid decrease in the rate of attack;

- flushing of water strongly increases the rate of disintegration in cases where the chemical attack is effective; and
- flushing of water has no significant effect on the rate of disintegration in cases where the chemical attack is slow (fresh water).

2. Purpose and scope

When an industrial process like the present one is to be developed, and — amongst other things — the robustness of a process with regard to reasonable variations in the conditions is to be determined, it is preferable that such a basis comprises theoretical as well as empirical substance. Moreover, in the present case, a retrieval might take place perhaps more than a decade after the emplacement of the bentonite blocks. This is a relatively long time in comparison with the duration of the experiments which in most cases is — or can be expected to be — considerably shorter. Thus, an understanding of the mechanisms involved may be necessary in order for reliable assessments to be made regarding the applicability of the process.

In the Swedish programme (SKB, 1998a, b) extensive studies have been made regarding the interaction of water and various ions with compacted bentonite (Eriksen and Jansson, 1996; Karnland, 1995; Pusch, 1995; Pusch and Jacobsson, 1978; Pusch et al., 1988, 1990, 1992, 1995, 1998a,b; Yu and Neretnieks 1997). Most of the work has concerned bentonite with a low water ratio and having pore waters with low salt concentrations. However, some of the studies have concerned the effect of intruding salty groundwater (Pusch et al., 1992; Karnland 1998) and the possibility of enrichment of salt onto the hot canister (Karnland 1995). In the past, there has generally been little reason to investigate liquid systems or slurries although some work has been carried out on bentonite slurry injection (Pusch et al., 1988) into fractures in the rock.

The properties of bentonite slurries are, however, of great commercial interest in other areas and have therefore been the subject of extensive studies (Chilingarian and Vorabutr, 1983; Darley and Gray 1991, Dobiáš, 1993, Bailey, 1991, Grüven and Pollastro, 1992; Low 1961, 1979; Lummus and Azar, 1986; Van Olphen, 1977). For example, bentonite suspensions are used extensively in the oil industry to provide drilling fluids with strongly non-Newtonian behaviour. Such drilling fluids may show little resistance to flow at around the drilling head and at the same time provide a high resistance elsewhere so that debris formed in the drilling process is removed from the hole. Bentonite suspensions also cause filter cakes to build on the walls of the drill hole so that loss of drilling fluid into the geological formation is avoided.

The purpose of the work presented in this paper is to put together the behaviour of bentonite clay in the bentonite–water–salt system and to use this material as a basis for determining the mechanisms involved in the chemical–hydrodynamical method already described for uncovering the canister in a retrieval process. The identification and description of the mechanisms should be based on the present understanding of the systems as well as on the empirical data available on the disintegration of bentonite in salt solutions. The main emphasis in the literature search has been on dilute systems since this aspect has not been subjected to as many studies in the past as have systems with a low water content, cf above. Further details on the present work can be found in Sjöblom and Pusch (1998).

3. Some properties of the bentonite–water–salt system

For the purpose of the present paper only a limited number of chemical reactions are considered. Thus, the infinite silicate sheet molecules are assumed to take part in chemical reactions at the surface only and the actual basic structure is assumed to remain intact. The reactions are assumed to involve water together with ions of sodium and calcium. Excessive positive charge is assumed to be balanced by chloride ions.

Under these assumptions, the chemical reactions can be expected to involve ionic bonding together with dipolar bonding, especially hydrogen bonding. Under such conditions, it can be expected

Table 1
A summary of the interactions between montmorillonite, water, sodium chloride and calcium chloride

Water content	Total salt	Ca or Na	Inter-lamellar	Diffusive layer	Pore water
Low	Either	Either	Small	Small	Little
Some	High	Either	Small	Small	Some
Some	Low	Na	Extends	Extends	Little
Some	Low	Ca	Small	Some extension	Some
Abundant	High	Either	Small	Small	Abundant
Abundant	Low	Ca	Small	Some extension	Abundant
Abundant	Low	Na	Large extension	Large extension	Some or abundant

that most reactions which are thermodynamically possible also take place within a short period of time. There are two important exceptions, however. Firstly, reactions which require that species diffuse over large distances and, secondly, reactions which involve reorientation of large entities together with the simultaneous breaking and formation of a significant number of bonds (Sjöblom and Pusch, 1998).

