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**Bentonite swelling pressure in strong NaCl solutions**

**Correlation between model calculations and experimentally determined data**

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Clay Technology, Lund, Sweden

December 1997

# BENTONITE SWELLING PRESSURE IN STRONG NaCl SOLUTIONS

## CORRELATION BETWEEN MODEL CALCULATIONS AND EXPERIMENTALLY DETERMINED DATA

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# ABSTRACT

A number of quite different quantitative models concerning swelling pressure in bentonite clay have been proposed by different researchers over the years. The present report examines some of the models which possibly may be used also for saline conditions. A discrepancy between calculated and measured values was noticed for all models at brine conditions. In general the models predicted a too low swelling pressure compared to what was experimentally found. An osmotic component in the clay/water system is proposed in order to improve the previous conservative use of the thermodynamic model. Calculations of this osmotic component is proposed to be made by use of the clay cation exchange capacity and Donnan equilibrium.

Calculations made by this approach showed considerably better correlation to literature laboratory data, compared to calculations made by the previous conservative use of the thermodynamic model. A few verifying laboratory tests were made and are briefly described in the report.

The improved thermodynamic model predicts substantial bentonite swelling pressures also in saturated sodium chloride solution if the density of the system is high enough. In practice, the model predicts a substantial swelling pressure for the buffer in a KBS-3 repository if the system is exposed to brines, but the positive effects of mixing bentonite into a backfill material will be lost, since the available compaction technique does not give a sufficiently high bentonite density.

# SAMMANFATTNING (SWEDISH)

Ett antal olika kvantitativa modeller för beräkning av svälltryck i bentonit har förslagits av olika forskare genom åren. Den aktuella rapporten undersöker ett antal modeller vilka möjligen skulle kunna användas också för salta grundvattenförhållanden. En påtaglig skillnad mellan beräknade och uppmätta värden noterades för samtliga modeller vid mycket höga salthalter (brines). I allmänhet gav modellerna för låga beräknade svälltryck i jämförelse med vad som uppmätts vid laboratorieundersökningar. En osmotisk komponent i lera/vatten systemet förslås för att förbättra den tidigare alltför konservativa användningen av den termodynamiska modellen. Beräkningar av denna osmotiska komponent föreslås ske med hjälp av katjonbyteskapaciteten hos leran och Donnan-jämvikt.

Beräkningar som gjorts med denna teknik uppvisar avsevärt förbättrad samstämmighet med litteraturdata i jämförelse med beräkningar med den tidigare använda konservativa användningen av modellen. Ett fåtal verifierande laboratorietest har genomförts och redovisas i rapporten.

Den förbättrade modellen förutsäger ett avsevärt svälltryck hos bentonit även i en mättad natriumklorid-lösning under förutsättning att densiteten hos systemet är högt. Detta innebär i praktiken att bufferten i ett KBS-3 förvar skulle ge ett tillräckligt svälltryck vid kontakt med mycket salta grundvatten (brines), men att de positiva effekterna av att blanda bentonit i återfyllnadsmaterial försvinner eftersom tillgänglig packningsteknik inte kan åstadkomma tillräckligt hög densitet hos bentonitfasen.

# TABLE OF CONTENTS

# 1    BACKGROUND

## 1.1    GENERAL

Bentonite clays generally have a high swelling capacity in low electrolyte water solutions, i.e. the bentonite swells in water to a volume several times the original dry clay volume. The swelling gives rise to a macroscopic swelling pressure acting uniformly on the surroundings if the swelling is restricted to a volume smaller than that of maximum swelling. The volume of a KBS-3 deposition hole in rock is in principle fixed and the bentonite mass may be balanced to give a desired swelling pressure, and the coupled low hydraulic conductivity leads to an efficient seal of the volume. This swelling ability is one of the basic reasons for using bentonite clay as buffer material in a repository for spent nuclear fuel.

It is a well known fact that salt solutions reduces the swelling capacity of bentonite, and no swelling pressure will obviously develop if the capacity is reduced to an extent where the actual volume is not filled by the maximum swollen clay. Several laboratory test series have consequently been made in order to determine the effects on bentonite swelling of typical ground-water at repository depth, and of water solutions with considerably higher salt content (Pusch 1980, Karnland 1992, Dickson 1996). The effects have also been considered by means of thermodynamics and the results correspond quite well with the laboratory data also for conservative ground-water conditions.

However, for very high salt content solutions (brines) a conservative use of the thermodynamic model predicts a total loss of swelling pressure which is not in accordance with laboratory test results.

The discrepancy between model and measured values may appear as an academic problem since the discrepancy is only significant at very high salt contents which have never been found at repository depth. An explanation is, however, desirable from at least the following two quite different aspects:

- The discrepancy may throw suspicion upon the reliability of all measured data, also those at lower salt content. Normally, one would reject the model since laboratory results are looked upon as hard facts. This is not appropriate in this case, since the model is based on simple thermodynamic principles and has been commonly used and accepted, and because the laboratory data may represent conditions where equilibrium has not been reached.

- The salt content in the ground-water is observed to increase substantially with depth at several possible repository sites. Although there is no obvious scenario, it can not simply be excluded that there will be a draw-up of deep ground-water into a future repository. Consequently, in order not to reject such places on this ground, it is important to model bentonite swelling also for brine conditions.

1

## 1.2    AIM

Several models, both conceptual and quantifying, have been proposed to explain the nature of the swelling pressure and to calculate specific values for different physico-chemical conditions. The basic aims of this work are to quantitatively correlate existing laboratory data and model data concerning swelling pressure in bentonite exposed to NaCl brines and to discuss discrepancies, if any. Special respect is paid to the thermodynamic model.

## 1.3    PRINCIPLES FOR BENTONITE SWELLING

The physical properties of bentonite are determined by the interaction between water and the smectite component, which usually is montmorillonite. The montmorillonite is derived from pyrophyllite through isomorphic replacement of aluminum by magnesium in the octahedral layer and an ideal formula can be written

$$n(H_2O) \ c_x \ Si_8 \ Al_{4-x}Mg_x \ O_{20}(OH)_4.$$
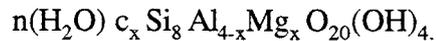
The induced negative layer charge (x) is in the range of 0,4 to 1,2 unit charges per $O_{20}(OH)_4$-unit and is balanced by interlayer cations (c). The octahedral sheet is composed of magnesium and aluminum coordinated octahedrally with oxygen atoms or hydroxyl groups. The silica tetrahedra are interconnected in a silica sheet structure. Three of the four oxygen atoms in each tetrahedron are shared to form a hexagonal net.
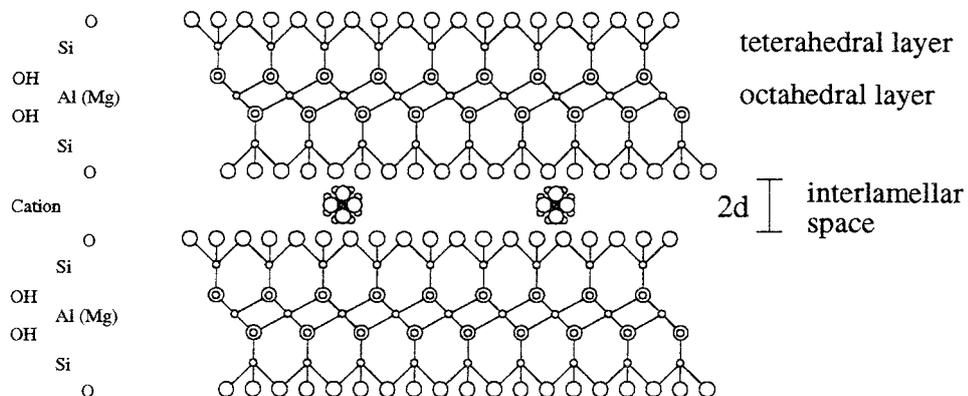


Figure 1-1.    Generalized structure of montmorillonite perpendicular to the c-axis. The octahedral Mg (dark circles) substitution for Al results in a net negative charge, which is compensated by interlamellar cations.

The hydration state, or amount of interlayer water, is a function of the extent and location of the 2:1 layer charge (Foster 1953, Harward 1966,) interlayer cation species (Glaeser 1968, Schultz 1969), vapor pressure (Keren 1975, Ormerod 1983), temperature (Rowland 1956, Colten 1986) and salinity of saturating solution (Norrish 1954, Posner 1964, Shang 1995). Continuous variation in basal spacing with salinity and vapor pressure changes has been observed for Na-saturated smectites with basal spacings greater than 40 Å (Norrish 1954).

2

If expansion is prohibited, the hydration forces will instead give rise to a macroscopic swelling pressure. At equilibrium and full water saturation this pressure is closely related to the water ratio ($m_w/m_s$, mass of water and mass of solid, respectively) in the clay, which is related to the density of the clay-water system ($\rho_m$). The swelling pressure may be determined experimentally in different types of geotechnical equipment such as swelling pressure oedometer and triaxial cell. It may also be determined indirectly for an actual bentonite by known relations between swelling pressure and e.g. water vapor pressure, interlamellar spacing, water ratio or density.

# 2 SWELLING PRESSURE MODELS

## 2.1 GENERAL

Several models for predicting swelling pressure in bentonite clay have been proposed. In this study a few models, representing quite different groups of approaches, are looked at. The models are chosen because they have been presented in connection with repository construction and, more or less, are claimed to handle different physico-chemical conditions including electrolyte solutions in the system. The model groups they represent may be called:

empirical models,
diffuse double-layer models,
thermodynamic models.

The models are briefly presented and some results from calculations of swelling pressure are shown, both for non-saline and saline conditions in order to relate the measured results to the different models.

