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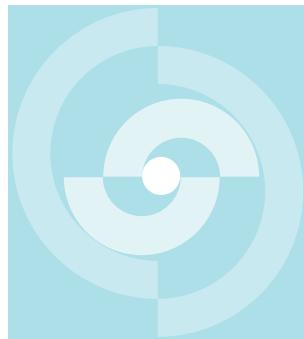
Nationale  
Genossenschaft  
für die Lagerung  
radioaktiver Abfälle

**Cédra**

Société coopérative  
nationale  
pour l'entreposage  
de déchets radioactifs

**Cisra**

Società cooperativa  
nazionale  
per l'immagazzinamento  
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# TECHNICAL REPORT 86-15

## Degradation of Concrete in a LLW/ILW Repository

L.O. Höglund

June 1987

KEMAKTA Konsult AB, Stockholm



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Der vorliegende Bericht wurde im Auftrag der Nagra erstellt.  
Die Autoren haben ihre eigenen Ansichten und Schlussfolgerungen dargestellt. Diese müssen nicht unbedingt mit denjenigen der Nagra übereinstimmen.

Le présent rapport a été préparé sur demande de la Cédra.  
Les opinions et conclusions présentées sont celles des auteurs et ne correspondent pas nécessairement à celles de la Cédra.

This report was prepared as an account of work sponsored by Nagra. The viewpoints presented and conclusions reached are those of the author(s) and do not necessarily represent those of Nagra.

SUMMARY

The release rate of radionuclides from a Type B repository depends on the long-term properties of the concrete. The critical properties of the concrete are diffusivity and hydraulic conductivity.

From calculations assuming a groundwater flow through the repository, it has been concluded that, besides the obvious risk of a fast nuclide release, the rate of concrete deterioration would also be increased compared to a situation where transport through the technical barriers takes place by diffusion only.

The deterioration of concrete by aggressive species in the groundwater except by carbonation has been found to be less important than leaching by water. Also, possible chemical attack by sulphate, which is an expected constituent of the waste, could be reduced by the choice of a sulphate-resistant concrete.

By appropriate design of barriers, the flow of groundwater through the repository can be minimized. This would assure that the only possible mass transfer mechanism would be diffusion. This would also decrease the influence of carbonation to an insignificant level. The rate of deterioration is low in this case.

The possibility of microbial degradation of concrete has not been considered in this report.

RESUME

Le taux de libération des radionucléides hors d'un dépôt final de type B dépend des propriétés à long terme du béton. Les propriétés critiques du béton sont la diffusivité et la conductivité hydraulique.

Des calculs supposant un écoulement des eaux souterraines à travers le dépôt final ont permis de conclure que, outre le risque évident que comporte une libération rapide des nucléides, le taux de dégradation du béton augmenterait lui aussi par rapport à une situation où le transport à travers les barrières techniques n'a lieu que par diffusion.

En plus de la carbonatation, on a constaté que la dégradation du béton par des agents agressifs dans les eaux souterraines était moins importante que la lixiviation par l'eau. Une éventuelle attaque chimique par le sulfate, dont on doit assumer la présence dans les déchets, pourrait être réduite en choisissant un béton résistant au sulfate.

La planification appropriée des barrières peut limiter à un minimum l'écoulement des eaux souterraines à travers le dépôt final. Cela garantirait que la diffusion est le seul mécanisme de transfert de matière possible et réduirait aussi l'influence de la carbonatation à un niveau insignifiant. Le taux de dégradation du béton est dans ce cas très bas.

La possibilité de dégradation microbienne du béton n'a pas été considérée dans le présent rapport.

ZUSAMMENFASSUNG

Die Radionuklidfreisetzungsrates aus einem Endlager Typ B hängt von den Langzeiteigenschaften des Betons ab. Die kritischen Eigenschaften des Betons sind die Diffusivität und die hydraulische Konduktivität.

Aus Berechnungen unter Annahme eines Grundwasserflusses durch das Endlager ist geschlossen worden, dass, neben dem Risiko einer schnellen Nuklidfreisetzung, die Rate des Betonzerfalls auch zunehmen würde, im Vergleich zu einer Situation wo der Transport durch die technischen Barrieren nur durch Diffusion stattfindet.

Es wurde festgestellt, dass der Betonzerfall bedingt durch aggressive Spezies im Grundwasser unbedeutender ist als die Auslaugung durch Wasser mit Ausnahme der Carbonatisierung. Ein möglicher chemischer Angriff durch Sulfat, dessen Vorkommen in den Abfällen angenommen werden muss, könnte durch die Wahl eines sulfatresistenten Betons reduziert werden.

Der Grundwasserfluss durch das Endlager kann durch geeignete Auslegung der Barrieren auf ein Minimum beschränkt werden. Damit wird sichergestellt, dass Diffusion der einzige Stofftransportmechanismus ist. Dies würde auch den Einfluss der Carbonatisierung auf ein unbedeutendes Niveau reduzieren. Die Betonzerfallsrate ist in diesem Fall klein.

Die Möglichkeit einer mikrobiellen Degradierung des Betons wurde in diesem Bericht nicht berücksichtigt.

SUMMARY  
ZUSAMMENFASSUNG  
RESUME

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## 1

## INTRODUCTION

The release rate of radioactive nuclides from a repository depends, to a large extent, on the diffusion resistance in the matrix, backfill, and other barrier materials. When concrete, which is foreseen as barrier material in a NAGRA repository for L/ILW, is exposed to ground-water, several chemical reactions occur. Most of these reactions result in changed physical and chemical properties of the concrete. This could cause a gradual change in the resistance of the concrete to radionuclide diffusion.

For Project 'Gewähr 1985', it was necessary to quantify the long-term properties of concrete with respect to its function as a barrier. Studies of this kind have been carried out in the past but have been focused on the long-term mechanical strength /1,2/. In this report, the influence of chemical processes on the concrete, with special emphasis on the diffusion characteristics, has been studied and some rough estimates of expected changes in barrier properties are made. It should be noted, however, that the contents of this report document a preliminary study performed within the scope of Project Gewähr and represent neither a full understanding of the complicated chemistry of concrete, nor the complete picture of how the barrier properties depend on the changes in concrete composition due to various processes.

It is obvious that the hydraulic situation in the vicinity of the repository is an important factor when estimating the long-term integrity of the concrete barriers. The hydraulic properties assumed in this report do not correspond to those of the model site at Oberbauen Stock, but should merely be regarded as an example for calculation. Due to the very long time perspective, the results are uncertain. Therefore, the results have been used in a conservative manner in the safety analysis for Project Gewähr.

Section 2 gives a short review of the most important reactions in the complex chemical system which concrete represents.

The results presented in sections 3 and 4 are estimated rates of concrete deterioration assuming different chemical reactions and mass transfer mechanisms.