The infinite silicate sheets carry negative charge which is counterbalanced by cations at or near the surface. In concentrated salt solutions, the counterions are close to the surface and in dilute systems the counterions form an electrostatic double layer further away from the surface.

The sheets form stacks which in the case of sodium rich bentonite may comprise a few sheets stacked on top of each other. The number of sheets in a stack tends to be higher in cases where the calcium/sodium ratio is high and where the individual sheets fit well on top of each other.

The distances between the sheets in a primary particle are strongly dependent on the availability of water, the sodium to calcium ratio and the ionic strength. The strongest swelling is encountered when the distance is below ca 1 nm which is the region of crystalline swelling. There is evidence suggesting that the water molecules are relatively ordered in this case (Sjöblom and Pusch, 1998; and references therein) which in turn suggests that the strong swelling pressures experienced are related to the tendency of hydrate water to form ordered structures involving hydrogen bonds. For distances above >1 nm, osmotic swelling takes place. This effect is strongest for low calcium to sodium ratios and low ionic strengths. The interactions in the bentonite–water–salt system are summarized in Table 1.

In systems with a low water content these effects are often observed in terms of swelling pressure.

In suspensions, the same basic phenomena show themselves in terms of dispersion, agglomeration and flocculation. In systems with a high ionic strength and in dilute systems with a high calcium to sodium ratio, the primary grains associate in a face to face pattern and form agglomerates. In dilute systems with a low calcium to sodium ratio aggregates are formed in which the edge of one primary particle (positively charged) binds to the face (negatively charged) of an adjacent one. (In systems with a low water content this corresponds to exfoliation, see further below). Under the latter conditions, but at high pH, the primary particles disperse as individual entities.

4. The general microstructural model

A model describing the behaviour of a buffer system must be considerably more specific than the compilation above based on the general clay literature. Moreover, the behaviour of a buffer is strongly dependent on the way in which it was prepared. The general microstructural model (GMM) developed by Pusch et al. (1990, 1995, 1998a,b) includes these features. The model is strongly phenomenological in nature, that is, a strong emphasis is put on the basic mechanisms involved and an understanding of the system as a whole. These features are highly advantageous in the present case when the model is to be extended to be applied as a tool to assess what mechanisms may be involved when a buffer is converted into a slurry using the chemical–hydrodynamical method.

Relevant tentative manufacturing details for the bentonite blocks include the following. Natural bentonite having a favourably low calcium to sodium ratio is excavated and partially dried in air. Further drying takes place in a rotary kiln whereafter the bentonite is crushed to a grain size <0.2 mm. Before compaction, the bentonite may be moistened again and compacted to high density blocks at a high pressure. During the compaction, the bentonite grains change shape[4], but the process is not driven to completion, that is, there is still porosity, and this porosity is not entirely filled with water. Moreover, the forces on the grains lead to migration of water into voids or regions of lower density. When the pressure is being released, some relaxation takes place but the patterns just described are nonetheless locked into the microstructure to a large extent. This microstructure still persists after the bentonite block has become saturated with water (under limited volume conditions).

In this structure, the grains are isotropic and expanded to hold two or three interlamellar hydrates. Spontaneous exfoliation of stacks of lamellae takes place from parts of the grains which were not compressed. This process leads to the formation of clay gel in the 'external' voids between the expanded grains as shown schematically in Fig. 1. These gels are assumed to have card-house structures with interconnected voids that form tortuos systems of channels with varying aperture, some of them representing dead ends and others continues water-bearing pores. The latter are responsible for the hydraulic and gas conductivities of the clay in bulk.

