Research

The Effects of High Salinity Groundwater on the Performance of Clay Barriers

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SKi

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SKI Perspective

Background

The buffer and backfill are key components of a KBS-3 type repository for spent nuclear fuel. The buffer, composed of compacted bentonite blocks, protects the copper canisters, and the backfill prevent excessive groundwater flow within the repository environment. The function of a bentonite based buffer and backfill rely on the sealing ability of these materials due to the development of a swelling pressure. Since it is well-known that an increase in groundwater salinity tends to reduce the swelling pressure, it is essential to confirm that the functional requirements of the buffer and backfill will be maintained in spite of the increases in groundwater salinity that can reasonably be expected. An increase in groundwater salinity at a repository site may occur due to the ingress of seawater or saline groundwater from great depth. This report describes the mechanistic understanding of bentonite swelling and its relationship with groundwater salinity. The experimental basis for the theoretical interpretations and the application of the theory to buffer and backfill respectively, are also covered.

The bentonite within buffer and backfill may under unfavourable circumstances be partially eroded through a recently discovered mechanism termed "piping/erosion". This might happen in particular during the operational phase of the repository and the mechanism is also related to the salinity of groundwater within the repository at that time. This report summarises the relatively limited information which is available on this subject. The possible influence of groundwater salinity on smecitite stability is also briefly addressed.

Purpose of the project

The purpose of this project is to summarise the current state-of-the-art and in particular review other sources of information apart from those originating from the SKB programme.

Results

The results indicate that sufficient swelling pressure will be maintained in the buffer in spite of very high levels of groundwater salinity due to the high density of the compressed bentonite blocks. For the lower density backfill, however, results indicate that present backfill designs (e.g. tested in the Äspö HRL) could be sensitive to increases in groundwater salinity. More work is clearly needed for the optimisation of the backfill performance and ensuring its robust function throughout the timescales that must be addressed within safety assessment.

Future work

More detailed review and evaluation of the development of new backfill designs will be a high priority subject in the not to distant future. There is also a need to follow-up ongoing efforts to better understand and control the "piping/erosion" mechanism.

Project Information

SKI Project Manager: Bo Strömberg
Project Identification Number: 200509042

Summary

Potential changes in groundwater chemistry during the operational or post-closure periods of the Swedish repository for spent fuel could affect the performance of both the bentonite buffer and repository backfill. For example, the up-coning of saline groundwater could lead to decreased swelling pressures in both the bentonite buffer and tunnel backfills, and could also induce 'piping'. SKB is considering these issues as part of its 'SR-Can' safety assessment. This report reviews evidence for the behaviour of swelling clays in groundwaters of varying salinity with special relevance to the SKB programme.

Smectite clays can absorb water into clay inter-layers with the most important parameters being: the surface density of charge of the clay (swelling decreases with increasing charge density); the charge and solvation behaviour of the inter-layer ions (swelling is greatest for ions such as sodium); and the electrolyte concentration or activity of water (swelling decreases with increasing salinity of the contacting solution). Two categories of swelling are generally observed: *innercrystalline swelling* caused by the hydration of the exchangeable cations in the dry clay; and *osmotic swelling*, resulting from concentration gradients in ion concentrations between clay surfaces and pore water. Several models exist to interpret and predict the swelling behaviour of clays and these consist of: empirical models; diffuse double-layer models; the DLVO model; and thermodynamic models. Of these, only thermodynamic models have the capacity to predict clay swelling behaviour in saline pore fluids.

SKB currently prefer an interpretation of clay swelling pressure where clay particles are viewed as 'macro-ions' and the entire clay-water system can be considered as a 'polyelectrolyte'. SKB use the term 'Donnan exclusion' to estimate the amount of introduced ions into the clay and hence the amount of reduced swelling pressure due to contact with a saline solution. Donnan exclusion is the process whereby the migration of anions through the narrow aqueous film surrounding clay platelets is restricted due to the repulsion by the negative charge of the clay platelets. SKB's experimental work shows that:

- There is an exponential relation between swelling pressure and mean basal inter-lamellar spacing of the clay.
- Ions from the external electrolyte solution enter the clay volume, leading to decreased water activity in the clay.
- Introduced ions enter the swelling pressure-inducing volume in the clay.
- Swelling pressure is systematically reduced at all clay densities by interaction with saline fluids.

SKB believes that if the buffer density exceeds 1.9 Mg m^{-3}, the functional requirements for the swelling pressure to exceed 1 MPa will be fulfilled, even with groundwater salinities equivalent to 3 M NaCl. Similarly, the functional requirement for buffer hydraulic conductivity of 10^{-12} m s^{-1} will also be fulfilled if the buffer density is greater than 1.8 Mg m^{-3}, and with NaCl equivalent salinity equal to 3M (~175 g l^{-1} TDS).

A review of work carried out elsewhere related to the swelling of montmorillonitic clays shows that the mechanistic understanding of such processes is less well advanced than that presented by SKB. The interpretation of clay swelling by Japanese researchers relies upon the application of the diffuse double layer theory, which has been shown by SKB and others to be inadequate to describe clay swelling pressures in saline pore fluids. Work in Germany has focused on the acquisition of a large dataset of swelling pressures in saline pore fluids, rather than mechanistic interpretation of such data.

Consideration of all this information indicates that groundwater salinity (up to 3M NaCl equivalent) will not have a significant impact upon buffer swelling capacity if densities at emplacement are 1.9 Mg m^{-3} or greater.

Backfill materials are even more susceptible to loss of swelling pressure in saline groundwaters. SKB is currently studying several different designs for tunnel and repository backfill. With regard to salinity effects, they state that a hydraulic conductivity of 10^{-10} m s^{-1} and a swelling pressure > 0.1 MPa at a groundwater TDS of 35 g l^{-1} is the target for this assessment. According to the results of the Backfill and Plug test, the 'concept A' backfill (SKB's current reference backfill concept) had a density of 1.7 Mg m^{-3}, a hydraulic conductivity of 4 10^{-10} m s^{-1}, a compressibility of 30 MPa and a swelling pressure of 0.15 - 0.2 MPa (all with a groundwater salinity of 1.2 %

NaCl). These values are deemed acceptable by SKB, except for the slightly too high hydraulic conductivity. However, it should be noted that SKB had to increase the proportion of clay in the mixture from 15 % (reference composition) to 30 % to achieve these properties. It seems certain therefore that during routine backfilling operations with the potential for non-ideal grain size distribution, piping, and a groundwater salinity in excess of 1.2 %, the reference backfill composition (15 % clay) will not perform to SKB's functional requirements. SKB continues its research in this area in conjunction with Posiva to assess different backfill formulations. Research on tunnel backfilling in Canada suggests that an initial density of at least 0.9 Mg m^{-3} is required to maintain a nominal swelling pressure of 0.1 MPa. Canadian tunnel backfill contains much less clay (6 % by dry mass) than the SKB variety, but a much higher density of 2.1 Mg m^{-3} (equivalent to an effective clay dry density of 0.46 Mg m^{-3}).

SKB considers that if groundwater inflow in fractures in deposition holes exceeds that which can be absorbed by bentonite swelling, there will be a water pressure in the fracture acting on the buffer which may lead to piping. Piping is the erosion of the clay along a linear feature. SKB believe that piping will only occur before full saturation of the buffer and is of concern during the operational phase of the repository. Piping is a complex process which increases with water pressure and groundwater salinity. SKB continue to research this problem through laboratory and in situ tests. The problem of piping is also germane to repository backfilling. SKB consider that it may be difficult to derive a solution to water inflow during backfill installation. Consequently, the backfill needs to have enough swelling ability so that piping channels can be healed once a tunnel has been sealed by plugging. All this must be placed in context of the rate of backfilling which SKB hopes to be in the order of 6 m per day.

Research conducted by SKB and elsewhere suggests that the long-term effects of montmorillonite degradation due to the presence of saline groundwater will consist mainly of formation of beidellite or kaolinite.

Contents

1   Introduction

Potential changes in groundwater chemistry during the operational or post-closure periods of the Swedish repository for spent fuel could affect the performance of both the bentonite buffer and repository backfill. For example, the introduction of dilute groundwaters during drawdown could increase the potential for bentonite erosion and/or the production of colloids. Alternatively, the up-coning of saline groundwater could lead to decreased swelling pressures in both the bentonite buffer and tunnel backfills, and could also induce 'piping'. SKB is considering these issues as part of its 'SR-Can' safety assessment (SKB, 2004a, b, c). Currently, SKB envisages the presence of two water types at its repository sites: fresh waters with a bicarbonate imprint at less than 200 m depth; and brackish-marine waters with Cl^- contents up to 6 g l^{-1} (10 g l^{-1} TDS) (SKB, 2004b). The most saline groundwater being considered by SKB in any up-coning process has 47.2 g/l TDS and is exemplified by a water from the Laxemar borehole at 1350 m depth (SKB, 2004b).

For SR-Can, SKB concludes that if the buffer density exceeds 1.9 Mg m^{-3}, the functional requirements for the swelling pressure to exceed 1 MPa will be fulfilled, even with groundwater salinities equivalent to 3 M NaCl (SKB, 2004b). Similarly, the functional requirement for buffer hydraulic conductivity of 10^{-12} m s^{-1} will also be fulfilled if the buffer density is greater than 1.8 Mg m^{-3}, and with NaCl equivalent salinity equal to 3M (SKB, 2004b). SKB also concludes that the swelling pressure criterion is likely to be met for a MX-80 bentonite/crushed rock backfill of 1.7 Mg m^{-3} mixed dry density at low salinities, but not for a backfill employing Milos bentonite (SKB, 2004b). The hydraulic conductivity functional criterion is likely to be met for both backfill types at all salinities (SKB, 2004b).