## 2 DESCRIPTION OF POSSIBLE MECHANISMS OF CONCRETE DETERIORATION

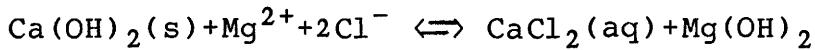
### 2.1 Characterisation of different types of concrete-deteriorating mechanisms

The long-term stability of concrete used for waste conditioning, backfill and construction material will be influenced by the different chemical components in the waste and by the groundwater. The deterioration of concrete is of both chemical and mechanical character. It can be divided into three different categories /3/:

- Ia Leaching of alkali hydroxides and calcium by groundwater
- Ib Reaction with dissolved species in the groundwater, forming soluble reaction products
- II Reaction with dissolved species leading to the formation of new crystalline phases which causes crack formation due to expansion.

The first type of deterioration, Ia, is a special case of type Ib and will take place in acid, neutral and slightly alkaline waters, which covers most natural waters. The ground-water reported for marl rocks falls within this category /NTB 84-20/. The rate of deterioration depends on the amount of groundwater available, the amount of aggressive species in the groundwater, the initial content of alkali and calcium in the groundwater, the diffusion resistance in the barrier material and the kinetics of calcium dissolution.

The second type of deterioration, type Ib, is caused by reactions giving soluble products which are then leached out of the concrete. An example is the reaction between calcium hydroxide and magnesium chloride:



The third type of deterioration, type II, is caused by different reactions of dissolved species with the minerals in the concrete. Initially, the attack will comprise reactions forming products which recrystallize in the pores of the concrete. This leads to closure of the pores. When the pore space is filled, further recrystallization can initiate strong mechanical stress in the concrete and eventually cause cracking of the concrete.

## 2.2 Gradual attack on concrete by groundwater

For concrete in contact with groundwater, the first attack is a leaching of soluble alkali- and calcium-hydroxides from the concrete. Due to this leaching, the pH-value will drop. This causes the hydrolysis of the concrete to continue, giving a gel of silicates and aluminates as a final reaction product, in the form of  $\text{Si(OH)}_4 \cdot n\text{H}_2\text{O}$  and  $\text{Al(OH)}_3 \cdot n\text{H}_2\text{O}$ .

As a result of the leaching and gel formation, the concrete loses its strength. The influence on the pore structure is not fully understood, but the resistance to diffusion will probably decrease. Simultaneously, there may be an attack by dissolved species in the groundwater which results in an expansion of the cement structure and may cause the concrete to crack (type II reactions), all depending on the composition of the groundwater.

## 2.3 Identification of aggressive species in groundwater

In groundwater a number of dissolved species may attack the concrete and cause deterioration. The most important species in groundwaters are  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{H}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{HCO}_3^-$ , /1,2,3/.

In Appendix B, reported compositions for groundwaters found in Valanginian marl are given. It should be noted that for these groundwaters no  $\text{Mg}^{2+}$  is reported. The waters are slightly alkaline with a high content of hydrogen carbonate. Interesting is the reported content of sulphide, which could be aggressive to concrete.

## 2.4 Attack by carbonates on concrete

Carbonate in groundwater may occur as free carbon dioxide, hydrogen carbonate or carbonate. In reaction between carbonates and calcium hydroxide, calcium carbonate is formed. The calcium carbonate is less soluble than calcium hydroxide and will precipitate in the pores, thus gradually closing them. This results in an increased strength and a decreased porosity of the concrete.

However, the calcium carbonate can be dissolved by water or, if the groundwater contains free carbon dioxide, the calcium carbonate can be dissolved as calcium hydrogen carbonate. The dissolution of calcium carbonate by pure water is slow.

The possible attack by free carbon dioxide depends on the amount of carbon dioxide as well as the initial content of hydrogen carbonate in the groundwater. A high content of hydrogen carbonate in the incoming groundwater reduces the dissolvable amount of calcium hydrogen carbonate and thus reduces the rate of calcium dissolution /2/. The rate of attack will also depend on the pH-value of the groundwater since the carbon dioxide / hydrogen carbonate / carbonate equilibrium is strongly pH-dependent. For pH-values above 7.5, the content of free carbon dioxide in the groundwater is negligible and the rate of calcium dissolution is low.

## 2.5

Attack by sulphates on concrete

The attack by sulphates on concrete is complex and comprises a number of possible recrystallization reactions. The concrete is penetrated by sulphate dissolved in the groundwater, whereupon the sulphate attacks tricalcium aluminate, forming expanding ettringite. The expansion during ettringite formation may result in the formation of cracks in the concrete. In such cracks further precipitation can take place, thus increasing the expansion. This expansion is also a result of the formation of sulpho-aluminates, brucite, gypsum and other reactions caused by sulphates /2/. These reaction products have a higher molar volume than the reactants.

The effect of sulphate attack is that the porosity will decrease initially due to precipitation of solid reaction products in the pores, but will increase if the concrete starts to crack. The use of sulphate-resistant concrete with a low content of tricalcium aluminate can reduce the risk of crack formation in the concrete.

However, another reaction has been suggested as a possible mechanism for crack formation in concrete, namely the reaction between tetracalcium aluminate and sulphate at high sulphate concentrations /2/. The reaction product is a highly hydrated tricalcium monosulphate with high molar volume. This reaction is, however, very slow if the calcium hydroxide concentration is high. The reason is the low solubility of tetracalcium aluminate at high pH-values. Further supply of sulphate can recrystallize the monosulphate as ettringite. It seems that no firm answer can be given with present knowledge to the question of which mechanism is the most probable under prevailing conditions.

## 2.6 Attack by chloride on concrete

### 2.6.1 Attack by chloride alone

Chloride can attack calcium aluminate forming calcium aluminate chlorohydrates. This has a deteriorating effect on the concrete because the calcium aluminates, which are one of the binding components in the concrete, are consumed. Chloride can also attack concrete by formation of calcium chloride, which is soluble.

On the other hand, chlorides can enhance the hydration of calcium silicates, which improves the concrete properties.

### 2.6.2 Combined attack by chloride and sulphate

The first attack comprises a formation of mono-chloro-aluminates which crystallize in the pores. If, thereafter, sulphate penetrates the concrete, the monochloro-aluminates will react with the sulphate, forming expanding ettringite. Therefore, combined attack by sulphates and chloride is more severe than the attack by chloride itself, although the depth of penetration of sulphates is less than that of chloride. The attack by chloride is severe only if the chloro-aluminates formed are strongly expanding.

Considering possible crack formation, the overall effect is that the porosity will increase through the attack.

## 2.7 Attack by sulphides on concrete

Hydrogen sulphide is an acid which is partly dissociated at high pH. Hydrogen sulphide is able to dissolve calcium carbonate and form soluble calcium hydrogen carbonate and calcium sulphide or calcium bisulphide.

The overall effect is that the porosity of the concrete increases due to the sulphide attack.

## 2.8 Attack by ammonium and amines on concrete

Ammonium and amines can attack both calcium carbonate and calcium hydroxide by forming ammonium /amine salts, thereby increasing the calcium solubility.

The overall effect is an increased porosity of the concrete.

2.9 Attack by alkali hydroxides on concrete ballast materials

Alkali hydroxides in the cement paste can attack certain ballast materials if these contain reactive silicic acid. This reaction leads to expansion and may cause cracks in the concrete. This type of problem has been reported for concretes mixed with ballast materials containing opal, flint and dolomite /5/. This deterioration can probably be avoided and a careful choice of aggregate minerals for the concrete is recommended.

