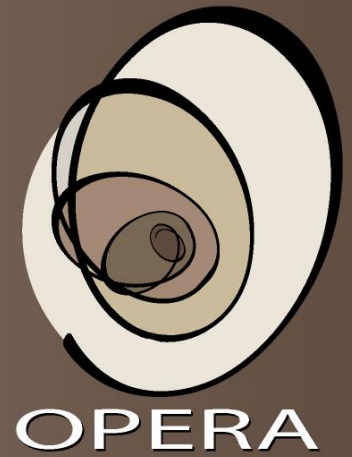




Potential Degradation Processes of
the Cementitious EBS Components,
their Potential Implications on Safety
Functions and Conceptual Models for
Quantitative Assessment

OPERA-PU-SCK514

Radioactive substances and ionizing radiation are used in medicine, industry, agriculture, research, education and electricity production. This generates radioactive waste. In the Netherlands, this waste is collected, treated and stored by COVRA (Centrale Organisatie Voor Radioactief Afval). After interim storage for a period of at least 100 years radioactive waste is intended for disposal. There is a world-wide scientific and technical consensus that geological disposal represents the safest long-term option for radioactive waste.

Geological disposal is emplacement of radioactive waste in deep underground formations. The goal of geological disposal is long-term isolation of radioactive waste from our living environment in order to avoid exposure of future generations to ionising radiation from the waste. OPERA (OnderzoeksProgramma Eindberging Radioactief Afval) is the Dutch research programme on geological disposal of radioactive waste.

Within OPERA, researchers of different organisations in different areas of expertise will cooperate on the initial, conditional Safety Cases for the host rocks Boom Clay and Zechstein rock salt. As the radioactive waste disposal process in the Netherlands is at an early, conceptual phase and the previous research programme has ended more than a decade ago, in OPERA a first preliminary or initial safety case will be developed to structure the research necessary for the eventual development of a repository in the Netherlands. The safety case is conditional since only the long-term safety of a generic repository will be assessed. OPERA is financed by the Dutch Ministry of Economic Affairs and the public limited liability company Electriciteits-Produktie maatschappij Zuid-Nederland (EPZ) and coordinated by COVRA. Further details on OPERA and its outcomes can be accessed at www.covra.nl.

This report concerns a study conducted in the framework of OPERA. The conclusions and viewpoints presented in the report are those of the author(s). COVRA may draw modified conclusions, based on additional literature sources and expert opinions. A .pdf version of this document can be downloaded from www.covra.nl

OPERA-PU-SCK514

Title: Potential Degradation Processes of the Cementitious EBS Components, their Potential Implications on Safety Functions and Conceptual Models for Quantitative Assessment

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Date of publication: July 2015

Keywords: concrete degradation, safety function

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Summary

This report presents current understanding of chemical and mechanical cement degradation processes based on a selected number of literatures. Specific attention is paid to studies carried out in the context of deep disposal applications, where possible. Preliminary implications of such degradation processes on safety functions of the repository components have also been discussed based on rather limited information. A geochemical conceptual model based on thermodynamics, and state of the art reactive transport model are proposed to help in the understanding of spatio-temporal behaviour of concrete geochemistry. Though not within the scope of this work package, an additional step is taken in carrying out preliminary geochemical calculations, including pertinent uncertainty analyses to gain a first level understanding of the chemical degradation processes of concrete. Also included are some simplified mathematical models, which are capable of exploring the chemo-mechanical behaviour, associated with decalcification and sulphate attack. Apart from the characteristics of the cement, aggregates and additives used in the makeup of the candidate concrete or mortar, the main drivers for these degradation processes are the native pore water composition, chemical nature of the waste form, presence of steel, saturated conditions, thermal field, availability of oxygen and diffusion. The literatures suggest that all the processes discussed have an impact on the performance of the cementitious components; however, many of the processes are going to be predominantly active in the long term. Short term impact can be specifically attributed to temperature variation, atmospheric carbonation and sulphate attack; the latter especially relevant during the operational phase from the point of view of retrievability.