SKB rely on a 'buffer rheology model' to predict likely behaviour of the buffer. This model is described in SKB (2004b) and in more detail in Hedin (2004), and relies upon the calculation of buffer density assuming that upward expansion of the buffer is balanced by friction against the walls of the deposition hole and the force exerted by the compressed tunnel backfill. This sub-model can handle the interaction with saline

groundwater through consideration of the osmotic effects described by Karnland et al. (2002).

This report reviews evidence for the behaviour of swelling clays in groundwaters of varying salinity with special relevance to the SKB programme.

2 Clay swelling

2.1 Fundamental clay behaviour

Smectite clays can absorb water into clay inter-layers with the most important parameters being:

- the surface density of charge of the clay (swelling decreases with increasing charge density);
- the charge and solvation behaviour of the inter-layer ions (swelling is greatest for ions such as sodium);
- and the electrolyte concentration or activity of water (swelling decreases with increasing salinity of the contacting solution).

Two categories of swelling are generally observed in clays (Madsen and Müller-VonMoos, 1989):

- innercrystalline swelling caused by the hydration of the exchangeable cations in the dry clay is determined to a large extent by the layer charge and the hydration properties of the interlayer cations. A maximum of 4 water layers may be emplaced by this process.
- More extensive swelling may occur by osmotic swelling resulting from concentration gradients in ion concentrations between clay surfaces and pore water.

Innercrystalline swelling is associated with expansion in discrete steps corresponding to the intercalation of monolayers of water into the clay structure, whereas osmotic swelling is associated with a continuous process. To avoid any inferences about causal mechanisms, the terms 'short-range swelling' and 'long-range swelling' have been used.

2.1.1 Innercrystalline swelling

Madsen and Müller-VonMoos (1989) describe the clay swelling process in montmorillonite. According to them, innercrystalline swelling may result in a doubling of clay volume and is generally stepwise (*Figure 1*). Emplacement of the first water layer leads to a layer widening of 0.25 nm. The cations are partly coordinated by the oxygens of the siloxane surface. With two water layers, the interlayer cations are coordinated octahedrally. With further water uptake, the coordinated octahedron alters its orientation. This stepwise nature of the layer widening process may be examined using water vapour adsorption isotherms (*Figure 2*).

The swelling pressure due to innercrystalline swelling can be calculated from the water vapour adsorption isotherms. In sodium montmorillonite, the sodium ions move to the layer surfaces as more water is taken up. Electrical double layers are built up which ultimately lead to disintegration of the montmorillonite into individual layers. Calcium montmorillonite behaves very differently from the sodium variety, in that swelling generally ceases once the distance between clay layers reaches about 1 nm. The calcium ions remain on the plane halfway between neighbouring layers and continue to exert an electrostatic attraction between them. Double layers are only formed on the outer surfaces of Ca-montmorillonite particles. Glaeser and Méring (1968) investigated the microscale swelling of Ca-smectite by XRD and showed that the transition from one to two layers of adsorbed water corresponded to a water activity of 0.2, whereas osmotic swelling started at water activities greater than 0.9.

Slade et al. (1991) have shown that layer charge affects swelling, with swelling decreasing as the surface density of charge increased. In their experiments, they noted that low layer charge clays like Wyoming bentonite, had greater swelling properties with 001 spacings increasing from 15.5 to 18.5 Å as NaCl concentrations in the pore fluid were decreased. This expansion corresponds to a transition from two to three sheets of water between the silicate layers. Slade et al. (1991) consider that both interlayer cations and the cations in the external solution compete for water molecules.
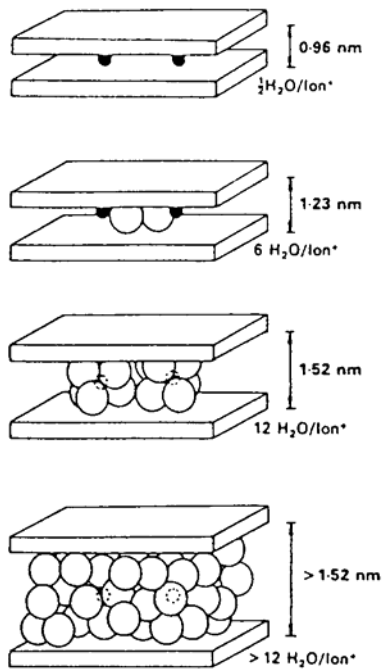
Figure 1: Innercrystalline swelling of sodium montmorillonite showing the change of interlayer distances with stepwise increases in the number of water molecules. From Madsen and Müller-VonMoos (1989).
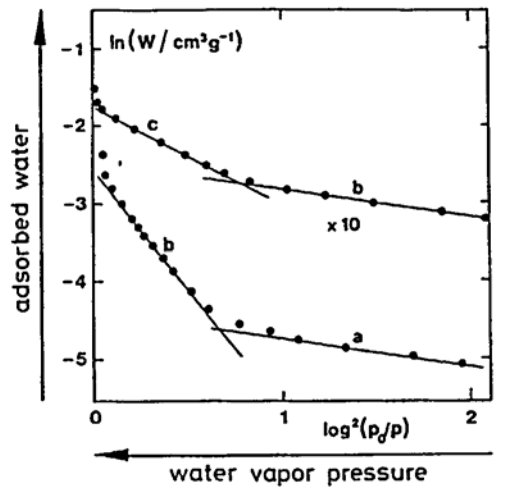

Figure 2: Water vapour adsorption isotherm for Wyoming bentonite at 20 °C. Sections b and c correspond to the interaction of the first and second water layers, respectively. The values on the top curve have been magnified ten times. W = water content, p = relative water vapour pressure, p_0 = water vapour pressure at saturation. From Madsen and Müller-VonMoos (1989).

The interlayer cation concentration is fixed by the charge on the clay and is very high (~ 4 M). If no forces other than cation hydration were involved, very high electrolyte concentrations would be required to limit swelling. However, interlayer forces are a balance between cation hydration, electrostatic, and van der Waal's forces. The tendency of the interlayer cations to hydrate is accompanied by interlayer expansion that is opposed to electrostatic attraction between the cations and the clay surfaces. Whereas the tendency to take up water increases linearly with interlayer cation concentration (i.e. clay charge), the opposing electrostatic forces increase with charge, much more rapidly than the forces causing swelling. Consequently, swelling becomes less with increasing charge. Commercial montmorillonites are at the low charge end of the smectite series, which gives them their desirable swelling properties.

2.1.2 Osmotic swelling

Osmotic swelling operates over larger distances than innercrystalline swelling and in sodium montmorillonite can result in total separation of clay layers. Because the interlayer ions are fixed for electrostatic reasons, water is taken up into the interlayer spaces to balance concentration, provided there is a higher concentration in the interlayer spaces. Osmotic swelling depends to a large extent on the electrolyte concentration and the valency of the dissolved ions. Innercrystalline swelling, on the other hand, depends only slightly on these factors. The driving force for osmotic swelling is the large difference in concentration between the ions held electrostatically to the clay surface and the ions in the pore water of the clay (*Figure 3*). The negatively charged clay surface and the cloud of ions form the diffuse electrostatic double layer. Increasing the salinity of the pore water removes water from between the clay layers and decreases the swelling pressure. Similarly, conversion of the Na-montmorillonite to the Ca-form reduces the swelling pressure. Since the osmotic pressure is a function of the ion concentrations, the repulsive force per unit area can be derived directly from the excess ion concentration in the plane midway between the clay layers:
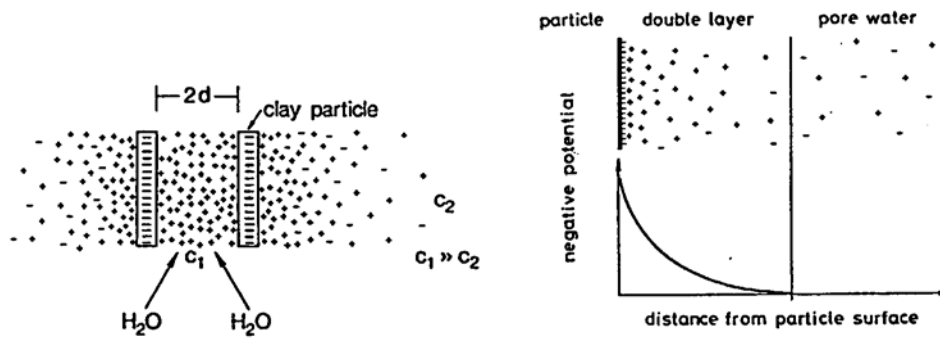
$$P_s = 2nkT(\cosh u - 1) \tag{1}$$

Figure 3: Two negatively charged clay layers with ion cloud and illustration of the diffuse double layer and ions in the pore water. The ion concentration C_1 between the layers is much higher than the ion concentration C_2 in the pore water. Equilibration of the concentrations can only be achieved though the penetration of water into the space between clay layers since the interlayer cations are fixed electrostatically by the negative charge of the layers (osmotic swelling). From Madsen and Müller-VonMoos (1989).

where n = ion concentration away from the clay surface; k = Boltzmann constant; u = electric potential at the plane midway between the layers (calculated using the Boltzmann distribution law).