### 3 ESTIMATION OF THE RATE OF DETERIORATION OF CONCRETE IN A REPOSITORY

The amount of groundwater entering the repository has been assumed to be  $1 \cdot 10^{-2} \text{ m}^3/\text{m}^2 \text{ year}$ . This is not based on the calculated amounts reported in /NGB 85-07/ and /NGB 85-08/ and should, therefore, be regarded only as an example for the calculations.

#### 3.1 Estimation of the leaching effect of non-aggressive groundwater flowing through a repository

##### 3.1.1 Amount of concrete in the repository

The volume of the repository is approximately 820'000  $\text{m}^3$ , with a horizontal cross-section area of 65'700  $\text{m}^2$ .

The volume of waste is about 200'000  $\text{m}^3$ , containing about 95'000  $\text{m}^3$  of concrete. Thus, including backfill and liner material, the repository contains about 715'000  $\text{m}^3$  of concrete.

##### 3.1.2 Amount of leachable calcium in the concrete

In the calculations the following assumptions have been made regarding the calcium content in the concrete;

###### Total calcium content

Total calcium content comprises calcium oxide/hydroxide, calcium aluminates and calcium silicates.

Portland cement paste contains about 65% by weight of calcium oxide. The concrete has been assumed to contain 300 kg cement paste per cubic metre. Thus, the total content of calcium in the concrete is 3500 moles per cubic metre. In the calculations, the total content of calcium has conservatively been rounded off to 3000 moles per cubic metre.

###### Content of free calcium oxide/hydroxide

Free calcium comprises calcium in the form of calcium oxide/hydroxide.

It is reasonable to assume a free calcium content of about 1-2% of the weight of the cement paste, corresponding to 60-120 moles per cubic metre of concrete. Here, the amount of  $\text{Ca(OH)}_2$  that can be produced during the hydration (up to 25% of the weight of the cement paste at complete hydration)

has been disregarded. This assumption is conservative. In the calculations, a content of 50-200 moles per cubic metre of concrete has been assumed.

#### CaO

The solubility of CaO (or  $\text{Ca}(\text{OH})_2$ ) in pure water is in the range of 0.020-0.025 kmoles/m<sup>3</sup>. Here, the conservative value 0.025 kmoles/m<sup>3</sup> has been assumed. This means that to dissolve the content of free CaO in 1 m<sup>3</sup> of concrete, we need to fully saturate about 2-8 m<sup>3</sup> of water. Assuming also that the calcium bound to silicates and aluminates has the same solubilities as free CaO, the calcium content in 1 m<sup>3</sup> could be dissolved in 120 m<sup>3</sup> of water. When all the calcium is dissolved, the quality of the concrete must be considered very poor. Already with leaching of 20% of the total calcium content, concrete has been reported to lose its mechanical strength /3/.

For the whole repository we have 715'000 m<sup>3</sup> of concrete and thus, to dissolve the total calcium content, we need  $8.6 \cdot 10^7$  m<sup>3</sup> of water.

#### 3.1.3 Estimation of the time for dissolution of calcium by percolation

For the assumed rate of groundwater flow,  $1 \cdot 10^{-2}$  m<sup>3</sup>/m<sup>2</sup>/year, the time for complete dissolution of calcium can be estimated to be 130'000 years. This is, however, a simplified calculation and overestimates the amount of water which percolates through the concrete. Therefore, the estimated time for dissolution of calcium by percolation is too short.

If the repository liner is intact, the flow of water through the repository will be insignificant. The transport mechanism accompanying the dissolution of calcium in this case will be diffusion. See 3.3-3.5

#### 3.2 Estimation of the chemical attack of aggressive species dissolved in groundwater percolating through the repository

In this section a number of possible reactions between concrete and species dissolved in groundwater are studied. The list of reactions is not complete, but by making the conservative assumption that all species dissolved in the ground-water

react with the concrete and dissolve calcium, the maximum leaching effect of these species can be accounted for.

Table 1 Estimated content in groundwater of species aggressive to concrete, see Appendix B.

| Species                   | Concentration<br>(mM) | (kmoles/year)<br>(Min-Max) |
|---------------------------|-----------------------|----------------------------|
| $\text{SO}_4^{2-}$        | 0.02-4                | 0.01-2.7                   |
| S-total                   | 0.6-3                 | 0.4-2                      |
| $\text{Cl}^-$             | 1.0-5.7               | 0.7-3.8                    |
| $\text{NH}_4^+$           | 0-0.3                 | 0-0.3                      |
| $\text{CO}_3^{2-}$ -total | 10-30                 | 6.6-20                     |

Some of the possible reactions between concrete and groundwater.

- (1)  $\text{CaO} + \text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + 2\text{OH}^-$
- (2)  $\text{Ca}(\text{OH})_2 + 2\text{HCO}_3^- \rightleftharpoons \text{CaCO}_3(\text{s}) + 2\text{H}_2\text{O} + \text{CO}_3^{2-}$
- (3)  $\text{Ca}(\text{OH})_2 + \text{SO}_4^{2-} \rightleftharpoons \text{CaSO}_4(\text{s}) + 2\text{OH}^-$
- (4)  $\text{Ca}(\text{OH})_2 + 2\text{Cl}^- \rightleftharpoons \text{CaCl}_2(\text{s}) + 2\text{OH}^-$
- (5)  $\text{Ca}(\text{OH})_2 + \text{H}_2\text{S} \rightleftharpoons \text{Ca}^{2+} + \text{HS}^- + \text{H}_2\text{O} + \text{OH}^-$
- (6)  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 + 3\text{CaSO}_4 + 3\text{H}_2\text{O} \rightleftharpoons 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 3\text{H}_2\text{O}$
- (7)  $\text{Ca}(\text{OH})_2 + \text{CO}_3^{2-} \rightleftharpoons \text{CaCO}_3(\text{s}) + 2\text{OH}^-$
- (8)  $\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O} + 2\text{OH}^- + 2\text{Na}^+ \rightleftharpoons 2\text{NaAl(OH)}_4$
- (9)  $\text{CaCO}_3 + 2\text{NH}_4^+ + 2\text{Cl}^- \rightleftharpoons \text{CaCl}_2 + (\text{NH}_4)_2\text{CO}_3$
- (10)  $\text{Ca}(\text{OH})_2 + 2\text{NH}_4^+ + 2\text{Cl}^- \rightleftharpoons \text{CaCl}_2 + 2\text{NH}_4\text{OH}$

The dissolution reaction (1) was estimated above and can be completed after 130'000 years.