Samenvatting

Dit rapport vat de huidige kennis over chemische en mechanische processen gerelateerd aan cementdegradatie samen. Gebaseerd op de bestaande literatuur werd, waar mogelijk, aandacht besteed aan studies uitgevoerd in de context van geologische berging. Tevens werd het gevolg op de veiligheidsfuncties van de degradatieprocessen besproken, hoewel veelal gebaseerd op beperkte informatie. Een geochemisch conceptueel model met elementen uit thermodynamica en geavanceerd gekoppeld reactief transportmodellering wordt voorgesteld om in een later stadium een diep inzicht te verkrijgen in de ruimtelijke-temporele spreiding van degradatie in beton. Een eerste illustratie van een geochemische berekening werd uitgevoerd gebaseerd op onvolledige informatie over de poriënwatersamenstelling; aandacht werd besteed aan het inbrengen van onzekerheden om een eerste inzicht te verwerven in chemische betondegradatie. Een aantal vereenvoudigde wiskundige modellen om het chemo-mechanisch gedrag ten gevolge van decalcificatie en sulfaataanval werden besproken. Naast de karakteristieken van het cement, aggregaten en additieven voor de voorgestelde beton- of mortelsamenstellingen zijn, te belangrijke factoren voor degradatie de poriënwatersamenstelling van de gastformatie, de chemische eigenschappen van het afval, aanwezigheid van staal, verzadigingsgraad, thermisch veld, beschikbaarheid van zuurstof en diffusieve processen. De elementen in de literatuur suggereren dat al deze processen een impact hebben op de duurzaamheid en dus performantie van de cementgebonden componenten; alhoewel vele processen slechts een belangrijke rol zullen spelen op lange tijdschalen. Effecten op een kortere tijdschaal zullen hoofdzakelijk te wijten zijn aan temperatuurvariaties, atmosferische carbonatie en sulfaataanval; die laatste is in het bijzonder relevant tijdens de operationele fase met betrekking tot het terughalen van het afval.

1. Introduction

1.1. Background

The five-year research programme for the geological disposal of radioactive waste - OPERA - started on 7 July 2011 with an open invitation for research proposals. In these proposals, research was proposed for the tasks described in the OPERA Research Plan. In this report, the execution and results of the research proposed for task 5.1.4 with the following title in the Research Plan: *Cementitious material degradation* is described (Verhoef and Schröder [1]).

Cementitious materials that are used in different components in the disposal are typically not in equilibrium with the disposal environment and its physical, mechanical and chemical properties will evolve. As it is most plausible that the properties of the cementitious materials will change to less favourable properties, the term cement degradation is used. In addition, the evolution of cementitious materials will have an effect on the properties of other components in the disposal system.

1.2. Objectives

In order to meet the general requirements of work package 5.1.4, SCK-CEN originally proposed to address the requirements methodically through the following three tasks:

- Task 1: to provide a synthesis report on the chemical and physical/mechanical degradation of cementitious materials in the engineered barrier system (EBS) of high level radioactive waste (HLW).
- Task 2: to describe the effect of such degradation processes on safety functions of the repository components.
- Task 3: to suggest a geochemical conceptual model that might help in quantifying the evolution of safety-relevant processes.

This report presents the results obtained from these tasks.

1.3. Realization

The literature study and a preliminary geochemical model presented in this report have been performed by SCK-CEN, Belgium within the GEPETO project.

1.4. Explanation contents

Chapter 2 describes the most pertinent chemical degradation processes. The goal here is to describe the known major degradation processes based on literatures, which should allow one to draw certain preliminary conclusions on their relevance and potential implications on safety functions. Chapter 3 describes the most pertinent mechanical degradation processes. Note that chemical and mechanical degradation processes are interrelated. However, in terms of presentation, they have been separated into distinct chapters for the sake of clarity.

In describing each of the degradation processes, specific attention is paid to studies carried out in the context of deep disposal applications, if available, and implications on the safety functions of the repository components. It is necessary to qualify upfront that task 2 is not trivial because interactions between various degradation processes over the long term are extremely complex and at this point in time there is a clear lack of understanding and data of such processes for the given material. These require most often thorough experimental, field and numerical studies. Therefore, the term potential implications should be viewed cautiously as these are preliminary in nature and should be

confirmed by further research. Chapter 2 and 3 together fulfil the objectives of task 1 and 2.

Chapter 4 briefly touches upon the issue of retrievability given the current understanding of cement degradation processes.

Chapter 5 proposes a conceptual model for exploring the complex geochemical processes of cement in contact with native Boom Clay water. A further step is taken in carrying out a preliminary analysis, including uncertainty analyses, based on the available information for a benchmark cement and Boom Clay pore water proposed in Koenen and Griffioen [2] and Verhoef et al. [3], respectively. Thus some preliminary interpretations of the geochemical analyses are also made available at this stage. However, note that the geochemical calculations do not provide a picture of spatial evolution of chemical degradation processes. Therefore, the same chapter also includes a description of a state of the art reactive transport model that can be used to analyse spatio-temporal behaviour of geochemicals, including feedback with transport and physical properties of cementitious components. Though not envisaged in task 3, this chapter also proposes some simplified chemo-mechanical models for exploring the potential impact of chemical degradation on mechanical degradation for two major processes.