Bentonites can be expected to behave as semi-permeable membranes. At high compaction, diffuse double layers may overlap and make up the whole pore solution (Keijzer and Loch, 2001). Compaction results in a higher concentration of cations and a lower concentration of anions in the double layer with respect to the equilibrium solution. At sufficient compaction, the water film present in the narrow pores between the clay layers is dominated by the double layers and the electrical restrictions they impose. Anions attempting to migrate through the narrow aqueous film are repelled by the negative charge of the clay platelets. This is known as 'negative adsorption' or 'Donnan exclusion' (Mitchell, 1993; Horseman et al., 1996). To maintain electrical neutrality in the external solution, cations will tend to remain with their co-ions. Thus, their movement across the clay will also be restricted (Fritz, 1986). Water and uncharged solutes have unrestricted access across the membrane.

2.2 Models of clay swelling behaviour

Several models are available for the prediction of swelling pressure in montmorillonite-type clays and these are reviewed in Grauer (1986) and Karnland (1997). Essentially, the models are of the following types:

- empirical models.
- Diffuse double-layer models.
- The DLVO model.
- Thermodynamic models.

2.2.1 Empirical models

Empirical models are attractive because of their simplicity, but data fitting sometimes necessitates the use of negative values for clay interlamellar distances, thus questioning the physical significance of the models (Karnland, 1997). Low (1980) proposed the following expression:

$$\ln(P_s + 1) = \alpha \frac{m_c}{m_w} + \ln B \qquad (2)$$

where P_s is swelling pressure, m_c and m_w are masses of clay and water, respectively, and α and B are adjustable parameters. Direct measurement of the swelling pressure of 35 different montmorillonites showed a relationship between P_s and the mass ratio of montmorillonite to water m_c/m_w (*Figure 4*). α and B are constants that are characteristic of the montmorillonite and probably of the solution applied. This means that the impact of solution composition on the swelling pressure is concealed in the empirical parameters. Moreover, this model does not take into consideration the degree of compaction of the montmorillonite.
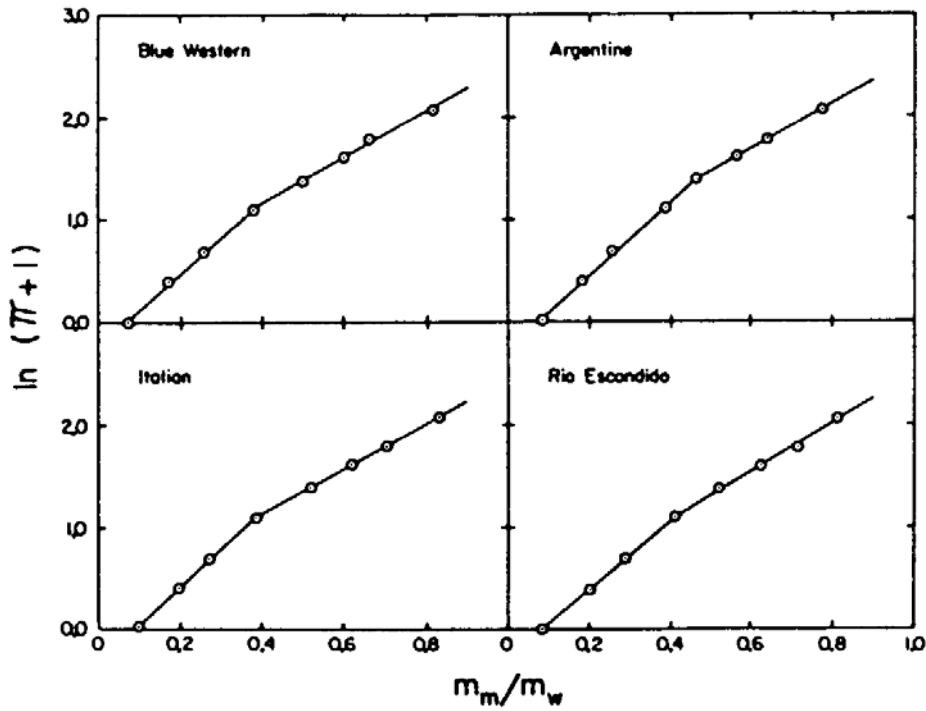
Figure 4: The relationship between swelling pressure and montmorillonite/water ratio for a group of different montmorillonites. From Low (1980).

More recently, workers at GRS in Germany researching the behaviour of MX-80 bentonite contacted by brines have come up with the following empirical expression to describe swelling pressures (Herbert and Moog, 2000):

$$\ln P_s = -\frac{A\left(m_{Na^+}, m_{K^+}, m_{Mg^{2+}+Ca^{2+}}\right)}{\rho_{red}} + B\left(m_{Na^+}, m_{K^+}, m_{Mg^{2+}+Ca^{2+}}\right) \qquad (3)$$

where m_i denotes the molality of species i in solution, ρ_{red} is the reduced dry density, and A and B are adjustable parameters which are a function of solution composition. Herbert and Moog (2000) recognise that a large matrix of experimental results is necessary to be able to derive the various parameters concerned.

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2.2.2 Double layer models

Double layer models use the theory developed by Gouy and Chapman in 1910 and account for both the repelling forces between clay particles and attractive van der Waals forces. Double layer models suffer from the fact that in compacted bentonite, there is a distribution of particle separation distances, which may be well below 10 Å. This means that the nominal clay double layer cannot extend undisturbed into pore space. These small dimensions therefore pose another problem regarding the definition of the concentration of any ion in the pore space. Depending on the size of the pores, the concentration cannot be the same as in a hypothetical bulk solution in equilibrium with the same cations attached to the clay surface. The theory of electrical double layers creates the idea of sorbed cations arranged within a diffuse swarm in the vicinity of the clay surface. When the mean diameter of the pores in the compacted bentonite becomes smaller than twice the value of the thickness of the double layer, the question arises whether pore water exists in any form. Indeed, Low (1987) argued that because < 2 % of exchangeable cations on smectites are dissociated, double layer repulsion can only make a small contribution to swelling pressure.

Karnland (1997) applied the DDL model to MX-80 bentonite in solutions of variable NaCl content and noted that the capacity of the double layer model to predict swelling pressures in saline solutions with NaCl > 0.5 % was very limited. Calculations of swelling pressure using this model fit measured values reasonably well up to pressures of 30 MPa, but at high salt concentrations, the measured pressures exceed calculated values (Karnland, 1997).

In an experimental study of the effects of different interlayer cations and electrolyte concentrations on the swelling pressure and interlayer distances in montmorillonite, Zhang et al. (1995) concluded that the effect of the electrolyte concentration was not described quantitatively by electric double-layer theory and considered that the electrolyte reduced swelling by disrupting the hydration shells surrounding the montmorillonite particles.

In general, double layer models involve inconsistencies in their mathematical treatment and there are issues concerning parameterisation of the models (Karnland, 1997). This

model does not produce sensible results for ions other than Na^+, or at high salt concentrations.

2.2.3 DLVO Theory

The DLVO model is named after its various proponents – Derjaguin, Landau, Vervey, and Overbeck and describes the interactions between charged surfaces in aqueous solutions by consideration of electrostatic repulsion and attraction by van der Waal's forces. The theory has its basis in colloid chemistry, but cannot in general be applied to evaluate clay swelling (Grauer, 1986). DLVO theory predicts a decreasing surface repulsion of clay platelets with increasing electrolyte concentration which becomes an attraction at high ionic strengths. For very small interparticular distances, the theory predicts an attraction for all ionic strengths, which is contrary to experimental evidence. The DLVO model thus suffers the same weaknesses as double-layer theory.

DLVO theory gives a quantitative interpretation of the swelling of Na-smectite, but the hysteresis between the first compaction and subsequent expansion indicates that other forces are involved in clay aggregates. For alkali ions, agreement between swelling results and theory decreases with the polarisability and the hydration energy of the counterion. In general, this can be explained by a surface adsorption mechanism. van Olphen (1977) discussed interlayer forces in bentonite for small interlayer separations and showed that hydration effects become important, leading to deviation from DLVO theory. DLVO theory cannot explain innercrystalline swelling.

2.2.4 Thermodynamic models

Thermodynamic models describe the macroscopic properties of the clay-water system and do not lend themselves to consideration of microscopic properties (Sposito, 1972). Sposito (1972) proposed the following definition for swelling pressure:

$$P_s = -\frac{\Delta\mu_w}{\bar{v}_w} \qquad (4)$$

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where $\Delta\mu_w$ is the change in water chemical potential when a unit mass of water is transferred from pure liquid water into the clay paste, and $\bar{v}_w$ is the partial molal volume of water at constant temperature, pressure and mass of clay. At low water contents, the density of the absorbed water is lower than in the fluid phase so that $\bar{v}_w > 1$ cm^3 g^{-1}. Oliphant and Low (1982) used the following empirical correction:

$$\bar{v}_w = 1.002\exp\left(0.036\frac{m_w}{m_s}\right) \tag{5}$$

where m_w and m_s are the mass of water and clay, respectively. Low and Anderson (1958) suggested a relationship between the swelling pressure and the osmotic pressure of the solution in equilibrium with the clay:

$$P_s = -\frac{RT}{M_w\bar{v}_w}\ln\frac{p}{p_0} \tag{6}$$

where M_w is the molecular weight of water, and p and p_0 are the vapour pressure of adsorbed and pure water, respectively. The above expression was derived from the following relationships between swelling pressure and relative partial free energy of water in the clay-water system, $\bar{G}_w - G_w^0$:

$$RT\ln\frac{p}{p_0} = \bar{G}_w - G_w^0 = M_w\left(\bar{g}_w - g_w^0\right) \tag{7}$$

and

$$\bar{g}_w - g_w^0 = -\bar{v}_w \cdot P_s \tag{8}$$

where $\bar{g}_w - g_w^0$ is the relative partial specific free energy of water in the clay-water system. Low (1987) considered clays equilibrated with binary electrolytes through the following:

$$P_s = -\frac{RT}{M_w \bar{v}_w} \ln\left(\frac{p}{p_0}\right) - \left(-\frac{RT}{M_w \bar{v}_w} \ln\left(\frac{p_e}{p_0}\right)\right) \qquad (9)$$

where p_e is the vapour pressure of the surrounding electrolyte solution. The first term in equation (9) represents the swelling pressure of the clay and the second term addresses the osmotic pressure of the surrounding salt solution.