For reaction (2), using the values given in Table 1, the time for complete reaction can be estimated with eq. 1:

$$T = \frac{\text{Total calcium content}}{\text{Amount of aggressive species annually in water}} \quad (\text{Eq. 1})$$

$$T = 2.1 \cdot 10^5 - 6.5 \cdot 10^5 \text{ years.}$$

The reaction (3) can similarly be estimated to be completed after

$$T = 7.9 \cdot 10^5 - 2.2 \cdot 10^8 \text{ years}$$

For (4) the time for complete reaction is;

$$T = 1.1 \cdot 10^6 - 5.4 \cdot 10^6 \text{ years}$$

$$\underline{\text{Reaction (5)}} \quad T = 1.1 \cdot 10^6 - 5.3 \cdot 10^6 \text{ years}$$

$$\underline{\text{Reaction (7)}} \quad T = 1.1 \cdot 10^5 - 3.3 \cdot 10^5 \text{ years}$$

$$\underline{\text{Reaction (10)}} \quad T = 1.4 \cdot 10^7 - \infty \quad (\text{NH}_4\text{-content})$$

Assuming that the reaction (3), (4), (5), (7) and (10) occur simultaneously and independently, we can calculate the deterioration times using the maximum and minimum values in Table 1. Thus, using Eq. 1, we obtain:

$$T_{\max} = 2.9 \cdot 10^5 \text{ years}$$

$$T_{\min} = 8.0 \cdot 10^4 \text{ years}$$

If we also consider the dissolution reaction (1), the corresponding times for complete reaction are;

$$T_{\max} = 9.0 \cdot 10^4 \text{ years}$$

$$T_{\min} = 5.0 \cdot 10^4 \text{ years}$$

It should be noted that sulphate may be consumed by either reaction (3) or reaction (6) or in partitions determined by the chemical equilibrium. Reaction (6) occurs only at high concentrations of sulphate and is probably of importance only in the vicinity of waste with a high content of sulphates. Only one of the reactions (2) or (7) will take place at a time and both reactions compete with respect to the available carbonate. In (9) and (10), both reactions must share the available ammonium. Reaction (8) is a possible second step of reaction (7) in sodium carbonate solutions. The effect of reaction (8) has not been considered in this report.

**3.3 Calculations of leaching of sodium- and potassium-hydroxide from the repository assuming mass transfer by diffusion**

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The leaching of alkali hydroxides from the repository has been calculated assuming that the hydroxides are completely soluble in the pore-water of the concrete. The cement (Portland type) contains about 1% by weight of alkali hydroxides. The content in concrete varies due to different mixtures of cement and ballast material. The transient release by diffusion has been calculated according to Eq. 2 /6/.

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{4}{a^2 \cdot a_n^2} e^{-(D_a \cdot a_n^2 \cdot t)} \quad (\text{Eq. 2})$$

where

$M_t$  = the amount of leached material at time  $t$  (kmoles)

$M_\infty$  = the leachable amount of material (kmoles)

$a$  = repository radii (m)

$a_n$  = the n:th root to the equation

$$J_0(X_n) = 0 \quad \text{where}$$

$$X_n = a \cdot a_n \quad \text{and}$$

$$J_0(X_n) = 1 - \frac{1}{\pi} \int_0^{\pi} \cos(X_n \cdot \sin\theta) d\theta \quad (\text{Eq. 3})$$

$$D_a = \text{diffusivity} \quad (m^2/s)$$

$$t = \text{time} \quad (s)$$

Equation (2) was solved using the first twenty roots of equation (3).

The results are given in Table 2 as the time required to leach a certain fraction of the initial content. See also Chapter 4.

A zero concentration has been assumed as a boundary condition. This assumption has been checked and has been found to overestimate the rate of leaching by less than 3%, when the rate of water flow is  $1 \cdot 10^{-2} m^3/m^2/\text{year}$  and the diffusivity is  $6.3 \cdot 10^{-4} m^2/\text{year}$ . A discussion of the effect of different boundary conditions is given in Chapter 4.

Table 2 Time required to leach out a certain amount of the initial content of alkali hydroxides, given for different diffusivities. See also Figure 1.

| D ( $\text{m}^2/\text{a}$ ) | $T_{3\%}$ | $T_{50\%}$ | $T_{80\%}$ | $T_{95\%}$ | (years) |
|-----------------------------|-----------|------------|------------|------------|---------|
| $6.3 \cdot 10^{-3}$         | 160       | 500        | 1700       | 3600       |         |
| $6.3 \cdot 10^{-4}$         | 1600      | 5000       | 17000      | 36000      |         |
| $6.3 \cdot 10^{-5}$         | 17000     | 50000      | 170000     | 360000     |         |

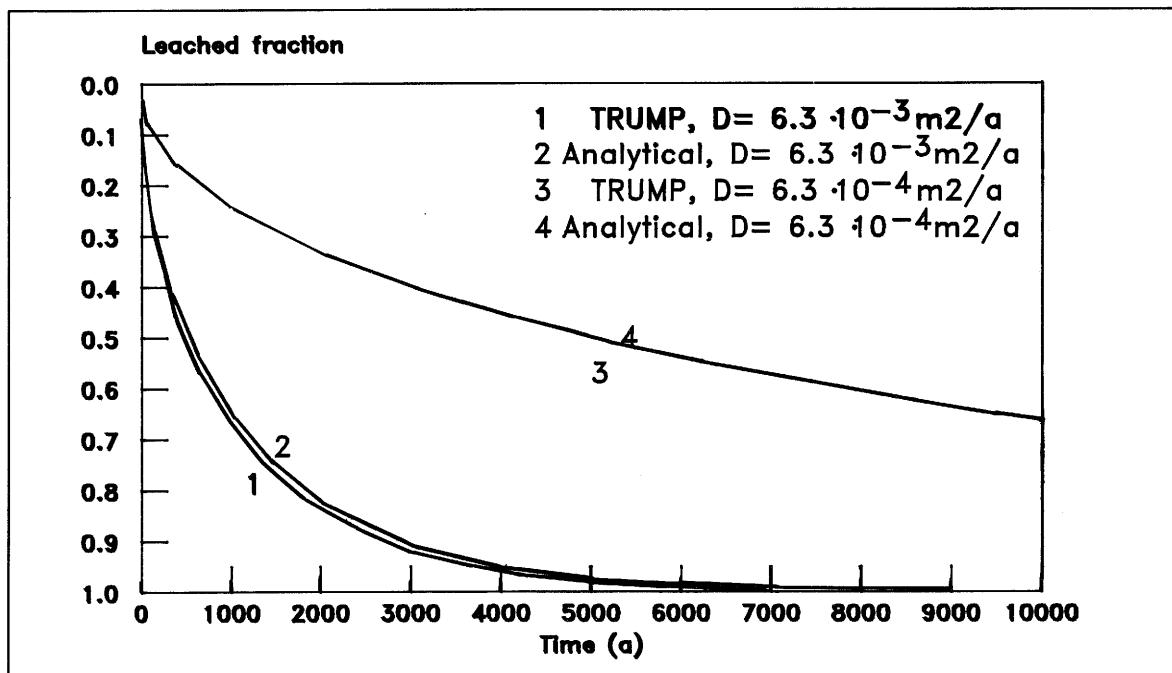


Figure 1. Fractional leaching of alkali hydroxides from the concrete.