Chapter 6 draws salient conclusions from this literature study. Some important recommendations are brought to the fore in Chapter 7 in order to help identify future research requirements.

2. Chemical degradation processes of the cementitious EBS components and their implications on safety functions

Chemical degradation is defined here as "*the gradual change in pore-water composition and concrete mineralogy, usually characterized by a decreasing Ca/Si ratio and a decreasing pH*".

Different chemical degradation mechanism may change the pore water and solid phase composition of concrete. The main chemical degradation phenomena considered in this section are decalcification/leaching, carbonation sulphate attack, chloride ingress and alkali aggregate reaction (AAR). Many overviews in other studies consider chloride ingress not as chemical degradation process, but link it directly to corrosion (e.g. Pabalan et al. [4]). However, chloride changes also the solid phase composition and, therefore, ingress of chloride was treated as a chemical detrimental process in Glasser et al. [5].

The following processes are deemed relevant under deep geological conditions:

- a) Decalcification and leaching
- b) Carbonation
- c) Sulphate attack
- d) Chloride ingress
- e) Interaction with waste form

It is to be borne in mind that the OPERA safety concept does not attribute any safety functions to the cementitious barriers, with the exception of concrete buffer that is expected to maintain a high pH environment during the engineering containment phase. Thus the main purpose of the literature review presented in this section is to examine the potential consequences of chemical degradation of cementitious components on the safety functions of other components of the repository.

2.1. Decalcification and leaching

2.1.1. Process description

Concrete pore water is characterized by its high alkaline conditions for a very long time. External environmental water is almost always much more acidic than the concrete pore water. Through interaction (*i.e.* diffusive mass fluxes due to concentration gradients or bulk fluxes due to pressure head gradients) with environmental water as ground water at the depth of the repository, most cement phases are progressively dissolved and leached out. Depending on the composition of the external water, the dissolution process coincides with the precipitation of other phases (*e.g.* calcite in case of bicarbonate, ettringite, thaumasite or gypsum in case of sulphate, brucite in case of magnesium). The process of leaching is a relatively slow process, but is relevant for time periods considered in safety calculations. The most important element is Ca, but also other elements in concrete (*e.g.* Na, K, Mg, Si, sulphate) will be leached out. A typical sequence of cement leaching and decalcification is [38]:

- Portlandite dissolution.
- Jennite dissolution with the formation of tobermorite, *i.e.* decalcification of the C-S-H phase.
- Simultaneously, the different AFm and AFt phases dissolve (monocarboaluminate, tricarboaluminate, ettringite, and strätlingite) also when jennite is completely dissolved.
- Tobermorite dissolution together with strätlingite dissolution.
- OH-hydrotalcite starts to dissolve, first together with tobermorite, then with calcite, and finally only OH-hydrotalcite remains (with hematite).

These chemical degradation reactions normally occur, to a certain degree, simultaneously in a cement system, *e.g.* portlandite dissolution during leaching can coincide with calcite precipitation when the inorganic carbon content in the infiltrating water is high. When viewed in a transport system (*e.g.* concrete in contact at one side with a water of constant composition), one typically obtains a zonation of different degradation states within the concrete as (from the boundary with the external water towards the inner core of the concrete; Adenot [6], Adenot and Faucon [7], Lagerblad [8], Kamila et al. [9], Escadeillas and Hornain [10]):

- Zone with residual, relatively insoluble phases (silica gel, hydroxides, calcite)
- Zone with decalcified C-S-H gel
- Zone with decalcified C-S-H gel and AFt (ettringite)
- Zone with decalcified C-S-H gel, AFt, and AFm (*e.g.* monosulfoaluminate or monocarboaluminate)
- Zone with portlandite, C-S-H gel, AFt and AFm

Leaching and decalcification are induced by mixing by diffusion and advective processes of external water with the concrete pore water and solid phases. A source of external water for leaching of the cementitious materials in the near field is mainly ground water.