3 Clay swelling and buffer behaviour

3.1 SKB approach

SKB currently prefers an interpretation of clay swelling pressure where clay particles are considered as macro-ions and the entire clay-water system may be viewed as a 'polyelectrolyte' (*Figure 5*). SKB has used the thermodynamic model of Low and Anderson (1958), with modifications using 'Donnan' relationships for saline systems. In broad terms, SKB state that the chemical potential or molar Gibbs energy of the clay-water system may be represented by (Karnland et al., 2002):

$$\mu_w = \mu_0 + RT \ln \frac{p_c}{p_0} + RT \ln \frac{p_e}{p_0} + m_w g h + \overline{V}_w \cdot P + zFE + \ldots \tag{10}$$

where μ_0 is the chemical potential of free water, the second and third terms represent the energy contribution from the clay and electrolyte respectively, p_c, p_0, and p_e represent the vapour pressure set by the clay, pure water, and an electrolyte, respectively. The fourth term represents the contribution from hydrostatic pressure, where g is the gravity constant and h is height. The fifth term represents water pressure of another origin, where $\overline{V}_w$ is the molar volume of water. The last term represents the contribution from electric origin. SKB has adapted the model of Low and Anderson (1958) by direct measurement of swelling pressure, water activity, and pore water concentrations in bentonite clays at different clay, salt, and water conditions. These measurements show that:

- there is an exponential relation between swelling pressure and mean basal inter-lamellar spacing of the clay.
- Ions from the external electrolyte solution enter the clay volume, leading to decreased water activity in the clay.
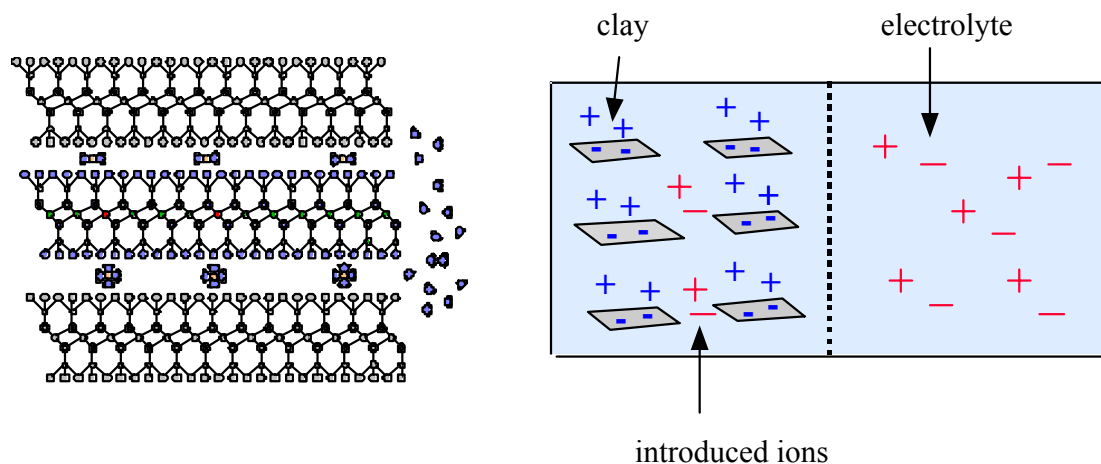
Figure 5 SKB's view of the clay-electrolyte system. The clay is seen as a 'soluble polyelectrolyte', contributing positively and negatively charged ions to the clay-water system. An osmotic equilibrium is set up between the clay and external electrolyte, involving diffusion of water molecules and ionic species. The osmotic pressure created reduces bentonite swelling in saline solutions.

- Introduced ions enter the swelling pressure-inducing volume in the clay.
- Swelling pressure is systematically reduced at all clay densities by interaction with saline fluids.

Consideration of *Figure 3* implies that decreases in swelling pressure in bentonites contacted by saline solutions are accounted for by diffusion of water molecules alone. However, SKB measurements show that ionic species from external saline solutions are transported into the clay. SKB view these introduced ions as 'an additional osmotic component' (Karnland et al., 2002), acting on the clay-water volume, such that the difference in concentration between external and introduced ions leads to a drop in swelling pressure.

Application of the thermodynamic relationship developed by Low (equation 6) in experiments with high salt concentrations by SKB underestimated measured swelling pressures as a consequence of the migration of ionic species from the external electrolyte into the clay-water system and the resulting reduction of partial molal free energy of water in the clay-water system. SKB therefore applied the following relationship to address the migration of ionic species into the clay:
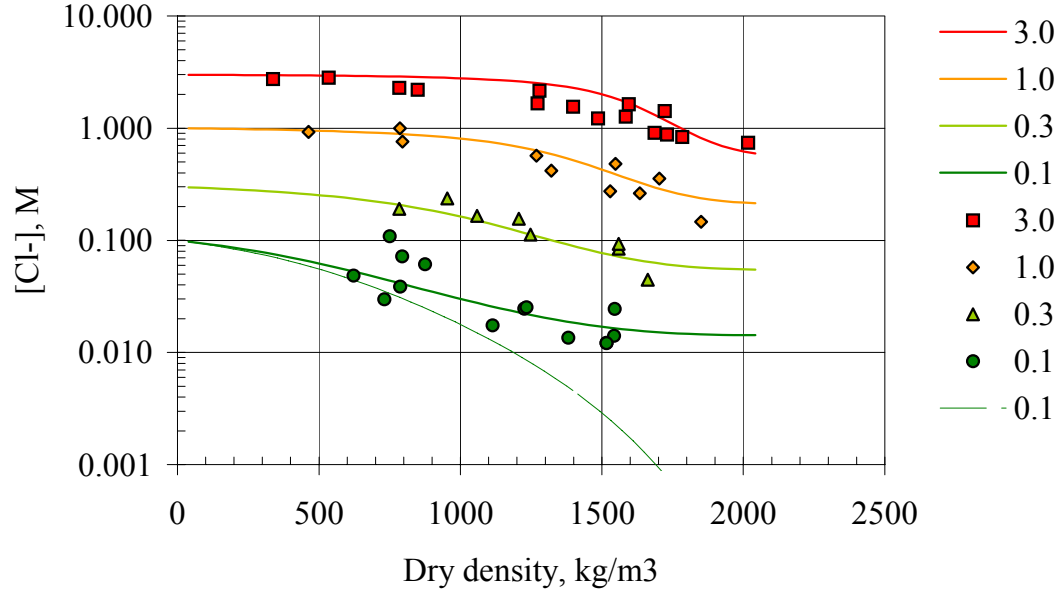
Figure 6: Measured (points) and calculated (lines) chloride concentrations in clay versus dry clay density from bentonite swelling experiments at different electrolyte concentrations. The concentrations of NaCl are shown to the right of the Figure. For comparison, 0.1 M results without adding the contribution from ion association is shown as a dashed line. From Karnland et al. (2002).

$$P_s = -\frac{RT}{M_w \overline{v}_w} \ln\left(\frac{p}{p_0}\right) - \left(-\frac{RT}{M_w \overline{v}_w} \ln\left(\frac{p_{ie}}{p_0}\right)\right) - \left(-\frac{RT}{M \overline{v}_w} \ln\left(\frac{p_e}{p_0}\right)\right) \qquad (11)$$

where p_{ie} is the vapour pressure in a water solution with a concentration corresponding to the increase in ion concentration in the clay-water system as saturated by an external electrolyte solution.