5. Proposed model for disintegration

The above described GMM model including the description on processes in the bentonite–water–salt system will be utilized here to derive a model for the conversion of compacted bentonite into a slurry using the chemical–hydrodynamical method.

The details of the disintegration process are highly dependent on the conditions, for example, degree of saturation of the bentonite, salt content of the bentonite, composition of the salt in the bentonite, salt content of the flush water, etc. In order to illuminate the principles of the interaction as well as the strategy of the approach, one particular case — a reference case — is described in some detail while the possible significance of other parameter combinations is discussed only in general (cf Discussion and conclusions).

5.1. Reference case

Let us assume that bentonite having a microstructure as described above is saturated with water. Let us also assume that the salt content of the saturated bentonite is considerably lower than that of the flush water. The composition and content of salt in the saturated bentonite is such that the low density parts of the microstructure form gels, that is, exfoliation has taken place and the primary particles are arranged in an edge to face pattern. The denser parts of the microstructure consists of aggregates (or grains) comprising stacks of primary particles.

Since the bentonite is assumed to be fully saturated, no capillary suction of water takes place. Instead, the salt water contacts the surface and at least the initial effect will have to be one of diffusion. For osmotic reasons, in combination with kinetic, water in low density regions is expected to diffuse into the salt water thus causing shrinkage of the material in contact with the salt water. In the denser parts of the microstructure, the aggregates will absorb water and swell. The most rapid encounter is expected to take place between the salt water and the low density regions.

The combined effect of these two processes is the opening up of a pore system in the low density regions. This pore system is being filled with water having a high salt content. This, in turn leads to aggregation of the previously flocculated material in the low density regions and a continued swelling

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[4] The change of shape may be mainly plastic (high water content) or include fracturing (low water content).

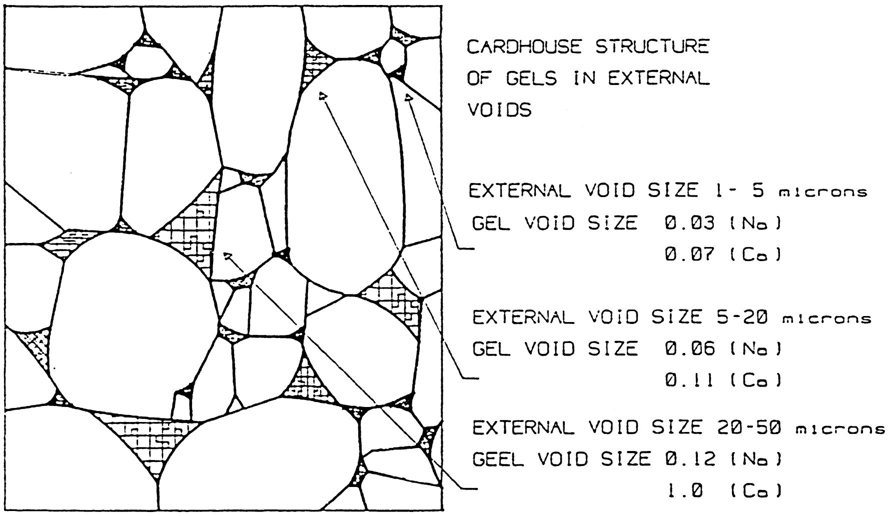

Fig. 1. Generalized microstructure of matured clay with gel in the 'external' voids.

in the high density regions. The latter swelling cannot be isotropic since the primary particles have extremely low height to diameter ratios and are stacked on top of each other at the same time as the expansion on swelling takes place mainly in a direction perpendicular to the silicate sheets.

The effects just described combine and lead to a differential expansion of the different constituents in the microstructure and a rapid opening up of a pore system. Simultaneously, these pores become filled with salt water which further promotes the pore and void formation processes which eventually leads to a disintegration of the bentonite microstructure.