## 2.2 EMPIRICAL MODELS

### 2.2.1 Low´s semiempirical model

Philip Low early suggested that the interaction of water with clay surfaces produces a hydrostatic repulsive force that contributes to clay swelling (Low 1953). Numerous experiments by Low and co-workers have shown that the properties of water in montmorillonite-water systems obey the empirical equation (Low 1979):

$$J_i = J_i^0 \cdot e^{\frac{\beta_i \cdot m_m}{m_w}}$$  [1]

where $J$ and $J^0$ are the values of a property, i, in the montmorillonite-water system and in pure water, respectively, and $\beta$ is a constant that is characteristic of the property. The relation is alleged to be valid for thermodynamic, hydrodynamic and spectroscopic properties of the water.

Direct measurement of the swelling pressure on 35 different montmorillonites showed a relationship between $P_s$ and the mass ratio of montmorillonite to water ($m_m/m_w$), (Low 1980), given by

$$\ln (P_s+1) = \alpha (m_m/m_w) + \ln B,$$  [2]

where $\alpha$ and B are constants that are characteristic of the montmorillonite. Since the proportion of crystal edges in montmorillonite is small, Low argues that the interlamellar distance (2d in Figure 1) is related to $m_w/m_m$, and that the relation in eq. [2] may be written

$$\ln (P_s+1) = k (1/2d) + \ln b$$  [3]

4

or

$$Ps + 1 = \exp(k\,(1/2d) - (1/\lambda_0))$$

where k is a constant, b is $\exp(-k/\lambda_0)$ and $\lambda_0$ is the modal interlamellar distance when the swelling pressure is zero ($P_s = 0$). Combination of equation [1] and [2] yields

$$P_s + 1 = B \cdot \left(\frac{J_i}{J_i^0}\right)^{\frac{\alpha}{\beta_i}}$$

which indicates that the swelling pressure in the system is related to any of the examined properties of the water in the system.

The validity of equation [3] has been examined in several laboratory studies by Low (e.g. Low 1983) by direct parallel measurement of the interlamellar distance and swelling pressure.

Consequently, according to Low it is possible to calculate the swelling pressure by use of equation [3] after the constants k and $\lambda_0$ have been determined in laboratory experiments.

### 2.2.2    Commentary on the models

The model is attractive because of its simplicity. However, two different values of k and $\lambda_0$ have to be used in order to describe the swelling of some montmorillonites. Further negative values of $\lambda_0$ have to be used in some cases which puts the physical significance in question (Grauer 1986). The effects of solutions with high salt contents are not thoroughly discussed and the model turns out to be of limited direct use for the actual application.

## 2.3    DOUBLE LAYER MODELS

### 2.3.1    General

There are several similar theories concerning the distribution of ions between charged surfaces which may generally be identified as double-layer models. The diffuse double layer model (DDL) was independently developed by Gouy and Chapman in 1910. The main purpose of the models, with respect to clay swelling, is to determine the mid point electrical potential ($\varphi_d$) between two parallel montmorillonite clay flakes. If the potential is properly determined for a certain physico-chemical condition it should in principle be possible to calculate the repulsive force arising between the flakes, according to the Langmuir equation (below). The repelling force between the flakes will be counteracted by attraction forces, (van der Waals force) which can be calculated if the distances between the flakes can be determined.

The sections 2.3.2 and 2.3.3 describe the approach by Komine and Ogata in which they calculate the swelling pressure on the basis of the Diffuse Double Layer (DDL) Theory. The reasons for using this as an example of DDL models are that the Komine and Ogata article is one of the most recently presented on the subject, and they have compared the results with laboratory data for different ion concentrations (Komine 1996).

The Komine and Ogata results have been reproduced and new calculations for the Posiva/SKB reference bentonite material MX-80 have been made with special respect to high NaCl concentrations in the saturating water solution. The original constants and MX-80 material specific data are shown in table 2-1, and the calculation results are shown in Figure 2-1.

Section 2.3.4 describes a model presented by Young and Warkentin where the swelling pressure is calculated as an osmotic pressure of the difference in concentration of ions between clay particles and in an external solution. Calculation of the concentration between the clay flakes is made by use of a DDL model.

## 2.3.2    Repulsive force between two parallel layers

A repulsive force is generated between two parallel layers if the two layers approach each other and their electrical potential distribution overlap. The repulsive force per unit area between two parallel layers is given by eqs. [1]-[3], which are derived from the electrical potential distribution around the two charged layers (Langmuir 1938, Olphen 1963, Mitchell 1993).

$$f_r = 2nkT(\cosh u - 1) \qquad [4]$$

$$u = 2y_d \qquad [5]$$

$$y_d = \frac{\upsilon e' \varphi_d}{kT} \qquad [6]$$

where $f_r$ is the repulsive force per unit area between the two parallel layers ($J/m^3$), $\upsilon$ is the ionic valence, $e'$ is the electric charge ($=1.602 \times 10^{-19}$), k is the Boltzmann constant ($=1.38 \times 10^{-23}$ J/K), T is the absolute temperature (K), n is the concentration of ions (number/$m^3$) in pore water, u is the variable obtained by $\varphi_d$, which is the electrical potential at the center of the two parallel layers.

According to the Gouy-Chapman theory of diffuse double layer (Chapman 1913, Mitchel 1993) the distribution of the electrical potential in the clay water electrolyte system around the clay layer is given by:

$$\frac{d\varphi}{dx} = -\sqrt{\frac{2nkT}{\varepsilon}} 2\sinh\left(\frac{\upsilon e'\varphi}{2kT}\right) \qquad [7]$$

6

$$\varphi_0 = \frac{kTz}{\upsilon e'}$$ [8]

for $\quad z = 2\sinh^{-1}\left(96.5 \times \frac{B}{S}\sqrt{\frac{1}{8\varepsilon nkT}}\right)$

where x is the position from the layer surface (m), $\varphi$ is the electrical potential at position x, $\varepsilon$ is the static permittivity of the water solution ($C^2 \cdot J^{-1} \cdot m^{-1}$), B is the cation exchange capacity (mequiv./g) and S is the specific surface ($m^2/g$) of the clay.

Eq. [4] has been solved for the conditions $\varphi = \varphi_0$ for x=0, and $\varphi = \varphi_d$ for x=d, which gave:

$$y_d = 4\tanh^{-1}\cdot\left[\exp(-\kappa d)\tanh\left(\frac{z}{4}\right)\right]$$ [9]

for $\quad \kappa = \sqrt{\dfrac{2n\upsilon^2 e'^2}{\varepsilon kT}}\quad (m^{-1})$

where d is half the distance between the two layers (m) (Figure 1-1), and $\kappa$ is the double-layer parameter. The characteristic length ($1/\kappa$) is a measure of the thickness of the double layer (Iwata 1988; Mitchell 1993).

Therefore, the repulsive force per unit area, or simply the resulting pressure, between two parallel layers is given by

$\quad f_r = 2nkT(\cosh u - 1) \qquad (J/m^3) \qquad$ [10]

$\qquad = 2nkT(\cosh u - 1) \times 10^{-6} \qquad (MPa)$

for $\quad u = 2y_d = 8\tanh^{-1}\left[\exp(-\kappa d)\tanh\left(\frac{z}{4}\right)\right]$

$\qquad \kappa = \sqrt{\dfrac{2n\upsilon^2 e'^2}{\varepsilon kT}}$

$\qquad z = 2\sinh^{-1}\left(96.5 \times \frac{B}{S}\sqrt{\frac{1}{8\varepsilon nkT}}\right)$

## 2.3.3 Attractive force between two parallel layers

It is well known that attractive forces act between two layers if they approach extremely close to each other (Iwata 1988; Mitchell 1993). London's theory for attractive energy between a pair of molecules (London 1937) was extended to obtain the attractive energy between two parallel layers (Casimir 1948). The attractive force per unit area, which is commonly termed the van der Waals force, is given by

$$f_a = \frac{A_h}{24\pi}\left[\frac{1}{d^3} + \frac{1}{(d+t)^3} - \frac{2}{\left(d+\frac{t}{2}\right)^3}\right] \quad (J/m^3) \quad [11]$$

where $f_a$ is the attractive force per unit area between the two parallel layers, $A_h$ is the Hamaker constant, d is half the distance between the two layers (m), and t is the thickness of layer (m). The value of $A_h$ calculated from theoretical analysis of coagulation measurements is $2.2 \times 10^{-20}$ J for montmorillonite (Novich 1984).

Therefore, the force P per unit area (resulting pressure) between two parallel layers can be obtained by

$$P = f_r - f_a \quad \text{(repulsion: positive)} \quad [12]$$

**Table 2-1.** Parameters in the prediction method for swelling characteristics of compacted bentonite

| | |
|---|---|
| Density of bentonite $p_s$ | 2.78 Mg/m³ |
| Specific surface of montmorillonite minerals $S_m$ | 750 m²/g |
| Specific surface of nonswelling minerals $S_{nm}$ | 0 m²/g |
| Montmorillonite content of bentonite $C_m$ | 75% |
| Cation exchange capacity B | 0.8 eq./kg |
| Ionic valence $\upsilon$ | 1 |
| Absolute temperature T | 295 K |
| Boltzmann constant k | $1.38 \times 10^{-23}$ J/K |
| Hamaker constant $A_h$ | $2.2 \times 10^{-20}$ J |
| Electric charge e' | $1.602 \times 10^{-19}$ C |
| Static permittivity of pore water $\varepsilon$ | $80 \times 8.8542 \times 10^{-12} C^2 \cdot J^{-1} \cdot m^{-1}$ |
| Thickness of montmorillonite layer t | $9.60 \times 10^{-10}$ m |
| Avogadros's number $N_A$ | $6.023 \times 10^{23}$ |
| Concentration of ions in pore water $n_0$ | 20, 40, 86 and 600 mol/m³ |