SKB used 'Donnan exclusion' to estimate the amount of introduced ions into the clay and hence the amount of reduced swelling pressure due to contact with a saline solution (Karnland, 1997; Karnland et al., 2002). Donnan exclusion is the term given to the restriction of the migration of anions through the narrow aqueous film surrounding clay platelets due to the repulsion by the negative charge of the clay platelets. In order for electrical neutrality to be maintained, cations remain with the anions so that their migration is also restricted. In other words, the measured concentration of cations and anions in the clay decreases with increasing compaction of the clay due to this process (*Figure 6*). Consequently, SKB determined the concentration of sodium ions in the clay using the following:
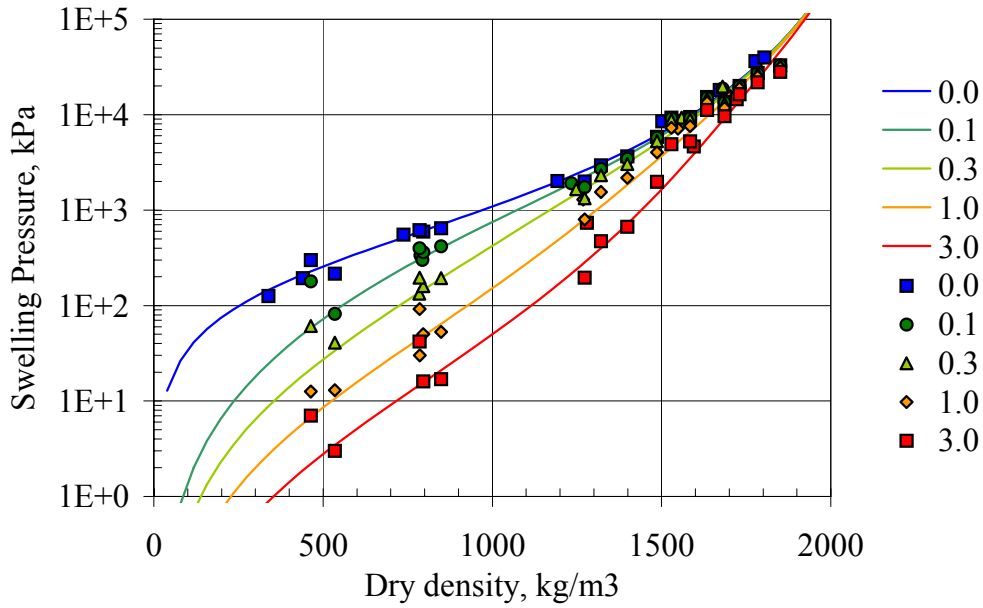
Figure 7: Effects of increased salinity on clay swelling pressure. The concentrations of NaCl solutions (M) are shown to the right of the Figure. From Karnland et al. (2002).

$$[Na^+_{ce}] = \frac{-[Na^+_{cc}] \pm \sqrt{[Na^+_{cc}]^2 + 4 \cdot [Na^+_e]^2}}{2} \qquad (12)$$

where $[Na^+_{ce}]$ is the concentration of introduced electrolyte ions, $[Na^+_{cc}]$ is the concentration of original charge-compensating ions in the clay, and $[Na^+_e]$ is the concentration of ions in the electrolyte.

SKB concludes that if the buffer density exceeds 1.9 Mg m^{-3}, the functional requirements for the swelling pressure to exceed 1 MPa will be fulfilled, with groundwater salinities up to 3 M NaCl (SKB, 2004b) (*Figure 7*). Similarly, the functional requirement for buffer hydraulic conductivity of 10^{-12} m s^{-1} will also be fulfilled if the buffer density is greater than 1.8 Mg m^{-3}, even for 3M NaCl equivalent salinity (SKB, 2004b).

Karnland et al. (2005) have extended this work to consider the swelling properties of bentonites from Greece (Deponit-CaN), India, Germany, the Czech Republic and Denmark. Experiments measured hydraulic conductivities as well as swelling pressure

in NaCl solutions of 0.1, 0.3, 1.0, and 3.0 M ionic strength. The swelling behaviour of Ca-montmorillonite is very different from Na-montmorillonite because innercrystalline swelling is much less than the Na-variety (see Section 2.1.1). SKB recognise that the Ca-bentonite from Milos must be conditioned with sodium for it to perform in a similar fashion to MX-80 bentonite. SKB has shown that Na-conditioned Milos bentonite has similar properties to Wyoming MX-80.

3.1.1 Treatment of clay swelling behaviour in SR-Can

For the SR-Can assessment, SKB considers that the swelling pressure of the buffer under fully-saturated conditions is a function of the cation exchange capacity of the clay, the clay density, and the ionic composition of the surrounding groundwater (Hedin, 2004). According to Hedin (2004), the relationship between swelling pressure and clay density for freshwater is:

$$P_s^{fresh} = AT \left(\exp \left(B \frac{\rho_{solid} \left(\rho_{clay} - \rho_{water} \right)}{\rho_{water} \left(\rho_{solid} - \rho_{clay} \right)} \right) - 1 \right) \tag{1}$$

where A and B are fitting parameters, T is temperature (°K), and ρ_{clay}, ρ_{water}, and ρ_{solid} are the densities of saturated clay, water, and solid clay particles, respectively.

For saline groundwater, Hedin (2004) considers that the swelling pressure will be reduced due to osmotic effects, leading to a Donnan equilibrium. This loss of pressure is confirmed by results from laboratory experiments (Karnland, 1997). Hedin (2004) deduces the following relationship for the clay swelling pressure in an external NaCl concentration C [M] where Na$^+$ is the adsorbed cation on the clay:

$$P_s^{saline} = \sqrt{\left(P_s^{fresh} \right)^2 + \left(2RTC\alpha_d \right)^2} - 2RTC\alpha_d \tag{13}$$

where P_s is the swelling pressure in kPa, R is the gas constant [8.314 J/(°K.mole)] and α_d (dimensionless) is the tabulated degree of dissociation for the external NaCl solution of concentration C, given by:

$$\alpha_d \approx 10^{\frac{-0.34\sqrt{C}}{1+1.83\sqrt{C}}} + 0.03C \qquad\qquad (14)$$

3.2 Experience elsewhere

In Japan, (Komine and Ogata, 1996) have used the diffuse double layer theory to calculate swelling pressures in bentonite clays and considered that the model predicts pressures well up to 3 MPa with groundwater salinity < 0.04 M. However, this approach was criticised by Sridaharan (1997) who noted that Komine and Ogata's mathematical relationships to describe clay swelling were applicable only for a single plate model and not the parallel plate variety. Komine and Ogata later presented a revised approach to describe clay swelling pressure (Komine and Ogata, 2003). This approach utilised theoretical equations describing the Gouy-Chapman diffuse double layer theory, coupled with van der Waal's force to evaluate the repulsive and attractive forces of clay behaviour. This revised approach purports to account for variations in composition of coexisting groundwater, although the salinity of fluids used in verification tests was less than 0.05 M. Komine and Ogata (2003) conclude, like other workers, that swelling pressure is strongly dependent upon montmorillonite content and the initial dry density. For the H-12 safety assessment in Japan, JNC referred to swelling pressure measurements made by Suzuki et al. (1992), where swelling pressures of > 4 MPa were attained at compaction densities in excess of 1.8 Mg m^{-3} in Na-bentonite, in both distilled water and seawater.

Di Maio (1996) investigated the effects of the exposure of water-saturated specimens of Ponza bentonite (Na-montmorillonite) alternately to pure water and saturated NaCl, KCl, or CaCl$_2$ solutions. Exposure to the three electrolytes produced consolidation of the specimens, a large decrease in deformability, and an increase in residual shear strength. Effects of exposure to NaCl were reversible when the samples were re-exposed to pure water, whereas those for KCl and CaCl$_2$ were not, due to ion exchange reactions. Di Maio (1996) considered that the results were consistent with changes in the thickness of the diffuse double layer of the clays due to diffusion of ions in and out of the clay. As a consequence of their smaller double layers, K- and Ca-montmorillonites are less susceptible to osmotic phenomena.
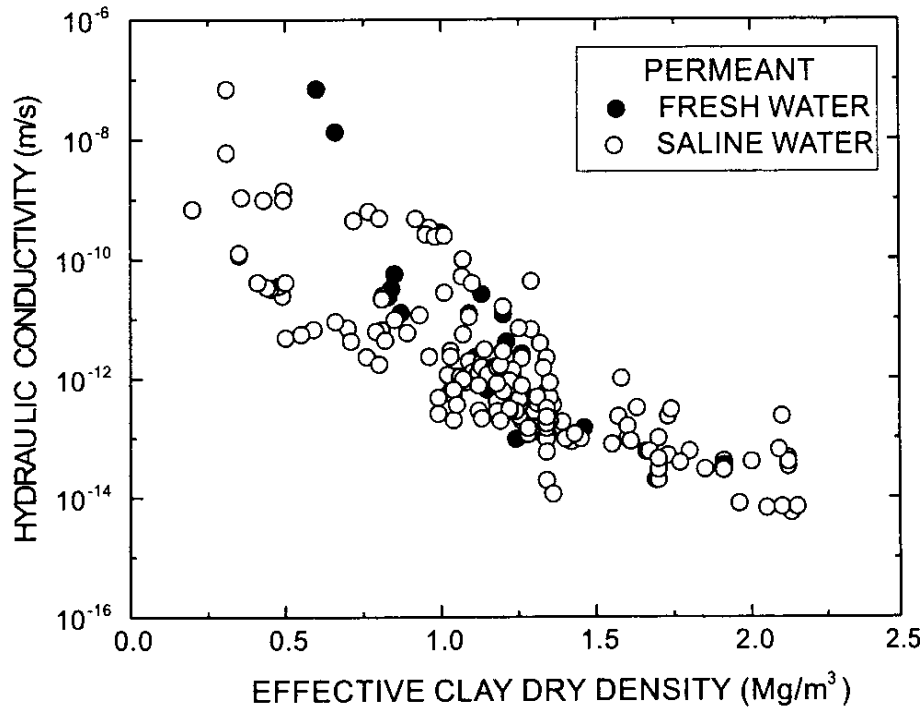
Figure 8: Measurements of hydraulic conductivity of bentonite at various compaction densities, and in 'fresh' and 'saline' groundwater. From Dixon et al. (1999).