It might be argued that the processes just described should not be as swift as observed since they to some extent include diffusion and also rearrangement of gel structure from flocculated to flocculated and aggregated form which involves rearrangement of large molecules. We still believe that they are indeed effective. Firstly, the aggregation process might not be necessary in order for the disintegration to take place. It may be sufficient that gel water is sucked out by osmosis (to diffuse into the salt water) so that pores are created. Secondly, formation or enlargement of channels in the microstructure can be expected to take place even if the aggregation process is grossly incomplete[5].

The flushing of water over the chemically modified surface enables reacted material to be removed and previously unaffected material to surface and thereby be made available for further chemical attack.

One important circumstance in both of the cases discussed (that is unsaturated and saturated bentonite) is that the product formed in the reaction between the bentonite and the salt water is aggregated and not just flocculated. This means that it cannot be expected that the aggregates would be held together (edge to face) so that the flow of water between the aggregates would be diffusion controlled. Instead, the aggregates can be expected to associate themselves to each other, face to face, and grow, even after they have been separated from the bulk bentonite. Such a process would lead to an increased water conductivity in, for example, a precipitate covering a bentonite surface.

Another ageing effect can also be expected to take place in the slurry formed. It has been

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[5] Already the reduction in the electrical repulsion between the primary grain surfaces as well as the improved possibilities for neutralization of the charges on the edges can be expected to have a significant effect.

described above that the water between the primary particles can be expected to move into the salt water. The completion of this process does not lead to equilibrium; actually it prevents equilibrium to develop. Complete equilibrium should involve not only water but also the salt. Thus salt should diffuse into the inter- and intralamellar water until the chemical activity is the same for all species in all sub-systems. This diffusion process will not take place initially, however, since water is then moving in the opposite direction. Only after this 'flow' has ceased will the salt move into the inter- and intralamellar regions. This secondary effect is not expected to lead to much change in the structure of the slurry; it will stabilize the stacking already developed.

5.2. Other cases

If the water contacting the bentonite has a high content of salt or if the calcium to sodium ratio is high, the low density regions might not appear in exfoliated face to edge form but instead in an aggregated form. In this case, an open pore system may exist and the hydraulic conductivity be considerably increased. Addition of salt water causes the aggregated low density material to shrink even further and the larger grains to swell. The combined effect is differential expansion, opening up of the pore system and inflow of flush water into the pore system.

If the bentonite is not fully saturated, the pore system enhances uptake of flush water into the microstructure by capillary suction which speeds up the process.

In contrast, if fresh water is used as flush water, the rate of disintegration becomes extremely slow. In cases where the bentonite is already saturated with water, the low density material is already exfoliated and arranged in a face to edge type of pattern. This pattern will persist even after the matter is contacted with fresh water. The larger aggregates will react and some exfoliation will be initiated. The gel formed will, however, cover the surface and provide a diffusion barrier which kinetically hinders further attack.

If fresh water is used as flush water and in cases where the bentonite is not initially saturated, some fresh water will enter the pore system. If the pores are wide, this uptake is an efficient process. The water will, however, react with the compacted bentonite and form gel which closes the pores and hinders further attack. If the pores are small, water will react only at or near the surface to form protective gel there.

Flushing of bentonite surfaces under fresh water conditions leads to slow disintegration. The primary grains are attached to each other by several contacts and the contacts to any individual grain will have to be broken more or less at the same time in order for the particle to disperse into the water. As mentioned above, this type of process can be expected to take place at a slow rate.

6. Discussion and conclusions

The work and conclusions presented above refers to work in progress. This means that all pertinent parameter combinations have not yet been subject to testing and there may still be room for alternative interpretations and certainly for supplementary ones. The picture which unveils is, however, one showing the chemical–hydrodynamical slurry forming process to be a robust and efficient one for use to uncover a deposited canister in conjunction with a retrieval operation.

Strong support to this picture is accrued from the 'theoretical' considerations made above provided that:

- the chemistry and microstructure is such that:
  - * differential expansion can be accomplished;
  - * flocculated conditions can be avoided; and that the chemically modified material can be removed by flushing.

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