Results from calculation by use of eq. [12] and the constants in table 2-1 for MX-80 Posiva/SKB reference bentonite are shown in Figure 2-1. The model is sensitive to ion charge and the use of monovalent cations give calculated values of around one order of magnitude higher pressure compared to divalent ones. Komine and Ogata used the value $\upsilon=1,5$ since the examined Kunigel material has approximately equal number of sodium and calcium ions

in exchange position. The presented values are based on monovalent sodium. High content of salt in the solution leads to major changes in swelling pressure and saturated NaCl solution (6.1 M, 36% b.w.) gives total loss of swelling pressure for all clay densities.
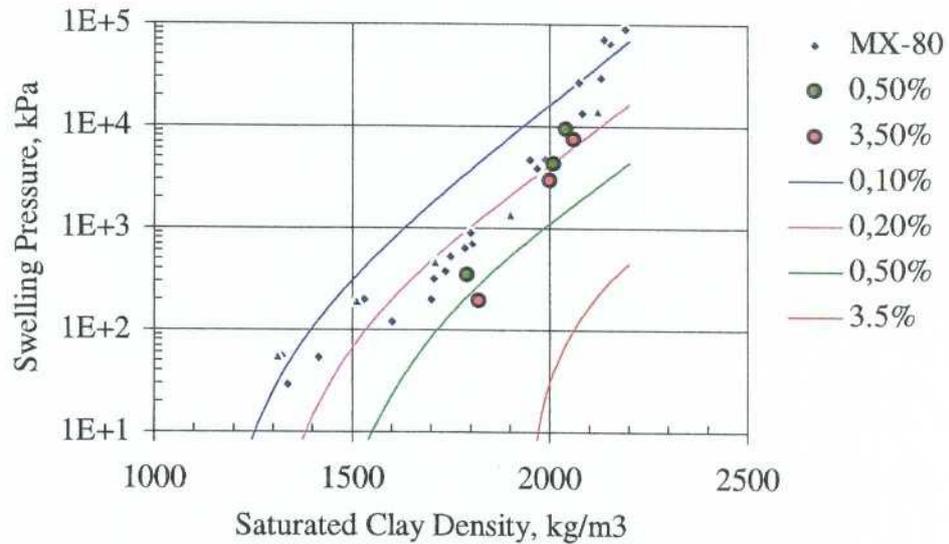


*Figure 2-1    Swelling pressure as a function of clay density at full saturation as calculated by the Komine and Ogata approach of the diffuse double layer theory. Dots indicate measured values and lines results from calculations.*

### 2.3.4    Osmotic DDL model

The swelling pressure can be calculated as an osmotic pressure by means of the Van´t Hoff equation (Yong 1975).

$$P_s = RT(C_c - 2C_0) \qquad [13]$$

where R is the gas constant, T is the absolute temperature, $C_c$ ( mole/liter) is the concentration of cations in the center between two clay flakes and $C_0$ (mole/liter) is the concentration of salt in the bulk water.

$C_c$ may be calculated by

$$C_c = \frac{\pi^2}{z^2 B(d + x_0)^2 \cdot 10^{16}} \qquad [14]$$

where z is the valence of the exchangeable cations, d is the half distance between the flakes in Å ($10^{-10}$ m), $x_0$ is a correction factor of 1 to $4*10^{-10}$ m depending on the ion valence and charge density of the flakes, and B is a constant with the value of $1*10^{15}$ cm/mmole and represents the combined effect of temperature and dielectric constant.

## 2.3.5 Commentary on diffuse double layer models

At very close particle separation distances there is an apparent problem with the basic principle of the diffuse double layers due to the spatial limitation. For densities of current interest in buffer material the theoretical mean spacing is around 9 Å which has to be considered as very close since it only allows for a few water molecules. Further, the interlamellar spacing between the flakes will be even shorter if there is a significant distribution in spacing due to inhomogeneity in the system,

Komine and Ogata conclude in their study that the model well predicts the swelling pressure up to a pressure of 3 MPa, which corresponds to a clay density in the lower range of possible buffer densities. The attractive forces are only dependent on basal spacing and are not affected by any of the conditions which affect the repelling forces. The calculated attractive forces were relatively small compared to the calculated total pressures also at small basal distances. In the present calculation of pressure in MX-80 bentonite there is no major difference in accuracy for high pressure values compared to lower. The ability to predict the effect of different salt content seems, however, to be very limited. Only NaCl contents in the water solution of less than 0.5% are tolerable in the range of measured values.

According to Yong it is possible to compensate for the conditions at very close spacing by adding a hydration energy component to the expressions, by paying particular attention to the counter ions in the Stern layer. To calculate the energies of interaction in this layer, it is necessary to estimate the concentration of ions at the inner and outer Helmholz plane, and to determine the energies involved in the hydration of the ions (Yong 1992). Calculations of swelling pressure for Na-montmorillonite, by use of an additional term, fits measured values quite well up to a swelling pressure of 30 MPa. However, at high salt concentrations, the measured pressures exceed calculated values. Yong proposes that this may be due to the use of concentrations instead of activities.

The models obviously suffer from the weaknesses of the double-layer theory; there are several double-layer models available, there are difficulties involved in their mathematical treatment, and in the selection of numerical values to be used. E.g. values between 2 and 50 are available for the relative dielectric constant of water on phyllosilicates (Sposito 1984). The problem is usually avoided in practice, as done above by Komine and Ogata, by using the value for pure water ($\varepsilon_w = 80$).

## 2.4 THERMODYNAMIC MODELS

### 2.4.1 General

A thermodynamic model describes the properties of the macroscopic clay water system. Consequently, it is not possible to draw any direct unambiguous conclusions on the swelling mechanism and the structure of adsorbed water from this concept. Introduction of microscopic parameters lead to unnecessary confusion (Sposito 1972).

Clay affinity for water leads to a low water vapor pressure in a dry clay. Water will thereby be transported into the clay volume, if the clay is contacted to a water solution with a higher vapor pressure. The uptake of water increases the vapor pressure in the clay-water system successively. A pressure will develop in this system if the vapor pressure is still lower, compared to that of the solution, at the time when the entire free space in the clay volume is filled with water. The magnitude of the pressure at equilibrium is governed by the difference in vapor pressure between the clay-water system and the solution, and may be calculated by means of thermodynamics (Sposito, 1972).

### 2.4.2 Clay-water potential

The following section is based on Yong's description of soil-water potential (1992).

Buckingham (1907) defined the capillary potential of a soil as the work required per unit weight of water to pull water away from the mass of soil. The potential in this approach is due to capillary forces at the air-water interfaces in the soil pores holding water in the soil.

In soil mechanics it is often more convenient to define the potential in terms of the water phase (soil-water potential, or free energy of the water in the soil), defined as the work required per unit weight of water to place water into a mass of soil. This leads to a change of sign and to increasing potential with increasing water content in the soil water system. The potential is consequently less negative in value as the water content increases, or in other words, the water vapor pressure is higher as the water content increases.

The soil-water potential of a soil-water system may be experimentally determined for various physico-chemical conditions. The values then represent the total soil-water potentials which may be divided in several water potential determining components.

- The matric potential, which is a matrix property and may be divided into one component due to air-water interface forces (matrix steric effect), and a second component due to swelling forces (matrix osmotic effect). Calculations of the matric potential for the two components will thereby be quite different. The water-air interface forces may be calculated for an

11

ideal system by use of capillary equations for the appropriate geometry, and swelling forces may be calculated by DDL theory.

There is no simple way to separate these components experimentally in studies on partly saturated soils. In a fully saturated system, the air-water interface component is obviously zero, which gives the possibility of determining the swelling component.

- The osmotic potential, which is related to the dissolved ions in the soil-water system and may be calculated from the concentration in the soil solution.

- The gravitational potential, which is the work required to transfer water from the reference elevation to the soil elevation.

- The pneumatic or pressure potential.

## 2.4.3 Quantitative model

The connection between swelling pressure $P_S$ and relative partial free energy on the basis of equilibrium thermodynamics have been derived and discussed in several articles (Low 1958, Sposito 1972, Kahr 1990) and may be summarized in the following way (Grauer 1986).

Low and Anderson have shown that:

$$\bar{g}_w - g_w^o = -\bar{v}_w \cdot P_S \qquad [15]$$

For changes in enthalpy, the following thermodynamic relation applies:

$$\left(\bar{g}_w - g_w^o\right) = \left(\bar{h}_w - h_w^o\right) - T \cdot \left(\bar{s}_w - s_w^o\right) \qquad [16]$$

there results

$$P_S = -\frac{\bar{h}_w - h_w^o}{\bar{v}_w} + T\frac{\bar{s}_w - s_w^o}{\bar{v}_w} \qquad [17]$$

Since

$$\bar{G}_w - G_w^o = M\left(\bar{g}_w - g_w^o\right) = RT\ln\frac{p}{p_0} \qquad [18]$$

with equation (15) there results

$$P_S = -\frac{RT}{M \cdot \bar{v}_w}\ln\frac{p}{p_0} \qquad [19]$$

12

where

$\overline{G}_w - G_w^o$: relative partial molar free energy of water in the clay/water system ($J \cdot mol^{-1}$).

$\overline{g}_w - g_w^o$: relative partial specific free energy of water in the clay/water system ($J \cdot g^{-1}$). The corresponding relative partial parameters enthalpy (h) and entropy (s) are similarly defined.

$\overline{V}_w$: partial specific volume of the water. Empirical correction

$$\overline{V}_w = 1.002 \, exp \, (0.036 \, \frac{m_w}{m_s}) \, (Oliphant \, 1982).$$

p, $p_o$: vapor pressure of adsorbed and pure water

M: molecular weight of the water

The vapor pressure in a certain clay-water system may be determined at equilibrium for various amounts of water adsorbed by the clay and the swelling pressure of the system may be calculated from eq. [19].

The equation can also be applied to salt-containing solutions (Low 1987). If the clay is equilibrated with an aqueous electrolyte solution instead of pure water, $G_w^o$ is replaced by the partial free energy of the water in the solution (Low 1958). This is equivalent to replacing the vapor pressure of pure water $p_0$ in eq. [19] by the vapor pressure in the electrolyte solution ($p_e$) as shown in eq. [20]. This leads to a reduction of the swelling pressure $P_S$ since the vapor pressure is lower in the salt solution.

$$P_S = -\frac{RT}{M \cdot \overline{v}_w} \ln \frac{p}{p_e} \qquad p_e < p_0 \qquad [20]$$

Since vapor pressure in electrolytes is tabulated for different concentrations it is possible to calculate the swelling pressure for a certain clay by use of equation [20] if the vapor pressure in the clay (p) is known.