Dixon et al. (1999) investigated the hydraulic conductivity of clays under low hydraulic gradients and noted little difference in permeability of bentonite with saline groundwaters, although the salinity of such groundwaters was actually relatively low (TDS = 902 mg l^{-1}). The hydraulic conductivity was in the range $10^{-14} - 10^{-12}$ m s^{-1} at a clay density of $1.5 - 2.0$ Mg m^{-3} (*Figure 8*).

Dixon (2000) reviewed swelling pressure data for a number of different bentonites at varying pore water salinities and concluded that salinities as high as 100 g l^{-1} would not compromise the ability of bentonites to produce a swelling pressure of at least 0.1 MPa, as long as the effective clay dry density ('ECCD' = dry mass of clay ÷ {volume occupied by clay + volume of voids}) exceeded 0.9 Mg m^{-3}. He also noted the relative scarcity of swelling pressure data acquired under 'brine' pore water conditions. Apart from SKB data, Dixon (2000) could only source data for bentonite swelling in brines from the German and US programmes. Because of a lack of data at effective clay dry density at less than 1.5 Mg m^{-3}, Dixon considers that interpretation of the swelling data under saline conditions is difficult. Moreover, he believes that a buffer density greater

than 1.6 Mg m^{-3} would render pore water salinity ineffective for reducing swelling pressure because of the lack of diffuse double layers between clay platelets at this density. Dixon (2000) considers that the debate concerning the validity of the various theoretical models describing clay swelling pressure is unlikely to be settled in the near future and suggests that effort may be best placed in the acquisition of a database of physical measurements. A compilation of bentonite swelling pressure data produced by Dixon (2000) suggests little distinction of swelling pressures with regard to groundwater salinity (*Figure 9*). These data would suggest that a clay density of 0.9 Mg m^{-3} would be sufficient to produce a swelling pressure of 0.1 MPa at any groundwater salinity. With regard to effects of salinity on hydraulic conductivity, Dixon (2000) concluded that above effective clay dry densities of 0.9 Mg m^{-3}, there is little difference in hydraulic conductivity of bentonites saturated with saline solutions as compared with fresh water (*Figure 10*).

There has been extensive work carried out in Germany regarding the performance of bentonite in highly saline solutions as a result of their potential use as seals in halite repository host rocks (Herbert and Moog, 1999, 2000). The precise composition of brines has been shown to affect bentonite swelling pressures. Herbert and Moog (2000) have drawn the following conclusions from their experiments with MX-80 and various brines:

- the swelling pressure is largely dependent on the degree of compaction and the applied fluid pressure (the experiments were conducted using raw densities of 1.6 Mg m^{-3} for the bentonite samples and 100 bars for the fluid pressure).
- All swelling pressures with brines were much lower that those obtained with pure water, but higher than with saturated NaCl solution.
- If the potassium content was kept constant in the NaCl-saturated brines, the water uptake, the interlayer spacing, and the swelling pressure increased with increasing Mg content.
- In brines with varying K and Mg contents, K played the dominant role.
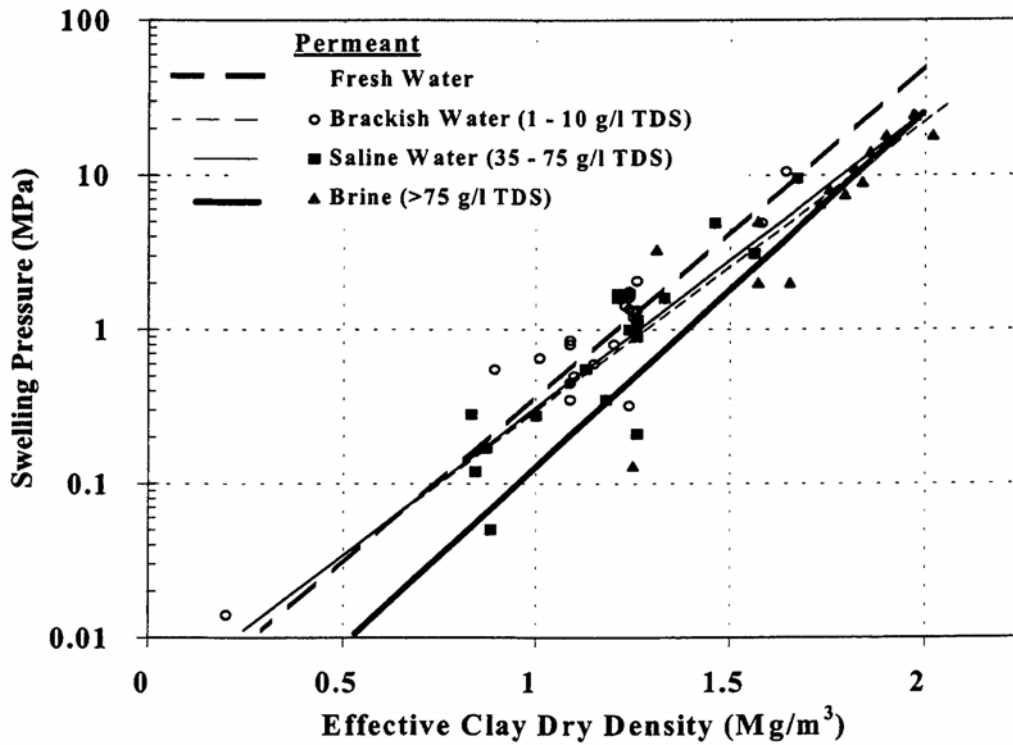
Figure 9: Relationship between bentonite swelling pressure and groundwater salinity. From Dixon (2000).
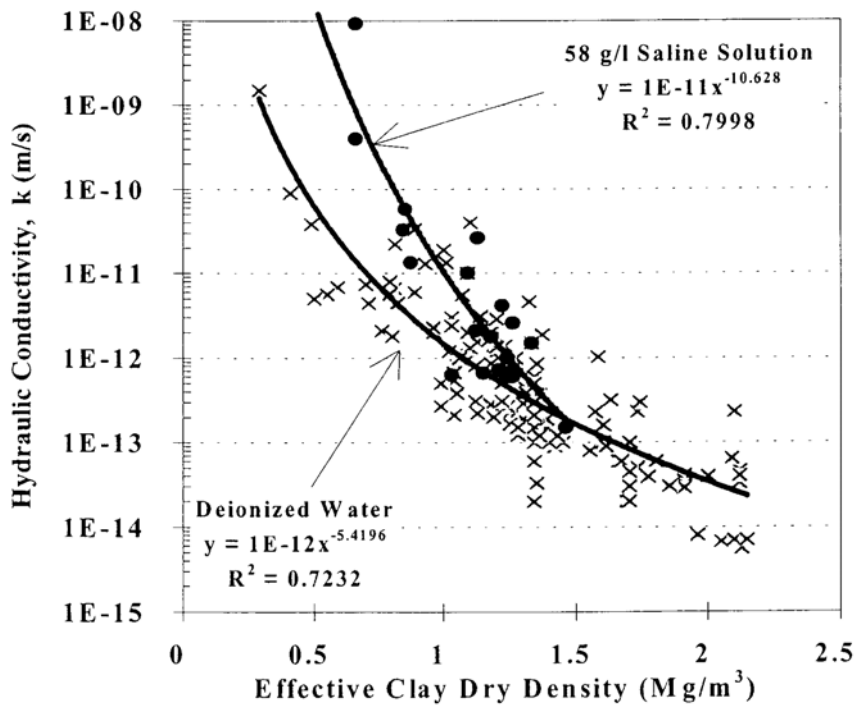

Figure 10: Influence of salinity on the hydraulic conductivity of bentonites. From Dixon (2000).

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4 Clay swelling and backfill behaviour

4.1 SKB approach

The issue of clay swelling behaviour is also of relevance to repository backfilling. SKB (Gunnarsson et al., 2004) states the following requirements for repository backfill:

- compressibility: the backfill should have a low compressibility to maximise the density of the buffer by limiting any upward expansion of the latter.
- hydraulic conductivity: the backfill should have a hydraulic conductivity over the entire length and cross-section of a tunnel in the same order of magnitude as that of the surrounding rock.
- effects on other barriers: the backfill should have no negative influences.
- long-term stability: the backfill should be stable and its functions maintained in the long-term.

SKB is currently studying different designs for tunnel and repository backfilling (Gunnarsson et al., 2004). With regard to salinity effects, they state that a hydraulic conductivity of 10^{-10} m s^{-1} and a swelling pressure > 0.1 MPa at a groundwater TDS of 35 g l^{-1} is the target for this assessment.

SKB considered 6 backfill types in their review:

- A. bentonite and crushed rock in various proportions (from 15 to 30 wt% bentonite) applied in inclined layers, e.g. Börgesson (1997).
- B. Compaction of swelling Friedland Clay, applied in a manner similar to concept A.
- C. Compaction of non-swelling soil (glacial till) with bentonite blocks at roof level.
- D. Pre-compacted blocks of bentonite across the entire tunnel section.
- E. A 'sandwich concept' of alternating zones of bentonite above the disposal holes and crushed rock elsewhere.
- F. A 'compartment concept' of alternating zones of bentonite and crushed rock, with the difference with the sandwich concept being the length of

the crushed rock zone (constant in the sandwich concept and varying in the compartment concept according to local geology and hydrogeology).