### 3.4 Calculations of leaching of free calcium hydroxide from a repository assuming mass transfer by diffusion

Considering the limited solubility of calcium in water, the successive attack on concrete by ground-water has been calculated. The attack has been assumed to proceed by a moving boundary process, where the concentration at the boundary is determined by the solubility of the calcium hydroxide. The time for successively increasing depth of leaching has been calculated by two different methods; one analytical model assuming pseudo-steady-state conditions /7/ and one numerical model using the integrated finite-difference computer program TRUMP/8/. The calculations have been made assuming a zero concentration boundary condition. The results are given in Table 3a. See also Chapter 4.

The available content of free calcium hydroxide in concrete is assumed to be about 1-2% by weight of the cement paste. Assuming a content of free calcium hydroxide of 100 moles per cubic metre of concrete, the time for complete leaching of the concrete has been estimated at 400'000 years using a diffusivity of  $6.3 \cdot 10^{-4} \text{ m}^2/\text{year}$ . Assuming a diffusivity of  $6.3 \cdot 10^{-3} \text{ m}^2/\text{year}$ , the corresponding value for complete leaching is 40'000 years.

The correlation between the analytical and the numerical model is good. The analytical model slightly underestimates the time for leaching in that this solution assumes pseudo-steady-state conditions, i.e. maximum gradient at every instant. The analytical model can be used for simplified calculations such as those presented in Table 3, whereas the numerical model is suitable for more complicated calculations as described in Chapters 4 and 6.

For concrete containing 200 moles of free calcium oxide per cubic metre, the calculated time for complete leaching is 80'000 years for a diffusivity of  $6.3 \cdot 10^{-3} \text{ m}^2/\text{year}$  using the analytical model. For a diffusivity of  $6.3 \cdot 10^{-4} \text{ m}^2/\text{year}$ , the calculated time for complete leaching is 800'000 years.

Assuming a free calcium content of 50 moles per cubic metre yields a time for complete leaching of 20'000 years, using a diffusivity of  $6.3 \cdot 10^{-3} \text{ m}^2/\text{year}$  and 200'000 years using a diffusivity of  $6.3 \cdot 10^{-4} \text{ m}^2/\text{year}$ .

3.5 Calculations of leaching of total calcium content in  
a repository assuming mass transfer by diffusion

In these calculations it was assumed that all calcium in the concrete is dissolved. The results are presented in Table 3b.

In the previous section it was observed that, for low diffusivities and long times, the pseudo-steady-state model slightly overestimates the rate of leaching. This is likely to be true also in this case and should be kept in mind when interpreting the results. The calculated time for total deterioration of the concrete in the repository is  $1 \cdot 10^6$  -  $1 \cdot 10^7$  years, depending on the assumed diffusivity. See also Figure 2.

However, when the calcium hydroxide is dissolved, it is reasonable to assume that the pore structure of the concrete will change and, when all calcium is dissolved, the diffusivity will probably increase further. Thus, the calculation made using the diffusivity of  $6.3 \cdot 10^{-3}$  m<sup>2</sup>/year would give a more reliable result, indicating a complete deterioration after approximately  $1 \cdot 10^6$  years.

Table 3a Calculated time for complete leaching of the content of free calcium hydroxide for different cases. See also Figure 2.

| Content of<br>free $\text{Ca(OH)}_2$<br>(moles/ $\text{m}^3$ ) | Pore<br>diffusivity<br>( $\text{m}^2/\text{year}$ ) | Finite-<br>difference<br>model<br>(years) | Analyti-<br>cal<br>model<br>(years) |
|--|---|---|-------------------------------------|
| 200  | $6.3 \cdot 10^{-3}$                                 | -   | 78 800                              |
| 200  | $6.3 \cdot 10^{-4}$                                 | -   | 788 000                             |
| 100  | $6.3 \cdot 10^{-3}$                                 | 42 000                                    | 39 000                              |
| 100  | $6.3 \cdot 10^{-4}$                                 | -   | 394 000                             |
| 50   | $6.3 \cdot 10^{-3}$                                 | -   | 19 700                              |
| 50   | $6.3 \cdot 10^{-4}$                                 | -   | 197 000                             |

Table 3b Calculated time for complete leaching of the total content of calcium, including calcium bound as silicates and aluminates

| Total content<br>of calcium<br>(moles/ $\text{m}^3$ ) | Pore<br>diffusivity<br>( $\text{m}^2/\text{year}$ ) | Analytical pseudo-<br>steady-state model<br>(years) |
|---|---|---|
| 3 000   | $6.3 \cdot 10^{-3}$                                 | 1 180 000   |
| 3 000   | $6.3 \cdot 10^{-4}$                                 | 11 800 000  |

4

## EFFECT OF DIFFERENT BOUNDARY CONDITIONS ON THE LEACHING OF ALKALI HYDROXIDES AND CALCIUM

So far, the mass transfer in the surrounding rock has been considered high enough to balance the rate of leaching and maintain the zero boundary condition. However, when estimated by the method given in /9/, the effect of the mass transfer in the vicinity of the repository has been found to be of importance. This method consists of an estimation of the mass transfer coefficient from the repository to the groundwater. (See Appendix A.) The effect has been calculated by assuming a convective boundary condition in the finite-difference model. In addition, the effect of a convective boundary condition has been calculated with an analytical model /6/.

The calculations presented in 4.2 also consider the effect of a 0.1 metre thick barrier, e.g. bentonite, around the repository.

4.1

### Leaching of alkali hydroxides assuming a convective boundary condition

---

Using the mass transfer coefficient of  $2.4 \cdot 10^{-2}$  m/year calculated in Appendix A for a water flux of  $1 \cdot 10^{-2}$  m<sup>3</sup>/m<sup>2</sup>/year, the rate of leaching has been calculated by two different models; with the analytical model presented below and with the numerical model TRUMP /8/. The analytical model is given by /6/:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{4L_n^2 e^{-(\beta_n^2 D \cdot t/a^2)}}{\beta_n^2 (\beta_n^2 + L_n^2)} \quad (\text{Eq. 4})$$

where

|            |                              |          |
|------------|------------------------------|----------|
| $M_t$      | = leached amount at time $t$ | (kmoles) |
| $M_\infty$ | = leachable amount           | (kmoles) |
| $t$        | = time                       | (s)      |

$$L = \frac{a \cdot k_v}{D}$$

where

$$\begin{aligned} a &= \text{repository radii} && (\text{m}) \\ k_v &= \text{mass transfer coefficient} && (\text{m/s}) \\ D &= \text{diffusivity} && (\text{m}^2/\text{s}) \\ \beta_n \cdot a &= B = \text{the roots of the equation} \\ B \cdot J_1(B) - L \cdot J_0(B) &= 0 && (\text{Eq. 5}) \end{aligned}$$

where  $J_0$  and  $J_1$  are the zero and first order Bessel functions.

The first twenty roots of equation (5) have been used in the calculations.

The effect of the convective boundary condition is best evaluated when the results are compared with the results from calculations with a zero concentration boundary condition. The results are presented in Table 4.

The results show a pronounced influence of the convective boundary condition on the rate of leaching during the early stage, especially for high diffusivities.