## 2.4.4 Commentary on the model

Alternatively, equation [20] may be expressed

$$P_S = -\frac{RT}{M \cdot \overline{v}_w} \ln \, (\frac{p}{p_0}) - \left( -\frac{RT}{M \cdot \overline{v}_w} \ln \, (\frac{p_e}{p_0}) \right) \qquad [21]$$

The first term represents swelling pressure of the clay according to eq. [19], and the second term represents the osmotic pressure of the surrounding salt solution (cf Figure 2-2). From eq. [21] it is obvious that the swelling

13

pressure of the system will be zero if the vapor pressure in the clay-water system (p) is equal to the one in the surrounding solution ($p_e$).
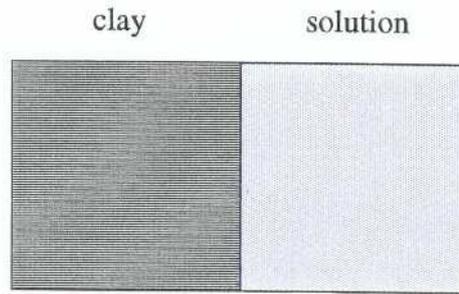


*Figure 2-2    Principle clay-water/water-solution system. cf. to eq. [21]. The two physical volumes are separated by a semipermeable membrane permeable to dissolved ions and water, but not to the mineral flakes. The membrane may represent a filter in a laboratory test, the rock-buffer interface or internal membrane functions in the clay volume.*

A conservative use of eq. [21], with respect to the preservation of swelling pressure, is to assume that the vapor pressure (p) in the clay-water system is not changed by the surrounding salt solution, i.e. the partial molar free energy of water ($\overline{G}_w$) in the clay-water system is not changed.

General calculations of swelling pressure as a function of density for different salt contents in the saturating solution, by use of this approach, are shown in Figure 2-3. The small dots represent measured pressure values of MX-80 bentonite saturated by pure water. The rightward curve shows calculated pressures in a clay equilibrated with a saturated NaCl solution (6.1 M, 36% b.w.). Round open and filled larger dots represent measured values of samples saturated by 0.5 and 3.5% NaCl solutions, respectively.
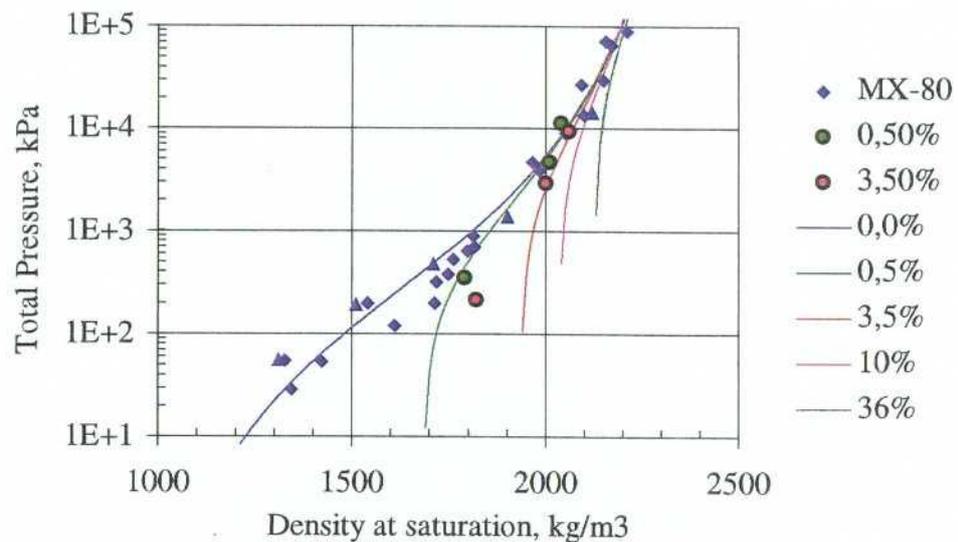


*Figure 2-3.    Results from measured swelling pressure (dots) and calculated pressures according to eq. [19] (lines). Figures show percent NaCl by weight in actual and imagined solutions.*

14

In a KBS-3 type repository the proposed bentonite buffer density is 2000 kg/m³ at full water saturation, corresponding to a water/clay ratio of 26%. The corresponding water vapor ratio ($p/p_0$) has been determined for MX-80 bentonite to be around 0.96, if saturated by pure water (Kahr, 1986). The corresponding water vapor ratio ($p_e/p_0$) in a NaCl solution is given by a concentration of approximately 1.25 M (70 g NaCl in 1 liter $H_2O$, between blue and red curve in Figure 2-3). The swelling pressure would consequently be zero for this combination of water vapor ratios in the clay-water system and in the surrounding water solution. At higher electrolyte concentrations the consequence of this use of equation [21] is, in addition to the lack of swelling pressure, also dehydration of the clay due to the dominant osmotic term.

However, literature data do not support the lack of swelling pressure, or dehydration, if bentonite clay at buffer conditions is saturated by brines (Dixon, 1996). In Figure 2-3 only the calculated data for 0.5% NaCl solution fits with experimental data. A first extreme verification test was made in this study, by use of a swelling pressure oedometer, in order to confirm the literature data. Airdry MX-80 bentonite was compacted to a density corresponding to 2000 kg/m³ at full water saturation, and the clay was contacted to a saturated NaCl solution (6.1 M, 36% NaCl b.w.). The macroscopic swelling pressure in the clay was measured during water uptake and the course is shown in Figure 2-4.
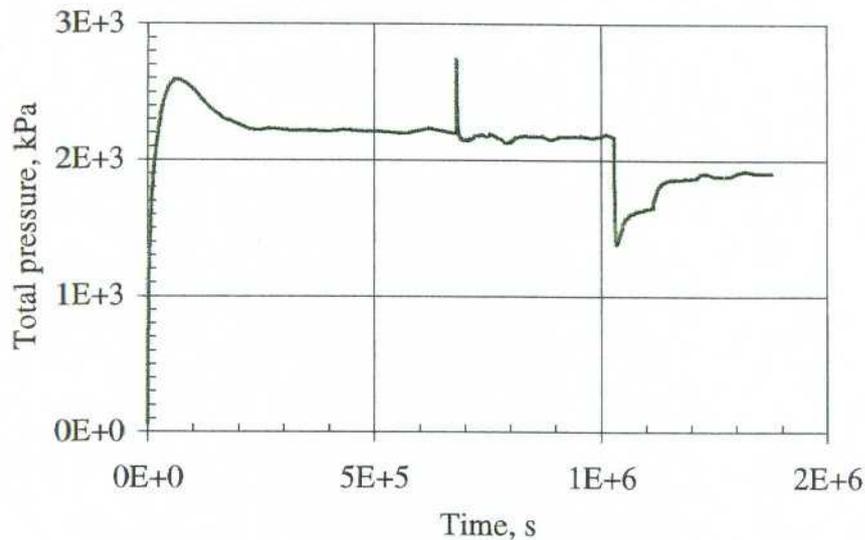


*Figure 2-4.    Swelling pressure built-up in MX-80 clay saturated by a 6.1 M NaCl solution. The clay density correspond to the proposed KBS-3 buffer (2000kg/m³ at full saturation).*

In order to ensure that the recorded pressure did not originate from released compaction tension, the clay-water volume was increased after pressure had stabilized (after around 1E6 s) and the pressure was thereby significantly reduced. The pressure was once again built up to a value of almost 2 MPa which strongly indicates that the pressure was related to true swelling. The expected pressure for a corresponding sample saturated with pure water is around 5MPa.

Consequently, the experimental data strongly indicate that the conservative use of eq. [21] is not adequate for high salt concentrations. The conservative approach does not take into account that ions may enter the clay-water system along with the saturating solution and thereby reduce the partial molar free energy of water $(\overline{G}_w)$ in the clay-water system. Introduced salt may be treated as an additional osmotic component acting in the clay-water volume according to section 2.4.1, and eq. [21] may then be completed by an osmotic term:

$$P_S = -\frac{RT}{M \cdot \overline{v}_w} \ln \frac{p}{p_0} + \left( -\frac{RT}{M \cdot \overline{v}_w} \ln \frac{p_{ie}}{p_0} \right) - \left( -\frac{RT}{M \cdot \overline{v}_w} \ln \frac{p_e}{p_0} \right) \qquad [22]$$

where p is the vapor pressure in the clay-water solution as saturated by pure water, $p_{ie}$ is the vapor pressure in a water solution with a concentration corresponding to the increase of ion concentration in the clay-water system as saturated by the electrolyte solution.

If the surrounding solution freely could enter the clay, without changes in ion content, this would lead to an internal osmotic component in the clay which fully would compensate for the external osmotic effect (i.e. $p_{ie} = p_e$). In other words, the swelling pressure would be unaffected by a salt solution, which nor is in agreement with the experimental data. Obviously, the laboratory data suggests that originally external ions are present in the clay pore water at equilibrium, and that the concentration is lower than in the surrounding water solution.

The validity of this approach may be examined by at least the three following techniques:

• Direct measurement of the vapor pressure in the clay at different physico-chemical conditions (e.g. densities and salt contents).

• Direct measurements of the ion content in the clay pore-water at different physico-chemical conditions.

• Calculation of the amount of ions in the clay pore solution for various external salt solution by use of the Donnan expression (section 2.4.4). The resulting calculated total pressures may then be compared with the actual measured swelling pressures.

The latter technique, if the principle turns out to well describe the actual conditions, admit calculation of the swelling pressure in a clay-water system for any given salt solution if the swelling pressure, or vapor pressure, is known for the clay as saturated by pure water.