From this review, SKB consider that concepts A, B, and D should receive further attention in Phase 2 of their joint studies with Posiva.

According to the results of the Backfill and Plug test, the 'concept A' backfill (SKB's current reference backfill concept) had a density of 1.7 Mg m^{-3}, a hydraulic conductivity of 4 10^{-10} m s^{-1}, a compressibility of 30 MPa and a swelling pressure of 0.15 - 0.2 MPa (all with a groundwater salinity of 1.2 % NaCl) (Gunnarsson et al., 2004). These values are deemed acceptable by SKB, except for the slightly too high hydraulic conductivity. However, it should be noted that SKB had to increase the proportion of clay in the mixture from 15 (reference backfill composition) to 30 % to achieve these properties. It seems certain therefore that during routine backfilling operations with the potential for non-ideal grain size distribution, piping, and a groundwater salinity in excess of 1.2 %, this notionally 'ideal' backfill will not perform to design specifications.

Pusch (2002) observed that the hydraulic conductivity of backfills consisting of rock ballast and bentonite clay is increased by one to two orders of magnitude if the saturating pore fluid is of the salinity of seawater rather than pure water. This is because the density of the 'clay filling' is relatively low (1.3 – 1.6 Mg m^{-3}), even when the average density of the clay/ballast mixture is high. The saline fluid acts to widen the voids in the clay by coagulation of particles. Pusch (2002) recommends that the clay in rock-clay backfills should be as fine as possible where the admixed proportion of clay is small. This effect is particularly pronounced with Ca-bentonites, so that backfills employing Ca-bentonite as the clay fill require a minimum content of at least 30 – 40 % to have a hydraulic conductivity less than 10^{-10} m s^{-1} (Pusch, 2002).

Although the swelling pressure of rock-clay backfills of density 2.0 – 2.1 Mg m^{-3} in freshwater can be sufficient to support roof tunnels, the swelling pressure totally disappears in pore fluids of seawater salinity in mixtures with only 10 – 15 % Na-bentonite at bulk dry densities less than 2 Mg m^{-3} (Pusch, 2002). Mixtures with at least 20 % clay have appreciable expandability saturated in freshwater and can maintain contact with tunnel roofs, even at densities of 0.8 Mg m^{-3} (Pusch, 2002).

Keto (2003) believes that the density of the bentonite needs to be increased in the bentonite-rock mixture type of backfill to address problems associated with higher groundwater salinities. One possibility to achieve a higher density is to use pelleted bentonite. Keto also considers that the proportion of bentonite in the mixtures could be reduced to 5 – 10 % to avoid the situation where rock grains 'float' in a clay matrix without any contact with each other. Such low contents of bentonite are similar to liners used in landfills. Keto questions whether the 'salt resistance' of backfill type A could be enhanced by adding non-swelling clay to the mixture in a similar fashion to the Canadian backfilling concept.

Pusch (2002) considers that backfills made from natural clays alone (e.g. the Friedland Clay) are more tolerant of saline conditions so that a hydraulic conductivity of at least 4 10^{-12} m s^{-1} can be maintained in 10 % $CaCl_2$ solution with a clay density of 2 Mg m^{-3}. The corresponding swelling pressure is 0.65 MPa for the $CaCl_2$ solution and 0.85 MPa in pure water. These values indicate that pure clay backfills are much tighter than rock-clay backfills of comparable density which is a result of the much more homogeneous microstructural constitution of the former.

4.1.1 Treatment in SR-Can

Two different backfill concepts will be analysed in SR-Can (SKB, 2004a):

- 'concept A', with 70 % crushed rock and 30 % bentonite. The material will be compacted in situ with a final clay density of 1.6 Mg m^{-3} when water saturated. This will also be used in the upper metre of the waste package deposition holes.
- Blocks of Friedland Clay ('concept B'). The entire tunnel will be filled with pre-compacted blocks. The uppermost metre will be filled with the same type of bentonite blocks used to fill above the waste package deposition holes.

All other voids (shafts, access ramps, ventilation tunnels etc.) will be backfilled with the same materials as the deposition tunnels after repository closure (SKB, 2004a).

4.2   Experience elsewhere

Dixon (2000) considers that the backfill is much more sensitive to variations in groundwater salinity than the bentonite buffer due to the lower clay content of the former and suggests an initial density of at least 0.9 Mg m^{-3} to maintain a nominal swelling pressure of 0.1 MPa. He reports that the Canadian tunnel backfill contains much less clay (6 % by dry mass) than the SKB variety, but a much higher density of 2.1 Mg m^{-3} (equivalent to an effective clay dry density of 0.46 Mg m^{-3}). However, the backfill of the Canadian concept is not expected to have any significant swelling pressure, since the sealing of the backfill-rock interface is via an 'upper backfill' material (20 % of the total volume of the backfill). This upper backfill would consist of 50 % bentonite and the remainder aggregate with a dry density of 1.4 Mg m^{-3} which would be capable of maintaining a substantial swelling pressure in pore waters with salinities as high as 100 g l^{-1} (Dixon, 2000).

5   Piping and erosion

SKB (2004c) states that if groundwater inflow in fractures in deposition holes exceeds that which can be absorbed by bentonite swelling, there will be a water pressure in the fracture acting on the buffer. Since the bentonite is initially in a gel-like state, the gel may be too soft to stop the water inflow and piping may result. Piping is the erosion of the clay along a linear feature and is a particular problem with saline groundwater. SKB (2004c) goes onto state that piping will take place if the following conditions are fulfilled:

- the water pressure in the fracture is higher than the total pressure in the clay and the clay's shear resistance.
- The hydraulic conductivity of the clay is low enough that water flow into the clay ceases to counteract the water pressure in the fracture.

SKB believe that piping will only occur before full saturation of the buffer. SKB view erosion as a different process which takes place if drag forces on clay particles from water movement is higher than the sum of frictional and attractional forces between the particle and the clay structure (SKB, 2004c). Erosion could occur as a consequence of piping, but also in the long-term at the interface between water-bearing fractures and the bentonite. Erosion will therefore concern clay gel which has penetrated these fractures during swelling. Clearly, for buffer functions to be maintained in the long-term, it is essential that buffer swelling closes any channel opened by piping. This will be the case if mass transfer by buffer swelling is greater than the erosion/piping rate and that piping does not re-occur (SKB, 2004c).

SKB has investigated piping at three experimental scales:

- in the laboratory with 10 x 5 cm cylindrical samples;
- at 1:10 scale for the KBS-3H concept;
- full-scale tests (Backfill and Closure test, KBS-3H test).

Piping is especially relevant to the horizontal emplacement concept where channels may contact a large number of canisters. This is currently being investigated by SKB (SKB, 2004c). More information may also be gained from excavation of the Prototype Repository test at Äspö (in 10 years time) where one of the deposition holes has a relatively large water inflow. SKB will investigate piping effects in SR-Can during the pre-saturation phase and will be based mainly on experience from the KBS-3H study (SKB, 2004c).

The problem of piping is also germane to repository backfilling. SKB consider that it may be difficult to derive a solution to water inflow during backfill installation and thus: "piping can probably not be avoided in the installation phase, irrespective what type of backfill material is used" (Gunnarsson et al., 2004). Gunnarsson et al. (2004) consider that a point source of groundwater inflow as low as 1 l/min would probably result in piping and surface erosion of the tunnel backfill. Backfill concepts 'A' and 'B' appear susceptible to piping effects (Gunnarsson et al., 2004). Consequently, the backfill needs to have enough swelling ability so that piping channels can be healed once a tunnel has been sealed by plugging. All this must be placed in context of the rate of backfilling which SKB hopes to be in the order of 6 m per day.

Keto (2003) considers that backfill erosion can take place in three ways (*Figure 11*):

- surface erosion, where water flowing on the surface of the backfill has the ability to transport material from the surface. This occurs during emplacement and could be counteracted by installing temporary drainage.
- Piping (internal erosion) requires a high hydraulic gradient and occurs by removal of material along the pore system of the backfill.
- Contact erosion occurs in the zone between coarse and fine materials, e.g. at the contact between the buffer and the backfill.
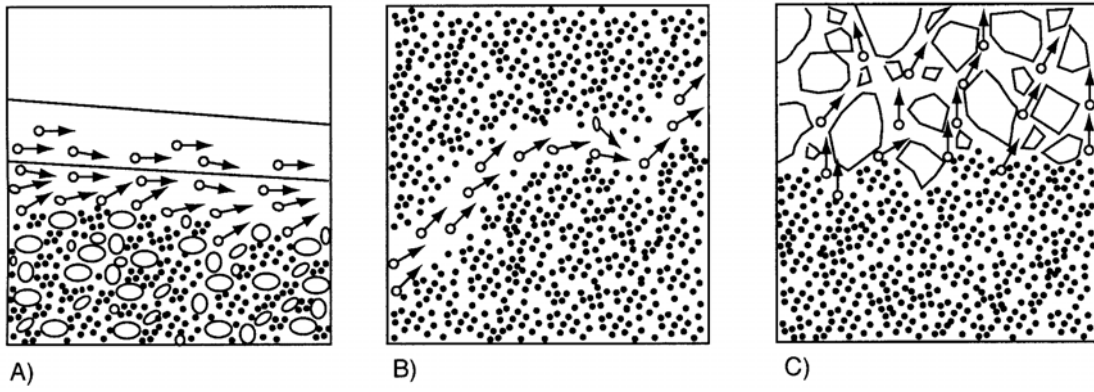
Figure 11: Types of backfill erosion. A). Surface erosion. B). Piping. C). Contact erosion. From Keto (2003).