Table 4 Time required to leach a certain percentage of the alkali content for different diffusivities, with and without convective boundary condition. A comparison is also made between the analytical solution and the solution obtained by the numerical model TRUMP/6/, /8/.

| Leached fraction<br>% | Pore diffusivity<br>( $\text{m}^2/\text{year}$ ) | Analytically calculated leach times for two boundary conditions |                                  | Equivalent calculation with numerical model TRUMP |                                  |
|-----------------------|--|---|----------------------------------|---|----------------------------------|
|                       |  | Zero conc. Convective<br>(years)                                | Zero conc. Convective<br>(years) | Zero conc. Convective<br>(years)                  | Zero conc. Convective<br>(years) |
| 30                    | $6.3 \cdot 10^{-3}$                              | 160   | 500                              | 160   | 500                              |
|                       | $6.3 \cdot 10^{-4}$                              | 1 600   | 1 950                            | 1 580   | 1 900                            |
| 40                    | $6.3 \cdot 10^{-3}$                              | 300   | 760                              | 300   | 750                              |
|                       | $6.3 \cdot 10^{-4}$                              | 3 000   | 3 500                            | 3 000   | 3 500                            |
| 50                    | $6.3 \cdot 10^{-3}$                              | 500   | 1 100                            | 500   | 1 100                            |
|                       | $6.3 \cdot 10^{-4}$                              | 5 000   | 5 600                            | 5 000   | 5 700                            |
| 60                    | $6.3 \cdot 10^{-3}$                              | 780   | 1 520                            | 780   | 1 500                            |
|                       | $6.3 \cdot 10^{-4}$                              | 7 800   | 8 500                            | 7 600   | 8 500                            |
| 70                    | $6.3 \cdot 10^{-3}$                              | 1 150   | 2 080                            | 1 150   | 2 000                            |
|                       | $6.3 \cdot 10^{-4}$                              | 11 500  | 12 400                           | 11 300  | 12 500                           |
| 80                    | $6.3 \cdot 10^{-3}$                              | 1 700   | 2 900                            | 1 700   | 2 500                            |
|                       | $6.3 \cdot 10^{-4}$                              | 17 000  | 18 100                           | 16 600*)  | 17 500*)                         |

\*) Extrapolated

#### 4.2 Leaching of calcium, assuming a convective boundary condition and/or a surrounding barrier

The effect of a convective boundary condition on the leaching of calcium from the repository has been calculated. The mass transfer coefficient is estimated to  $2.4 \cdot 10^{-2}$  m/year, see Appendix A. The leaching of calcium hydroxide as well as leaching of the total calcium will take place as a moving boundary process. Thus, a zone of attacked (or deteriorated) concrete will develop and the zone of intact concrete will gradually shrink. The calcium leaching has been calculated by two different models; one analytical pseudo steady-state model and one numerical model, TRUMP, which allows a transient analysis. The leaching has been calculated for five different cases;

1. - pure diffusion with a zero concentration boundary condition
2. - diffusion through a surrounding inert barrier, eg. bentonite
3. - diffusion with a convective boundary condition
4. - diffusion with both convective boundary condition and a surrounding inert barrier
5. - transient analysis with numerical model TRUMP for diffusion with a zero concentration boundary condition.

The calculated time for complete leaching of the contents of free calcium hydroxide and total calcium respectively are presented in Table 5, see also Figure 2. The calcium content of 100 moles/m<sup>3</sup> refers to the content of free calcium hydroxide, whereas the figure 3000 moles/m<sup>3</sup> corresponds to the total calcium content.

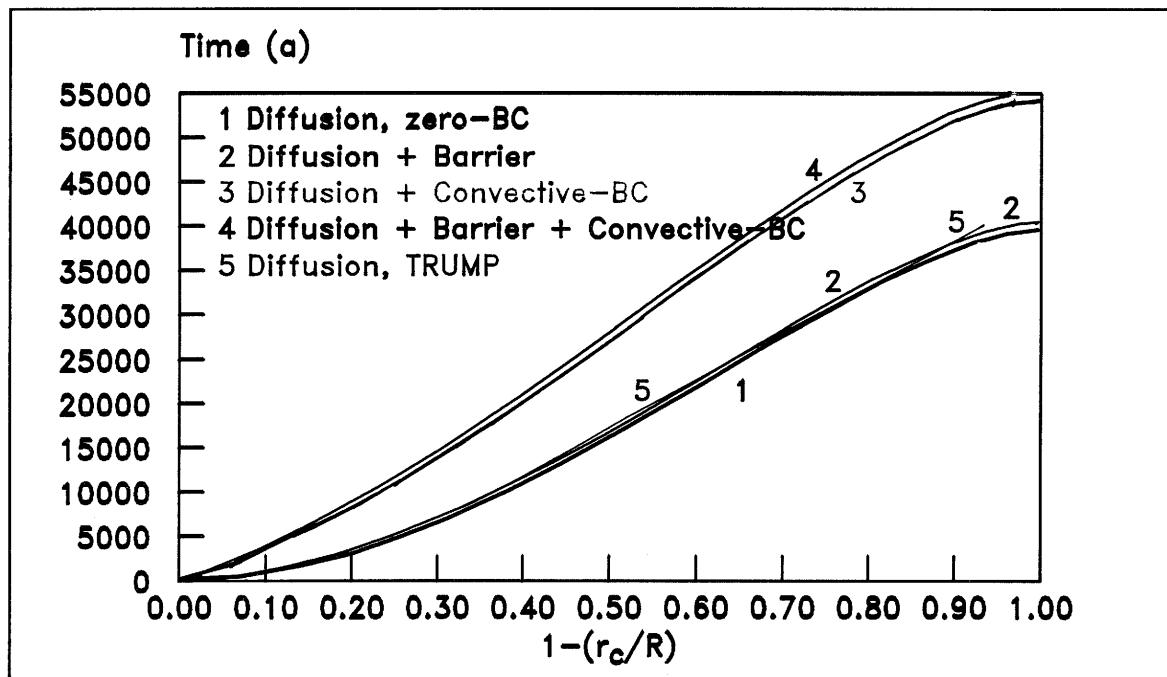
The convective boundary condition was found to increase the time for complete leaching by approximately 35 percent as compared with a zero concentration boundary condition.

The influence of a 0.1 metre inert barrier surrounding the repository lining with the same diffusivity as the concrete was found to increase the time for complete leaching of calcium by less than 3 percent.

However, it should be stressed that, during the early period, the mass transfer is large due to the steep calcium concentration gradient in the leached zone. As the leaching continues, the boundary between intact and leached concrete will move and, thereby, the distance over which the concentration profile is developed will increase and the calcium concentration gradient is decreased. Consequently, the influence of both the convective boundary condition and a surrounding barrier is more important during the early period. Therefore, these effects may prove to be important for estimations of the functional lifetime at the most exposed parts of the barrier system, i.e. the repository lining which will be leached first.