16

### 2.4.5 Donnan exclusion

The montmorillonite part in bentonite clay is composed of the negatively charged mineral flakes and charge compensating cations (Figure 1.1). The mineral flakes may consequently be seen as macro-ions and the system may be regarded as a polyelectrolyte. Donnan (1911) showed that a system similar to that in Figure 2-5 may lead to an unequal distribution of ions which are diffusable across a membrane separating the two volumes.
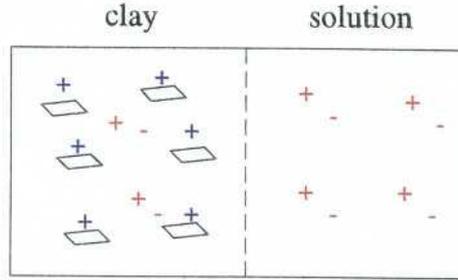


*Figure 2-5.   principle clay-water/water-solution system. Clay mineral flakes and charge compensating cations on the left side, and sodium and chloride ions on both sides of the filter. The number of chloride ions is lower on the clay side of the separating membrane compared to the external solution.*

The condition for equilibrium is that the chemical potentials be equal on both sides of the membrane for all components which can permeate. Since the macro-sized mineral flakes cannot pass the membrane, the equilibrium will be established only for ions in the saturating solution and the original montmorillonite cations. Idealized, this will only be $Na^+$ and $Cl^-$. The conditions of electrical neutrality in the entire system is

$$zC_m = C_{Cl-} - C_{Na+} \qquad [23]$$

where z is the valence of the macromolecule, $C_m$, $C_{Na+}$ and $C_{Cl-}$ is the concentration of the macromolecules, sodium ions and chloride ions, respectively.

In terms of activity the equilibrium condition for the diffusable ions will be

$$\{Na^+_c\}\{Cl^-_c\} = \{Na^+_e\}\{Cl^-_e\} \qquad [24]$$

Where the indices c and e refer to the clay-water system and to the surrounding salt solution, respectively. Approximation of the involved activity factors to a uniform value is reasonable since the concentrations of interest are all generally high. This gives

$$[Na^+_c][Cl^-_c] = [Na^+_e][Cl^-_e] \qquad [25]$$

The $[Na^+_c]$ factor is the sum of the concentration of original charge compensating ions $[Na^+_{cc}]$ and introduced electrolyte ions $[Na^+_{ce}]$. Local

electrical neutrality has to be established why $[Na^+_e] = [Cl^-_e]$ and $[Na^+_{ce}] = [Cl^-_{ce}]$ and eq. [25] may be written

$$([Na^+_{cc}]+[Na^+_{ce}])\ [Na^+_{ce}] = [Na^+_e]\ [Na^+_e] \qquad [26]$$

The total concentration of the original charge compensating ions $[Na^+_{cc}]$ are calculable for any water content from the clay CEC value, and the concentration of the surrounding solution may be determined. Consequently, it is possible to calculate the concentration of sodium ion introduced to the clay-water system according to

$$[Na^+_{ce}] = \frac{-\left[[Na^+_{cc}] \pm \sqrt{[Na^+_{cc}]^2 + 4 \cdot [Na^+_e]^2}\right]}{2} \qquad [27]$$

and thereby also the total number of ions in the clay-water system.

### 2.4.6 Calculation of swelling pressure

Since the concentrations of the ions introduced into the clay are possible to calculate, it is convenient to calculate the effect of the osmotic pressure directly from concentrations. This may be done by use of van't Hoff equation:

$$P_o = i \cdot C \cdot R \cdot T \qquad [28]$$

where $P_0$ is the osmotic pressure, i is the van't Hoff factor, C is the concentration of solute in moles per liter, R is the gas constant and T is the absolute temperature.

Eq. [22] may now be rewritten as

$$P_S = -\frac{RT}{M \cdot \overline{v}_w} \ln \frac{p}{p_0} - i \cdot R \cdot T(C_e - C_{ce}) \qquad [29]$$

where $C_e$ is the electrolyte concentration in the surrounding water solution and $C_{ce}$ is the concentration of the introduced solution.

The first term in eq. [29], representing the clay component of swelling pressure, may be replaced by experimental data of bentonite saturated by pure water. The advantage by doing this is that possible experimental artifacts will be similar in calculated and measured values and the effects of the salt solutions may be better compared.

In order to facilitate the calculations, the experimental swelling pressure values are adapted to a function of the water/clay ratio, by use of an expression based on the Langmuir equation [1]. The swelling pressure can thereby be calculated as a function of the same water/clay ratio as used in order to calculate the concentration of charge compensating ions in the

18

original clay. The accuracy of the adaptation is indicated by the actual measured values in the various diagrams.

A specific issue in eq. [29] is the van´t Hoff factor which by definition may vary between 1 and 2 for a 1:1 salt. The value is expected to be close to 2 in dilute solutions of strong electrolytes such as NaCl. Empirically it is found to decrease as the concentration increases. The most conservative use of eq. [29] is to set the van´t Hoff factor to be 2 (Figure 2-6).
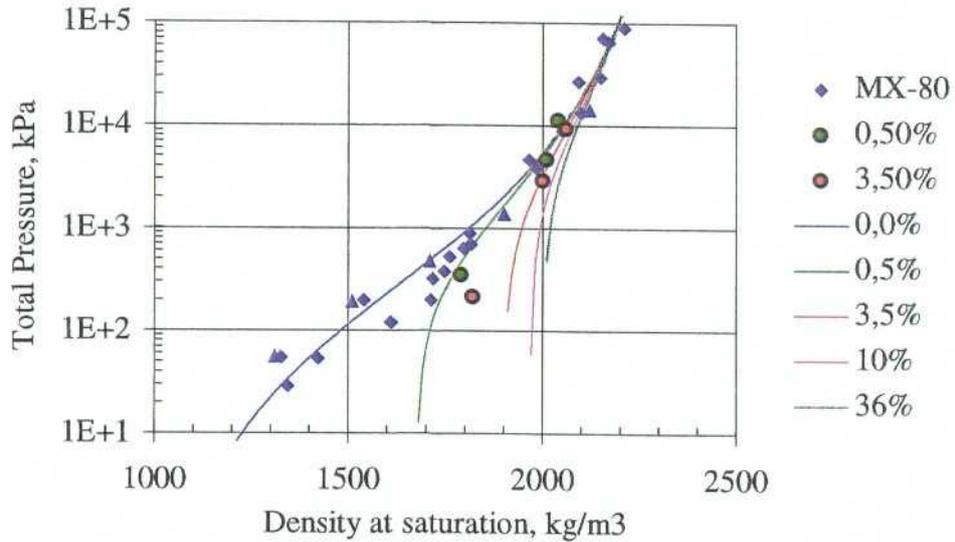


*Figure 2-6. Results from measured swelling pressure (dots) and calculated pressures according to eq. [19] (lines). Figures show percent NaCl by weight in actual and imagined solutions. Calculations are made by use of eq. [29] and i = 2.*

The best fit to experimental data, however, is arrived at if the van´t Hoff factor is set to 1. (Figure 2-7). The physical meaning of this is that no free ions exist in the solutions, or that the sodium and chloride ions act as pairs, which makes this value less probable.

Literature values of osmotic pressure for relatively concentrated NaCl solutions may be well reproduced by use of eq. [28] and a constant i-value of 1.9 as shown in Table 2-2. The use of this probable i-value gives the calculated pressures shown in Figure 2-8.

Table 2-2 Calculated osmotic pressure by use of eq. [28] and i=1.9, and literature values (Lang, 1967).

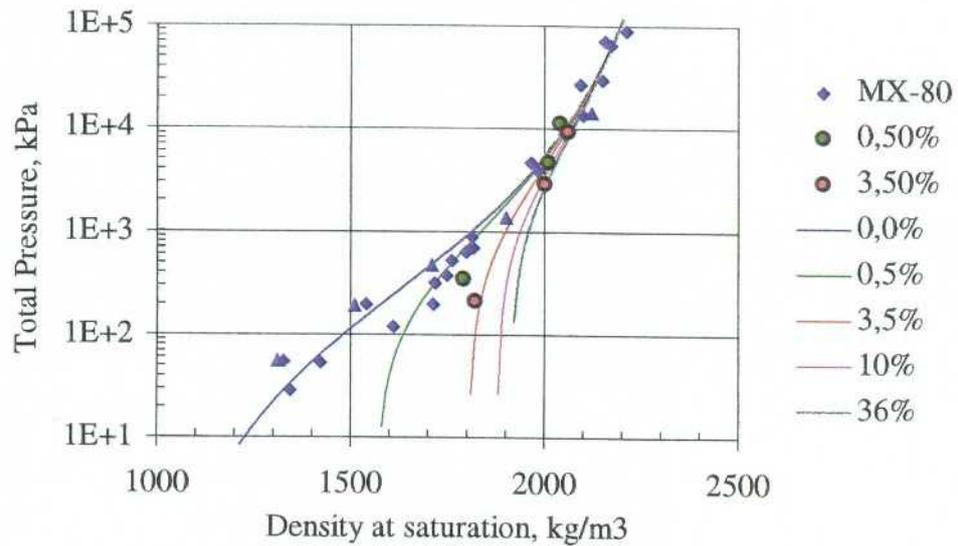| [NaCl] M | NaCl % b. w. | $p/p_0$, eq. [21] - | $P_o$, eq. [28] kPa | $P_o$ lit. values kPa |
|---|---|---|---|---|
| 0.5 | 2.93 | 0.984 | 2354 | 2281 |
| 1.0 | 5.85 | 0.968 | 4708 | 4640 |
| 1.5 | 8.78 | 0.952 | 7061 | 7134 |
| 2.0 | 11.70 | 0.937 | 9415 | 9780 |