6 Long-term stability of montmorillonite in saline groundwater

Pusch and Kasbohm (2002) reacted MX-80 bentonite with 10 and 20 % NaCl solutions at 110 °C for thirty days in closed and percolation experimental systems. There were two test series:

- one with compacted clay powder with a dry density of 1.2 to 1.3 Mg m^{-3} and saturation with 10 % and 20 % NaCl solutions, followed by heating to 110 °C under closed conditions for 30 days.
- In the second series air-dry compacted clay powder in a cell was heated at 110 °C for the same period of time and connected to vessels with 10 % and 20 % NaCl solutions.

Pusch and Kasbohm (2002) consider that the first series represents the conditions in the buffer clay after saturation with Na-rich water while the second one corresponds to the conditions in the course of saturation with such water. Results from physical testing showed that the hydraulic conductivity and swelling pressure of the hydrothermally treated clay samples were in the same order of magnitude as untreated clay. Comparison with illitic clays shows that the latter were at least a hundred times more permeable than the hydrothermally-treated clays. However, XRD analysis showed a clear difference in mineral composition between the two test series. Whilst no significant change from the typical mineralogy of untreated MX-80 was found for hydrothermal treatment of clay saturated with 10 and 20 % NaCl solution (except for some very slight neo-formation of illite-smectite mixed layers or irreversible partially collapsed phases in the 20 % NaCl solution), dry clay exposed to 20 % NaCl solution showed formation of Na-illite. It was concluded that Mg had migrated from octahedral lattice positions to interlamellar sites, implying partial dissolution of the original montmorillonite. Transmission electron microscopy showed that partial replacement of octahedral Mg by Al yielding a decrease in interlayer charge had occurred, especially in the air-dry clay powder heated to 110 °C under simultaneous exposure to NaCl solutions. Precipitated silica, partly in the form of quartz or cristobalite, may have originated from tetrahedral positions in the montmorillonite lattice where aluminum

could have replaced it, hence forming beidellite, or by dissolution of the smectite component. Although the temperature was somewhat higher than in a KBS-3 repository and the salt content appreciably higher than what is normally found at 500 m depth in Swedish bedrock, alteration may be less significant in real buffer clay. However, the laboratory study was only for a month in duration.

Under more extreme saline conditions, Herbert et al. (2004) investigated the reaction of Wyoming bentonite MX-80 with 6M NaCl- and $MgCl_2$-rich brines at 25, 90, and 150 °C at pH 1, 6.5 and 13 and concluded that a certain proportion of the montmorillonite is likely to be altered to kaolinite or pyrophyllite under these conditions, rather than illite. The MX-80 bentonite lost about 50 % of its water uptake capacity compared with pure water which increased with reaction time and temperature.

Hofmann et al. (2004) also investigated the stability of bentonite in brine solutions. They reacted samples of 'IBECO SEAL-80' (Na-activated) and 'TIXOTON TE' (Ca-activated) bentonites with brine saturated with $MgCl_2$ at 25 °C for 150 days in batch experimental systems. No mineral transformations were observed in these experiments, although cation exchange capacity and swelling were reduced. Both these latter properties could be returned to normal once the salt had been removed. Hofmann et al. (2004) note that there is considerable natural systems evidence for the preservation of bentonites over million-year timescales in marine to evaporitic environments as long as chemical and thermal conditions remain similar to those under which they were formed.

Pérez del Villar et al. (2005) and Fernandez et al. (2005) have investigated analogue evidence for the long-term stability of bentonite, by studying the Cala de Tomate and Archidona bentonite deposits (both in southern Spain), respectively. Both bentonites have been invaded by seawater in the geological past. Pérez del Villar et al. (2005) noted changes in exchangeable cations, BET-specific surface area and dispersibility, but no mineral transformations as a result of interaction of the Cala de Tomate deposit with saline waters. The Archidona bentonite has been invaded by seawater and meteoric water and different stages of its past history, but shows no sign of mineral alteration as a result of these processes.

7   Conclusions

Smectite clays can absorb water into clay inter-layers with the most important parameters being: the surface density of charge of the clay (swelling decreases with increasing charge density); the charge and solvation behaviour of the inter-layer ions (swelling is greatest for ions such as sodium); and the electrolyte concentration or activity of water (swelling decreases with increasing salinity of the contacting solution). Two categories of swelling are generally observed: *innercrystalline swelling* caused by the hydration of the exchangeable cations in the dry clay; and *osmotic swelling*, resulting from concentration gradients in ion concentrations between clay surfaces and pore water. Several models exist to interpret and predict the swelling behaviour of clays and these consist of: empirical models; diffuse double-layer models; the DLVO model; and thermodynamic models. Of these, only thermodynamic models have the capacity to predict clay swelling behaviour in saline pore fluids.

SKB currently prefer an interpretation of clay swelling pressure where clay particles are viewed as 'macro-ions' and the entire clay-water system can be considered as a 'polyelectrolyte'. SKB use the term 'Donnan exclusion' to estimate the amount of introduced ions into the clay and hence the amount of reduced swelling pressure due to contact with a saline solution. Donnan exclusion is the process whereby the migration of anions through the narrow aqueous film surrounding clay platelets is restricted due to the repulsion by the negative charge of the clay platelets. SKB's experimental work shows that:

- there is an exponential relation between swelling pressure and mean basal inter-lamellar spacing of the clay.
- Ions from the external electrolyte solution enter the clay volume, leading to decreased water activity in the clay.
- Introduced ions enter the swelling pressure-inducing volume in the clay.
- Swelling pressure is systematically reduced at all clay densities by interaction with saline fluids.

SKB believes that if the buffer density exceeds 1.9 Mg m^{-3}, the functional requirements for the swelling pressure to exceed 1 MPa will be fulfilled, even with groundwater salinities equivalent to 3 M NaCl (~175 g l^{-1} TDS). Similarly, the functional requirement for buffer hydraulic conductivity of 10^{-12} m s^{-1} will also be fulfilled if the buffer density is greater than 1.8 Mg m^{-3}, and with NaCl equivalent salinity equal to 3M.

A review of work carried out elsewhere related to the swelling of montmorillonitic clays shows that the mechanistic understanding of such processes is less well advanced than that presented by SKB. The interpretation of clay swelling by Japanese researchers relies upon the application of the diffuse double layer theory, which has been shown by SKB and others to be inadequate to describe clay swelling pressures in saline pore fluids. Work in Germany has focused on the acquisition of a large dataset of swelling pressures in saline pore fluids, rather than mechanistic interpretation of such data.

Consideration of all this information indicates that groundwater salinity (up to 3M NaCl equivalent) will not have a significant impact upon buffer swelling capacity if densities at emplacement are 1.9 Mg m^{-3} or greater.

Backfill materials are even more susceptible to loss of swelling pressure in saline groundwaters. SKB is currently studying several different designs for tunnel and repository backfill. With regard to salinity effects, they state that a hydraulic conductivity of 10^{-10} m s^{-1} and a swelling pressure > 0.1 MPa at a groundwater TDS of 35 g l^{-1} is the target for this assessment. According to the results of the Backfill and Plug test, the 'concept A' backfill (SKB's current reference backfill concept) had a density of 1.7 Mg m^{-3}, a hydraulic conductivity of 4 10^{-10} m s^{-1}, a compressibility of 30 MPa and a swelling pressure of 0.15 - 0.2 MPa (all with a groundwater salinity of 1.2 % NaCl). These values are deemed acceptable by SKB, except for the slightly too high hydraulic conductivity. However, it should be noted that SKB had to increase the proportion of clay in the mixture from 15 % (reference composition) to 30 % to achieve these properties. It seems certain therefore that during routine backfilling operations with the potential for non-ideal grain size distribution, piping, and a groundwater salinity in excess of 1.2 %, the reference backfill composition (15 % clay) will not perform to SKB's functional requirements. SKB continues its research in this area in

conjunction with Posiva to assess different backfill formulations. Research on tunnel backfilling in Canada suggests that an initial density of at least 0.9 Mg m^{-3} is required to maintain a nominal swelling pressure of 0.1 MPa. Canadian tunnel backfill contains much less clay (6 % by dry mass) than the SKB variety, but a much higher density of 2.1 Mg m^{-3} (equivalent to an effective clay dry density of 0.46 Mg m^{-3}).

SKB considers that if groundwater inflow in fractures in deposition holes exceeds that which can be absorbed by bentonite swelling, there will be a water pressure in the fracture acting on the buffer which may lead to piping. Piping is the erosion of the clay along a linear feature. SKB believe that piping will only occur before full saturation of the buffer and is of concern during the operational phase of the repository. Piping is a complex process which increases with water pressure and groundwater salinity. SKB continue to research this problem through laboratory and in situ tests. The problem of piping is also germane to repository backfilling. SKB consider that it may be difficult to derive a solution to water inflow during backfill installation. Consequently, the backfill needs to have enough swelling ability so that piping channels can be healed once a tunnel has been sealed by plugging. All this must be placed in context of the rate of backfilling which SKB hopes to be in the order of 6 m per day.

Research conducted by SKB and elsewhere suggests that the long-term effects of montmorillonite degradation due to the presence of saline groundwater will consist mainly of formation of beidellite or kaolinite.

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