Table 5. Calculated time for leaching of calcium from concrete.  $r_c/R$  denotes the ratio between the radius of intact concrete and the initial radius of the repository. Diffusivity is  $6.3 \cdot 10^{-3} \text{ m}^2/\text{year}$ . Columns marked 1, 3 and 2 are analytical pseudo steady-state solutions, whereas column 5 is a numerical transient solution.

| Curve<br>in<br>$r_c/R$ | Fig. 2 | Ca-content<br>(moles/m <sup>3</sup> ) | Calculated leach times (years) |                        |                       |                    |
|------------------------|--------|---------------------------------------|--------------------------------|------------------------|-----------------------|--------------------|
|                        |        |                                       | Diffusion+<br>zero BC          | Diffusion+<br>Conv. BC | Diffusion+<br>Barrier | Diffusion<br>TRUMP |
| 1                      | 3      | 2                                     | 5                              |                        |                       |                    |
| 0.95                   | 100    | 194                                   | 1 630                          | 302                    | 400                   | -                  |
|                        | 3 000  | 5 820                                 | 48 900                         | 9 060                  | -                     | -                  |
| 0.9                    | 100    | 760                                   | 3 550                          | 970                    | 1 200                 | -                  |
|                        | 3 000  | 22 800                                | 107 000                        | 29 100                 | -                     | -                  |
| 0.7                    | 100    | 6 330                                 | 13 800                         | 6 900                  | 7 000                 | -                  |
|                        | 3 000  | 190 000                               | 414 000                        | 207 000                | -                     | -                  |
| 0.5                    | 100    | 15 900                                | 26 900                         | 16 700                 | 18 000                | -                  |
|                        | 3 000  | 477 000                               | 807 000                        | 501 000                | -                     | -                  |
| 0.3                    | 100    | 27 300                                | 40 700                         | 28 300                 | 30 000                | -                  |
|                        | 3 000  | 819 000                               | 1 220 000                      | 849 000                | -                     | -                  |
| 0.1                    | 100    | 37 200                                | 51 700                         | 38 300                 | 39 000                | -                  |
|                        | 3 000  | 1 120 000                             | 1 550 000                      | 1 150 000              | -                     | -                  |
| 0                      | 100    | 39 500                                | 54 100                         | 40 500                 | 45 000                | -                  |
|                        | 3 000  | 1 190 000                             | 1 620 000                      | 1 220 000              | -                     | -                  |



where  $r_c/R$  denotes the ratio between  
the radius of unleached concrete and  
the radius of the repository

Figure 2. Gradual leaching of free calcium hydroxide from the concrete. Initial radius is 7 metres. The diffusivity is  $6.3 \cdot 10^{-3} \text{ m}^2/\text{year}$ .  
 1-4 Analytical model, pseudo steady-state  
 5 Numerical model, transient

## 5

## DISCUSSION

In the previous sections, mechanisms for concrete deterioration as well as some estimations of the time for degradation are presented.

The major difficulty in evaluating the results is to quantify a criterion which defines when concrete has to be considered deteriorated. The properties of importance for concrete used as conditioning and backfill material are the alkali content giving an alkaline pore-water, and the low diffusivity. For concrete used as a repository lining the most important properties are the low diffusivity, the low hydraulic conductivity and the mechanical strength. The mechanical strength is treated elsewhere /1/ and has not been considered in this report.

Hence, only the effect of leaching and chemical reactions on the parameters determining the diffusivity of the concrete will be treated. A first approximation can be that when the alkali hydroxides are leached out to a certain degree (e.g. 50%), the pore structure of the concrete is changed to such an extent, due to the changed chemistry, that the diffusion is increased. A major problem at the present stage of the work is that the quantitative influence of this chemical change on the diffusivity is not known. In our preliminary analyses we have arbitrarily assumed a factor of 10 increase. This approach may overestimate the rate of deterioration. It should be noted, however, that the diffusivity in concrete is to a very high degree determined by the internal porestructure, i.e. the tortuous and constructive pore system, and that it cannot be excluded that even small changes in the chemistry may cause changes in concrete, which could influence the diffusivity.

A second approximation is to consider the zone of concrete where free calcium hydroxide has been leached out to be deteriorated. In the deteriorated zone the diffusivity is assumed to be increased (again we have assumed at present a factor of 10 increase). This is a less conservative approach, due to the fact that a considerable part of the solid concrete itself is dissolved and might give a good measure of the rate of concrete deterioration.

A third approximation is to define the concrete as deteriorated only when the total content of calcium is leached out. This means that the only remaining part of the concrete would be silicates and aluminates -in other words, similar to sand.

From a conservative safety analysis point of view, it must be certainly assumed that the properties of concrete are considerably changed when the content of free calcium is leached out. Furthermore, the diffusivity in the concrete may be strongly influenced already at the stage when the alkali hydroxides are leached out. At the current early stage in the analysis it is, therefore, proposed to consider the concrete to be partly degraded when more than 50% of the content of alkali hydroxides has been leached out. In the most conservative case this means that the concrete will be deteriorated after 500 years. However, a more realistic case using less conservative data will give a deterioration after 5600 years.

In Project Gewähr, the diffusivity of the concrete was assumed to increase in two steps. Firstly, after 500 years, diffusivities were increased from  $2 \cdot 10^{-12}$  to  $2 \cdot 10^{-11} \text{ m}^2/\text{s}$  and, secondly, after 10'000 years, the diffusivities were further increased to  $2 \cdot 10^{-10} \text{ m}^2/\text{s}$ . The effect of continuous degradation of the barrier materials has also been demonstrated /4/. This approach probably gives a more physical description of the degradation process.

It must also be noted that this is only true when the hydraulic situation is such that no water is flowing through the repository. If a flow-through situation exists, the alkali hydroxides will be leached out at a time determined by the residence time for water in the repository, because no solubility limitation can be expected.

In section 2 the most probable mechanisms for concrete degradation are described. However, this is only a short compilation of the information given in /1,2,3/. These reactions were only considered when estimating the rate of concrete deterioration in the case of a flow-through of groundwater. As was concluded in section 3.2, the different mechanisms have varying importance, depending on the content of the different aggressive species in the groundwater. The major mechanism are the carbonation and dissolution of calcium in water. Besides these, the reactions with sulphate and chloride are the most important mechanisms.

However, the assumption that groundwater flows through the repository may be wrong. If the repository has a lower hydraulic conductivity than the surrounding rock, the major part of the groundwater will flow around the repository instead of through it. This means that the deterioration of the concrete will be determined by a diffusional mass transfer mechanism. The rate of this deterioration is estimated in Chapter 3. It can readily be seen that the

time for deterioration is much longer when mass transfer by diffusion only is considered than for the case of groundwater flowing through the repository. In Chapter 3 it was concluded that the contribution to mass transfer resistance from a surrounding barrier is important during the initial period of time. In a long term perspective, the effect of a surrounding barrier is not very pronounced, depending, however, on the thickness and the material properties of the barrier.

In Chapter 4 the influence of a convective boundary condition on the mass transfer was calculated. It was found to increase the time calculated for complete deterioration by approximately 35 percent.

The effect of an initial concentration of alkali and calcium in the groundwater is estimated in Appendix C. It can be concluded that it has a bearing upon the leaching of alkali hydroxides, whereas the influence on the leaching of calcium probably is negligible.

Clearly, a barrier which does not allow the groundwater to flow through the repository, thereby assuring mass transfer by diffusion, is most desirable. Whether this barrier should be made of bentonite, high density concrete or other material is not considered in this report.