19

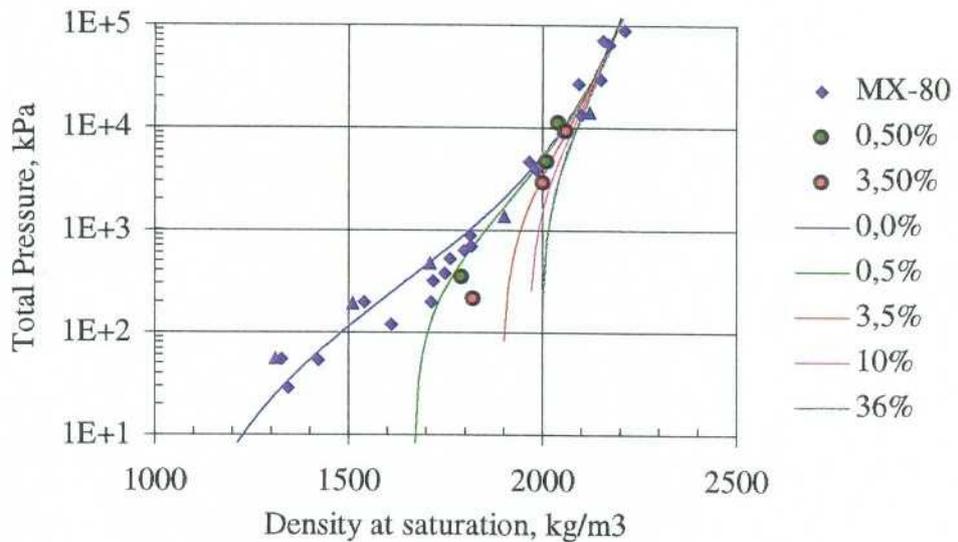*Figure 2-7.    Calculations made by use of eq. [29] and i = 1.*



*Figure 2-8.    Calculations made by use of eq. [29] and i = 1.9.*

In order to even better hit the experimental data the following approach may be discussed.

The calculations presented so far have considered the charge balancing cations in the montmorillonite as free ions. The van´t Hoff factor reflects that all possible ions are not acting as individual particles even in strong electrolytes as NaCl. In the montmorillonite polyelectrolyte-like system the conditions may be similar, i.e. not all charge balancing cations may act as free ions for all physico-chemical conditions. If so, the Donnan exclusion will be less significant than previously calculated. A "van´t Hoffs factor" may therefore be proposed to be used also for the montmorillonite. The effect of the negatively charged montmorillonite flakes is zero since the calculations only concerns the diffusable ions. Also with respect to osmosis the macro-

sized flakes may be considered as insignificant since the osmosis is a colligative property. Thus, the "clay van´t Hoff factor" ($i_{clay}$) has a theoretical value between 0 and 1 as calculated from sodium concentration.

Such a "clay van´t Hoff factor" may seem as a "fudge factor", but the physical meaning is clear and it is possible to indirectly determine the correctness of a certain value by chemical analysis of the clay at equilibrium. Further, a constant value, for all conditions with respect to NaCl concentration and clay density, seems to be sufficient in order to correlate calculated and measured pressure values. Speculatively, this indicates that an $i_{clay}$-value may be used as a material constant depending on the factors described in section 1.3 (cf. the constants proposed by Yong and Warkentin eq. [11]). The result from calculations with $i_{clay}$ = 0.3 for MX-80 bentonite is shown in Figure 2-9.
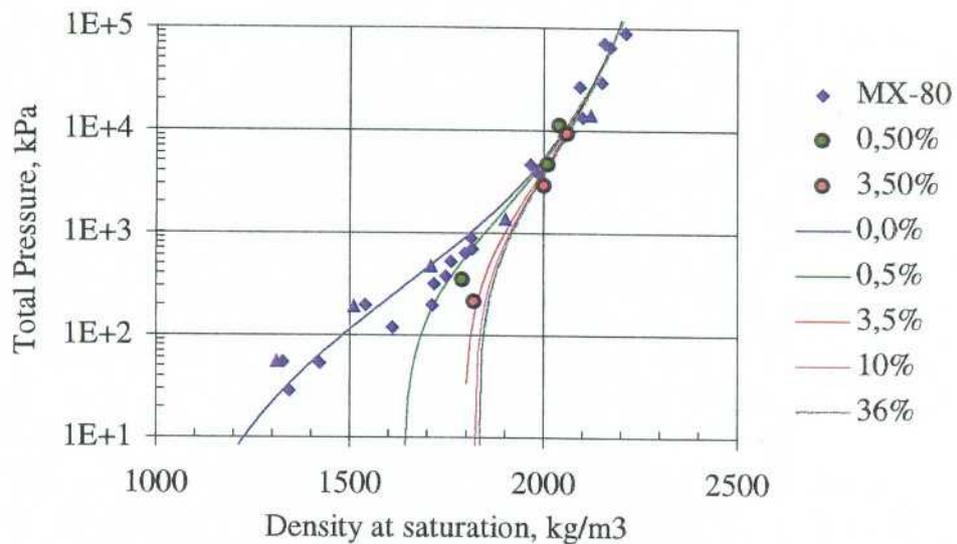


*Figure 2-9.   Results from measured swelling pressure (dots) and calculated pressures according to eq. [19] (lines). Figures show percent NaCl by weight in actual and imagined solutions. Calculations are made by use of eq. [29] and $i_{clay}$ = 0.3 and $i_{NaCl}$ = 1.9.*

*Comments on the swelling pressure calculations*

Figure 2-3 and 2-6, respectively, show the total pressure without (eq. [21]) and with (eq. [22]) an internal osmotic term as calculated by use of the Donnan equation. Although the results in Figure 2-6 represents the most possible conservative i-values (i = 2), with respect to the preservation of swelling pressure, they still show substancial swelling pressures at high clay densities also in brines, and thereby also much better correlation with experimental data. An alternative presentation of the two approaches, for specific buffer densities, is shown in Figure 2-10 (correspond to Figure 2-3) and Figure 2-11 (correspond to Figure 2-6).
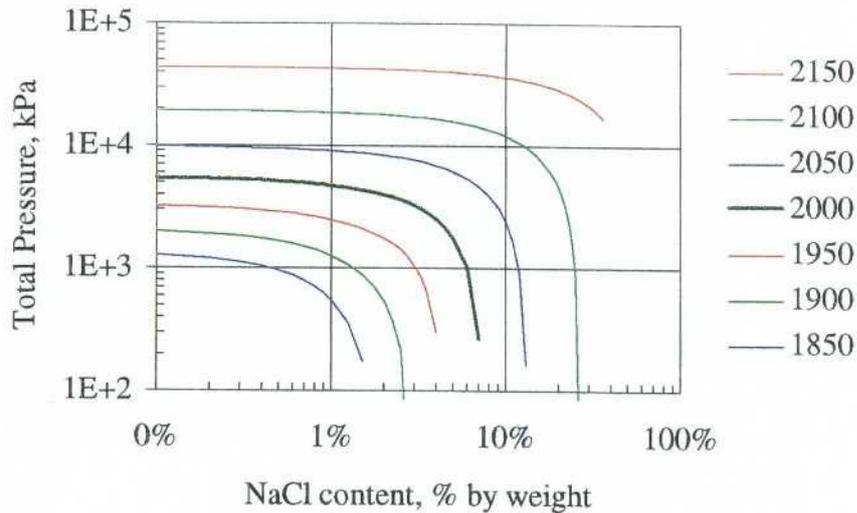
21

*Figure 2-10.  Calculated total pressure in the clay-water system without an internal osmotic term. Figures indicate clay density at saturation in kg/m³. Zero pressure is postulated for the proposed buffer density at a NaCl content of approximately 7%. Calculations are made by use of eq. [21].*
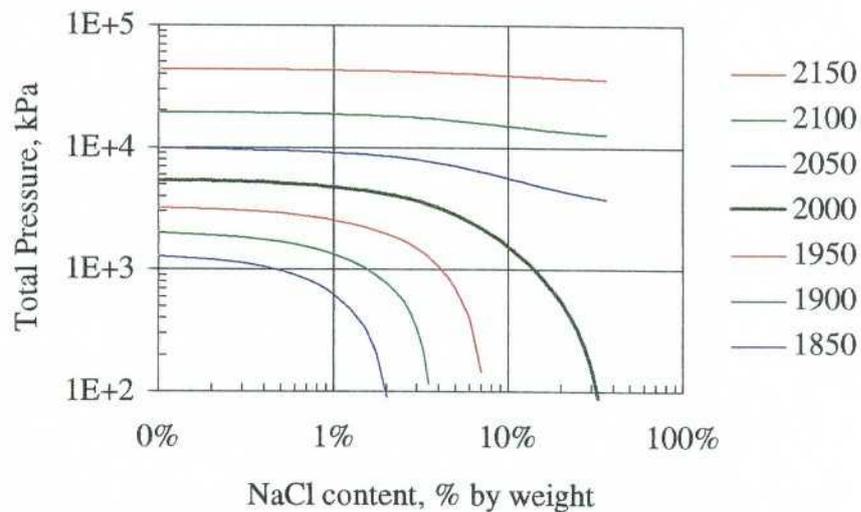


*Figure 2-11.  Calculated total pressure in the clay-water system including an internal osmotic term calculated by use of the Donnan expression. Figures indicate clay density (kg/m³) at saturation. A substantial swelling pressure is postulated for the proposed buffer density also for brine conditions. Calculations are made by use of eq. [29] and i = 2.*

### 2.4.7    Verification tests

The thermodynamic model indicates a number of implications for testing bentonite material and for buffer application. The following examples are of special interest.

- Original salt in the bentonite material may not unambiguously be regarded as conservative test conditions, with respect to swelling pressure preservation, since the salt may add an osmotic component.

- Presaturation of a bentonite buffer by use of pure water may under certain condition increase the negative effects of saline ground-water on swelling pressure instead of reducing them.

- No swelling pressure will be present at bentonite densities lower than 1.8 $g/cm^3$ in a saturated NaCl solution

- $CaCl_2$ solutions will have approximately the same effect on swelling pressure as NaCl solutions for bentonite at densities of current interest.

The latter consequence is an effect of the colligative nature of osmosis. If the solution concentration is expressed in moles per liter, the same concentration value for NaCl and $CaCl_2$ accordingly results in a slightly higher effect of the $CaCl_2$ solution (theoretically 3/2 times). If the values are given in percent by weight or as chloride contents the effect is reversed. This has been substantiated in previous laboratory tests for densities between 1800 and 2100 $kg/m^3$ (Karnland 1992).

Three additional verification tests were made to further check these consequences predicted by the model. The conditions and results were the following.

*Test V2*

MX-80 bentonite was prepared to a clay-water density corresponding to 2000 $kg/m^3$ after saturation with pure water. The sample was thoroughly mixed with finely ground sodium chloride powder before saturation. The amount of salt corresponded to a fully saturated solution in the pore-water at the actual density. The sample was thereafter saturated by a 6.1 M sodium chloride solution. The development of swelling pressure is shown in Figure 2-12.

The final swelling pressure was approximately 5 MPa, which is twice the measured value for conditions without internal salt, and what is expected if the osmotic internal and external effects of sodium chloride are the same. The recorded high pressure agrees with the model predictions, both in principle and in amount. However, an artifact may be the volume of non-dissolved sodium chloride which may act as bulk material, and thereby increase the bentonite density.
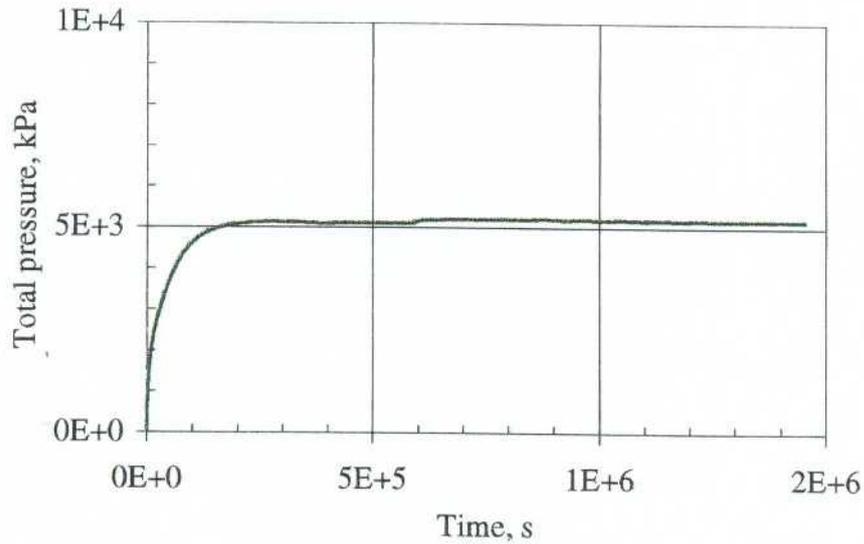
*Figure 2-12. Measured swelling pressure in oedometer test with MX-80 clay mixed with powdered NaCl at a clay-water density of 2000 kg/m³ and saturated by 6.1 M NaCl solution.*

*Test V3*

MX-80 clay-water density corresponding to 2000 kg/m3 after saturation with pure water. The sample was pre-saturated by deionized water and thereafter contacted to a saturated NaCl solution (6.1 M). The swelling pressure development is shown in Figure 2-13.

The marked drop in swelling pressure due to the contact to the salt solution is in agreement with model predictions. The residual final swelling pressure was in principle the same as what was measured when the clay was initially saturated by a 6.1 M NaCl solution and may be explained by a relatively fast diffusion of ions into the clay from the salt solution.
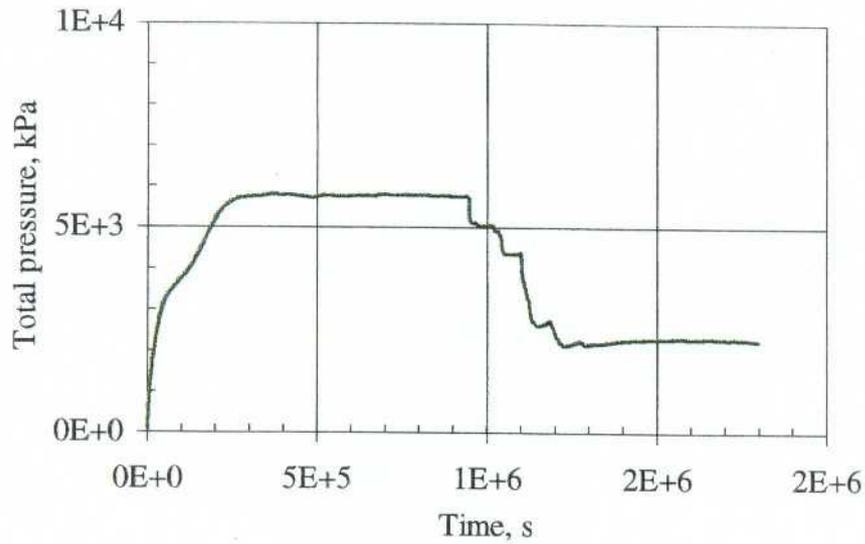
*Figure 2-13. Measured swelling pressure in oedometer test with MX-80 clay at a clay-water density of 2000 kg/m³. The clay was saturated by pure water and, at stable pressure condition, contacted to 6.1 M NaCl solution. The plateaus in the pressure line after contact to the salt solution are due to intermittent replacement of solution in the filters.*

*Test V4*

MX-80 clay-water density corresponding to 1800 kg/m3 after saturation with pure water. The sample was saturated by 6.1 M NaCl solution. The swelling pressure development is shown in Figure 2-14. The final swelling pressure was 130 kPa, which is a possible value according to the prediction shown in Figure 2-9.
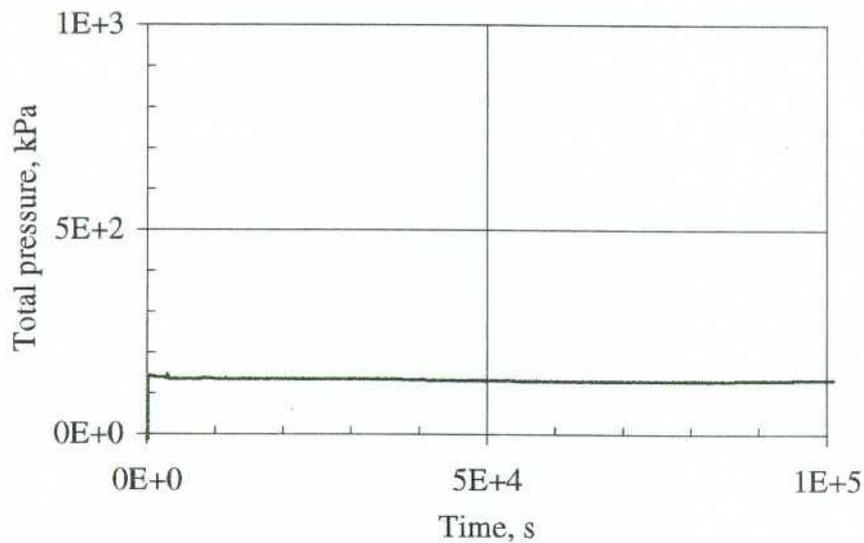


*Figure 2-14. Measured swelling pressure in oedometer test with MX-80 clay at a clay-water density of 1800 kg/m³ and saturated by 6.1 M NaCl solution.*

25

# 3    CONCLUSIONS

The performed literature study showed that the swelling capacity and swelling pressure of different types of bentonites and bentonite mixtures have been determined at several independent laboratories. A large number of investigations have also given detailed information concerning the physico-chemical conditions in the clay-water system. This have led to a consensus concerning the physical effects of bentonite swelling both on the macroscopic and microscopic levels. However, there is no general consensus concerning the detailed mechanisms leading to these effects, i.e. concerning the forces involved and how they may be determined or calculated. Several quite different approaches and theories have been proposed and there is an ongoing debate on the subject. In this study, only the thermodynamic model show satisfactory concordance between calculated and measured values of swelling pressure in bentonite exposed to concentrated salt solutions. It should, however, be noticed that other improved models are presently being developed.

The most important conclusion from this study is that the thermodynamic model may well predict the measured swelling pressures by use of eq. [20]. The only prerequisite for this is that the partial free energy of water in the clay-water system changes if the system is contacted to a salt solution compared to if the system is contacted to pure water. This means that there is no principle incongruity between the model and measured swelling pressures, and the main aim of this report is thereby fulfilled. The change may be treated as an osmotic component in the clay-water system according to the performed calculations.

The proposed quantification technique for swelling pressure at different clay densities and salt contents, as based on Donnan ion equilibrium and van't Hoff equation, gives significantly better correlation between calculated and measured values compared to previous models, also if the theoretically most conservative conditions are assumed. If a "clay van't Hoff factor" is introduced the correlation is further improved. The physical existence of such a factor and its value may be experimentally determined.

The experimental data and the performed calculations indicate that there will be a significant swelling pressure in the buffer also at saline ground-water conditions. The theoretical difference in effect from NaCl and $CaCl_2$ solutions is small according to the thermodynamic approach. However, the reduced swelling capacity in a brine type of ground-water significantly raises the lowest possible buffer density, and in practice, eliminate the positive effects of mixing bentonite into a backfill material.