The calculations presented in this report are based on very simple assumptions, such as:

- instantaneous reaction between concrete and reactants
- all reactions between concrete and aggressive species in groundwater are disadvantageous and lead to deterioration of the concrete
- the reaction/dissolution takes place evenly in a moving boundary layer between deteriorated and intact concrete.

In the next chapter, further studies on determining the critical mechanisms that lead to concrete degradation are outlined.

## 6

## FURTHER WORK

So far, the chemical reactions that will take place between the concrete and the groundwater have been considered deleterious to the concrete. However, some of the possible reactions can increase the strength of the concrete, at least at an early stage, e.g. carbonation. Other reactions may occur only under certain conditions or with certain types of cement, e.g. sulphate versus sulphate-resistant cement. Chemical reactions can occur within the concrete itself due to the changes in the pore-water composition, e.g. caused by leaching of alkali hydroxides and calcium. The need for chemical equilibrium calculations in this area is obvious and the results from screening calculations, not reported here, look promising. The calculations could be made in a series of steps; firstly, the chemical composition of the pore-water could be simulated and compared with available analyses on pore-water from different concretes /10/, secondly, the constituents of the solid phases in fully hardened concrete could be simulated and, thirdly, the influence of changes introduced to the chemical system could be studied. The results from these studies could then, in a second stage, be correlated with the calculations made on leaching of alkali hydroxides and calcium and with the work on near-field hydrology. The aim of these efforts would be to obtain a firm and consistent description of both the physical and chemical situation in the near-field as a function of time.

The leaching of alkali hydroxides and calcium could be calculated in more detail. Possible extensions are the simultaneous leaching of alkali hydroxides and calcium accompanied by reaction with species in the groundwater. To simulate the successive deterioration, the material properties of the concrete may be coupled to the leaching, thus obtaining a dynamic system. An indication of the changes in diffusivity and hydraulic conductivity can be obtained from the depletion of solid phases during leaching, leading to an increased porosity.

The information that can be obtained from these calculations includes the pore water chemistry and an indication of the material properties of the concrete, both items varying in time and space. This information should be used both when calculating the source terms of radionuclides in the repository and the radionuclide releases from the near-field.

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- /10/ Allard B., 'Radionuclide Sorption on Concrete', NAGRA Technical Report NTB 85-21, 1985.

References are made to the following Nagra Project Reports:

- NGB 85-07      Repository for low- and intermediate-level waste:  
                  Safety Barrier System
- NGB 85-08      Repository for low- and intermediate-level waste:  
                  Safety Report.
- NTB 84-20      Geowissenschaftliche Grundlagen des Sondier-  
                  standortes Oberbauenstein; T. Schneider, S.  
                  Kappeler; Dezember 1984.

## Appendix A

## CALCULATION OF MASS TRANSFER COEFFICIENTS

The mass transfer of a diffusing substance from a repository to the surrounding groundwater can be described as/9/;

$$N = K_V \cdot A \cdot \epsilon \cdot C$$

|                |  |                                |
|----------------|--|--------------------------------|
| N              | = Amount of diffusing substance                                  | kmoles/year                    |
| K <sub>V</sub> | = Mass transfer coefficient                                      | m/year                         |
| A              | = Repository cross-section area                                  | m <sup>2</sup>                 |
| ε              | = Porosity of the surrounding rock                               | m <sup>2</sup> /m <sup>3</sup> |
| C              | = Concentration of diffusing substance at the repository surface | kmoles/m <sup>3</sup>          |

$$K_V = \sqrt{\frac{4 D_V \cdot U_0}{\pi \cdot L \cdot \epsilon}}$$

$$D_V = \text{Diffusivity in bulk water} \quad m^2/\text{year}$$

$$U_0 = \text{Darcy velocity} \quad m^3/m^2/\text{year}$$

$$L = \text{Length in flow direction} \quad m$$

Assumptions for this report:

$$U_0 = 1 \cdot 10^{-2} \text{ m}^3/\text{m}^2/\text{year}$$

$$D_V = 3.15 \cdot 10^{-2} \text{ m}^2/\text{year}$$

For a repository radius of 7.0 metres,  $L = \pi \cdot r = 22$  metres.

For Valanginian marl the reported porosity is  $\epsilon = 0.033 \text{ m}^2/\text{m}^3$ .

Thus, the value of  $K_V = 2.4 \cdot 10^{-2} \text{ m/year}$ .

Now the value of c, the concentration at the surface of the repository, is unknown and varies in time. To enable the calculation of the amount of diffusing substance, a finite-difference program was used. The mass transfer coefficient was given as a convective boundary condition.

## Appendix B

## CHEMICAL ANALYSES OF THE GROUNDWATER IN VALANGINIAN MARL

TABLE B1

(Unit: mg/l)

Ref. /NTB 84-20/

| Species                   | Opening<br>gallery | Parallel<br>gallery | South hill<br>tube |
|---------------------------|--------------------|---------------------|--------------------|
| $\text{SO}_4^{2-}$        | 5                  | 382                 | 1.8                |
| S-total                   | 21                 | 92                  | 83                 |
| $\text{Cl}^-$             | 36                 | 145                 | 203                |
| $\text{NO}_3^-$           | 0.02               | -                   | -                  |
| $\text{NH}_4^+$           | 5.0                | -                   | -                  |
| $\text{CO}_3^{2-}$ -total | 655                | 1573                | 1900               |
| $\text{Na}^+$             | 295                | 810                 | 760                |
| $\text{Ca}^{2+}$          | 2.8                | -                   | 8.8                |

## Appendix C

## ESTIMATION OF THE INFLUENCE OF AN INITIAL CONCENTRATION OF ALKALI AND CALCIUM IN GROUNDWATER

If the groundwater has an initial concentration of leachable species, the driving force for the diffusion out of the repository of these particular species is reduced.

Calcium in groundwater

In Appendix B, the content of calcium in the groundwater is 7 mg per litre, corresponding to a concentration of  $2 \cdot 10^{-4}$  moles per litre. The assumed solubility of calcium in water is  $2.5 \cdot 10^{-2}$  moles per litre.

The ratio between groundwater concentration and solubility concentration can be used as a rough estimation of the influence on leaching. This ratio shows that the influence on leaching of calcium is less than 1%.

Alkali in groundwater

Using the various values of the sodium content given in Appendix B, the concentration of sodium in the groundwater was calculated to  $1.3 \cdot 10^{-2} - 3.6 \cdot 10^{-2}$  moles per litre.

A typical concrete has a pH-value of 13, which equals a sodium concentration in the pore-water of 0.1 moles per litre where sodium is the counterion to hydroxide. When comparing the concentration in the concrete with the concentration in the groundwater it can be concluded that, in this case, the maximum leachable amount of sodium is some 60-90 percent of the initial content.

To enable a quantitative estimation of the influence of an initial groundwater concentration on the leaching of alkali from the repository, Figure 1 in Section 3.3 can be used. The leached fraction should then be interpreted as;

1- Initial concentration in groundwater

## Initial concentration in concrete

A corresponding estimation was made for hydroxide, giving a similar result.