# ACKNOWLEDGEMENT

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# List of SKB reports

## Annual Reports

*1977-78*
TR 121
**KBS Technical Reports 1 – 120**
Summaries
Stockholm, May 1979

*1979*
TR 79-28
**The KBS Annual Report 1979**
KBS Technical Reports 79-01 – 79-27
Summaries
Stockholm, March 1980

*1980*
TR 80-26
**The KBS Annual Report 1980**
KBS Technical Reports 80-01 – 80-25
Summaries
Stockholm, March 1981

*1981*
TR 81-17
**The KBS Annual Report 1981**
KBS Technical Reports 81-01 – 81-16
Summaries
Stockholm, April 1982

*1982*
TR 82-28
**The KBS Annual Report 1982**
KBS Technical Reports 82-01 – 82-27
Summaries
Stockholm, July 1983

*1983*
TR 83-77
**The KBS Annual Report 1983**
KBS Technical Reports 83-01 – 83-76
Summaries
Stockholm, June 1984

*1984*
TR 85-01
**Annual Research and Development Report 1984**
Including Summaries of Technical Reports Issued during 1984. (Technical Reports 84-01 – 84-19)
Stockholm, June 1985

*1985*
TR 85-20
**Annual Research and Development Report 1985**
Including Summaries of Technical Reports Issued during 1985. (Technical Reports 85-01 – 85-19)
Stockholm, May 1986

*1986*
TR 86-31
**SKB Annual Report 1986**
Including Summaries of Technical Reports Issued during 1986
Stockholm, May 1987

*1987*
TR 87-33
**SKB Annual Report 1987**
Including Summaries of Technical Reports Issued during 1987
Stockholm, May 1988

*1988*
TR 88-32
**SKB Annual Report 1988**
Including Summaries of Technical Reports Issued during 1988
Stockholm, May 1989

*1989*
TR 89-40
**SKB Annual Report 1989**
Including Summaries of Technical Reports Issued during 1989
Stockholm, May 1990

*1990*
TR 90-46
**SKB Annual Report 1990**
Including Summaries of Technical Reports Issued during 1990
Stockholm, May 1991

*1991*
TR 91-64
**SKB Annual Report 1991**
Including Summaries of Technical Reports Issued during 1991
Stockholm, April 1992

*1992*
TR 92-46
**SKB Annual Report 1992**
Including Summaries of Technical Reports Issued during 1992
Stockholm, May 1993

*1993*
TR 93-34
**SKB Annual Report 1993**
Including Summaries of Technical Reports Issued during 1993
Stockholm, May 1994

*1994*
TR 94-33
**SKB Annual Report 1994**
Including Summaries of Technical Reports Issued
during 1994
Stockholm, May 1995


*1995*
TR 95-37
**SKB Annual Report 1995**
Including Summaries of Technical Reports Issued
during 1995
Stockholm, May 1996


*1996*
TR 96-25
**SKB Annual Report 1996**
Including Summaries of Technical Reports Issued
during 1996
Stockholm, May 1997


# List of SKB Technical Reports 1997

TR 97-01
**Retention mechanisms and the flow
wetted surface – implications for safety
analysis**
Mark Elert
Kemakta Konsult AB
February 1997


TR 97-02
**Äspö HRL – Geoscientific evaluation
1997/1. Overview of site characterization
1986–1995**
Roy Stanfors[1], Mikael Erlström[2],
Ingemar Markström[3]
[1] RS Consulting, Lund
[2] SGU, Lund
[3] Sydkraft Konsult, Malmö
March 1997


TR 97-03
**Äspö HRL – Geoscientific evaluation
1997/2. Results from pre-investigations
and detailed site characterization.
Summary report**
Ingvar Rhén (ed.)[1], Göran Bäckblom (ed.)[2],
Gunnar Gustafson[3], Roy Stanfors[4], Peter Wikberg[2]
[1] VBB Viak, Göteborg
[2] SKB, Stockholm
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[4] RS Consulting, Lund
May 1997


TR 97-04
**Äspö HRL – Geoscientific evaluation
1997/3. Results from pre-investigations
and detailed site characterization.
Comparison of predictions and
observations. Geology and
mechanical stability**
Roy Stanfors[1], Pär Olsson[2], Håkan Stille[3]
[1] RS Consulting, Lund
[2] Skanska, Stockholm
[3] KTH, Stockholm
May 1997


TR 97-05
**Äspö HRL – Geoscientific evaluation
1997/4. Results from pre-investigations
and detailed site characterization.
Comparison of predictions and observa-
tions. Hydrogeology, groundwater
chemistry and transport of solutes**
Ingvar Rhén[1], Gunnar Gustafson[2], Peter Wikberg[3]
[1] VBB Viak, Göteborg
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[3] SKB, Stockholm
June 1997


TR 97-06
**Äspö HRL – Geoscientific evaluation
1997/5. Models based on site character-
ization 1986–1995**
Ingvar Rhén (ed.)[1], Gunnar Gustafson[2],
Roy Stanfors[3], Peter Wikberg[4]
[1] VBB Viak, Göteborg
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[3] RS Consulting, Lund
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October 1997


TR 97-07
**A methodology to estimate earthquake
effects on fractures intersecting canister
holes**
Paul La Pointe, Peter Wallmann, Andrew Thomas,
Sven Follin
Golder Associates Inc.
March 1997


TR 97-08
**Äspö Hard Rock Laboratory
Annual Report 1996**
SKB
April 1997


TR 97-09
**A regional analysis of groundwater flow
and salinity distribution in the Äspö area**
Urban Svensson
Computer-aided Fluid Engineering AB
May 1997

## TR 97-10
**On the flow of groundwater in closed tunnels. Generic hydrogeological modelling of nuclear waste repository, SFL 3–5**
Johan G Holmén
Uppsala University/Golder Associates AB
June 1997

## TR 97-11
**Analysis of radioactive corrosion test specimens by means of ICP-MS. Comparison with earlier methods**
R S Forsyth
Forsyth Consulting
July 1997

## TR 97-12
**Diffusion and sorption properties of radionuclides in compacted bentonite**
Ji-Wei Yu, Ivars Neretnieks
Dept. of Chemical Engineering and Technology, Chemical Engineering, Royal Institute of Technology, Stockholm, Sweden
July 1997

## TR 97-13
**Spent nuclear fuel – how dangerous is it? A report from the project "Description of risk"**
Allan Hedin
Swedish Nuclear Fuel and Waste Management Co,
Stockholm, Sweden
March 1997

## TR 97-14
**Water exchange estimates derived from forcing for the hydraulically coupled basins surrounding Äspö island and adjacent coastal water**
Anders Engqvist
A & I Engqvist Konsult HB, Vaxholm, Sweden
August 1997

## TR 97-15
**Dissolution studies of synthetic soddyite and uranophane**
Ignasi Casas[1], Isabel Pérez[1], Elena Torrero[1], Jordi Bruno[2], Esther Cera[2], Lara Duro[2]
[1] Dept. of Chemical Engineering, UPC
[2] QuantiSci SL
September 1997

## TR 97-16
**Groundwater flow through a natural fracture. Flow experiments and numerical modelling**
Erik Larsson
Dept. of Geology, Chalmers University of Technology, Göteborg, Sweden
September 1997

## TR 97-17
**A site scale analysis of groundwater flow and salinity distribution in the Äspö area**
Urban Svensson
Computer-aided Fluid Engineering AB
October 1997

## TR 97-18
**Release of segregated nuclides from spent fuel**
L H Johnson, J C Tait
AECL, Whiteshell Laboratories, Pinawa, Manitoba, Canada
October 1997

## TR 97-19
**Assessment of a spent fuel disposal canister. Assessment studies for a copper canister with cast steel inner component**
Alex E Bond, Andrew R Hoch, Gareth D Jones, Aleks J Tomczyk, Richard M Wiggin, William J Worraker
AEA Technology, Harwell, UK
May 1997

## TR 97-20
**Diffusion data in granite Recommended values**
Yvonne Ohlsson, Ivars Neretnieks
Department of Chemical Engineering and Technology, Chemical Engineering, Royal Institute of Technology, Stockholm, Sweden
October 1997

## TR 97-21
**Investigation of the large scale regional hydrogeological situation at Ceberg**
Anders Boghammar[1], Bertil Grundfelt[1], Lee Hartley[2]
[1] Kemakta Konsult AB, Sweden
[2] AEA Technology, UK
November 1997

TR 97-22
**Investigations of subterranean microorganisms and their importance for performance assessment of radioactive waste disposal. Results and conclusions achieved during the period 1995 to 1997**
Karsten Pedersen
Göteborg University, Institute of Cell and Molecular Biology, Dept. of General and Marine Microbiology, Göteborg, Sweden
November 1997


TR 97-23
**Summary of hydrogeologic conditions at Aberg, Beberg and Ceberg**
Douglas Walker[1], Ingvar Rhén[2], Ioana Gurban[1]
[1] INTERA KB
[2] VBB Viak
October 1997


TR 97-24
**Characterization of the excavation disturbance caused by boring of the experimental full scale deposition holes in the Research Tunnel at Olkiluoto**
Jorma Autio
Saanio & Riekkola Oy, Helsinki, Finland
September 1997


TR 97-25
**The SKB Spent Fuel Corrosion Programme.**
**An evaluation of results from the experimental programme performed in the Studsvik Hot Cell Laboratory**
Roy Forsyth
Forsyth Consulting
December 1997


TR 97-26
**Thermoelastic stress due to a rectangular heat source in a semi-infinite medium. Application for the KBS-3 repository**
Thomas Probert, Johan Claesson
Depts. of Mathematical Physics and Building Physics, Lund University, Sweden
April 1997


TR 97-27
**Temperature field due to time-dependent heat sources in a large rectangular grid. Application for the KBS-3 repository**
Thomas Probert, Johan Claesson
Depts. of Mathematical Physics and Building Physics, Lund University, Sweden
April 1997


TR 97-28
**A mathematical model of past, present and future shore level displacement in Fennoscandia**
Tore Påsse
Sveriges geologiska undersökning, Göteborg
Sweden
December 1997


TR 97-29
**Regional characterization of hydraulic properties of rock using well test data**
David Wladis, Patrik Jönsson, Thomas Wallroth
Department of Geology, Chalmers University of Technology, Göteborg, Sweden
November 1997


TR 97-30
**ZEDEX - A study of damage and disturbance from tunnel excavation by blasting and tunnel boring**
Simon Emsley[1], Olle Olsson[2], Leif Stenberg[2], Hans-Joachim Alheid[3], Stephen Falls[4]
[1] Golder Associates, Maidenhead, United Kingdom
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December 1997