There exist a few studies on the leaching behaviour of concrete structures under real conditions. Lagerblad [8] studied the leaching depth in a few existing concrete structures up to 100 years old under stagnant and flowing water conditions in the surroundings of Stockholm, Sweden. Alteration depths varied between 4 to 10 mm. The study of Yokozeki et al. [11] investigated the leaching depths of portlandite and C-S-H phases in concrete structures up to 100 years old. Leaching depths for portlandite and C-S-H phases were up

to 100 and 5 mm, respectively. Such differences are attributed to various reasons as discussed below:

- The aggressiveness of the external water which is determined by the pH (a lower pH gives a higher aggressiveness), inorganic carbon content (the so-called aggressive carbon dioxide [4, 22, 10] which is that portion of the total dissolved carbon dioxide available to react with the cement; the other portion reacts with other aqueous species), and concentration of aggressive species in the water (e.g. sulphate and magnesium as the most important ones, but also some other ones as discussed in e.g. [10]).
- The transport properties of the concrete: chemical leaching and decalcification of the concrete are strongly dominated by the transport properties of water and aqueous species in the concrete. Most critical transport parameters are the total porosity (e.g. Haga et al. [12]), the tortuosity (to obtain the pore diffusion coefficient) and the permeability (to derive the saturated hydraulic conductivity). These transport properties are influenced mainly by the concrete microstructure (e.g. initial transport properties depend on the aggregates, capillary porosity and gel porosity; the latter is linked to the amount and quality of the C-S-H gel) and thus on factors such as water to cement ratio and curing time. Also supplementary cement materials influence the leaching rate ([10], [5]).
- External boundary conditions. The degree of saturation of concrete controls both the transport and diffusion of dissolved species and the amount of cement minerals to dissolve to achieve equilibrium.

The main consequences of leaching and decalcification are:

- Physical consequences: Although secondary phases may precipitate during leaching (e.g. strätlingite), the overall net evolution is an increase in total porosity. Consequently, an increase in porosity changes the flow and transport properties of water and solutes in the concrete.
- Mechanical consequences: Leaching of Ca decreases the mechanical strength (e.g. 3.1).
- Chemical consequences: As discussed in [39,13], the pore water composition, solid phase composition and other geochemical variables (e.g. pH) change during decalcification and leaching. The most important consequence is that sorption of radionuclides change with leaching and decalcification. Wang et al. [65] defined four cement/concrete degradation states based on the cement phases which control the pore water composition and pH. Sorption parameters (partition coefficient) were defined for several critical radionuclides for each of the degradation states.

2.1.2. Specific studies related to deep disposal

In a general review of long term stability of concrete, Shin [14] indicated the following behaviour under deep geological conditions. In the early stages, the Cl in ground water shows very fast and deep penetration into the concrete as compared to SO₄. Cl reacts in this case with Ca(OH)₂ to release Ca²⁺ into the aqueous phase and hence the specimen will slightly become porous, although most of the Cl is retained in the concrete as Friedel's salt. The behaviour of the C-S-H in the concrete under high temperature and pressure over extremely long periods of time is uncertain and in a repository where the initial temperatures are elevated a certain number of reaction products created can determine the long-term stability. There is a possibility that deleterious effects resulting in increased permeability may accompany recrystallization of the metastable phase. Porosity would increase by 3 to 3.5% and it is not known whether internal microcracks will be created by

this increased porosity. Ca(OH)_2 leaching by diffusion would be about 5 mm over 1,000 years and 15 mm over 10,000 years. According to a recent calculation by Perko et al. [15] the leaching depth is approximately 40 mm in 900 years. This difference is attributed to the nature of the incoming water; in Perko et al. [15] the pH of the incoming water is 4.

In a related study, Hoglund [16] presented leaching calculations for various scenarios in the context of a Swiss low- and intermediate-level waste (L/ILW) repository located in large disposal caverns at a depth of around 400 metres. Using a simplified model, the calculated time for total deterioration of the concrete in the repository is 10^6 - 10^7 years depending on the assumed diffusivity. Assuming pore structure changes (i.e. higher diffusivity), the calculations indicated a complete deterioration after approximately 10^6 years. In their calculation they assumed a total calcium content of 3000 moles/ m^3 and a pore diffusion coefficient of $6.3 \times 10^{-3} \text{ m}^2/\text{a}$. Temperature effects are not relevant in their study because of the waste being L/ILW.

In a deep disposal experimental study at the Tournemire experimental platform (IRSN, Aveyron, France) concrete samples are located in a mechanically undisturbed zone at constant saturation under in situ conditions for 18 years (Bartier et al. [17]). The modification of the hardened cement paste was found to be mainly controlled by carbonation and portlandite dissolution, as well as successive ettringite precipitation and dissolution, and, finally, by C-S-H decalcification.

In the context of French geological disposal of intermediate-level long-lived waste, cement based materials are considered as candidate materials. Leaching experiments were carried out in Hoek cells comprising a 20-mm thick sulphate-resisting Portland Cement paste in contact with mudstone (Dauzeres et al. [18]). The test temperature was set at 25°C and the duration of the tests was 2, 6 and 12 months. Carbonation was found to be low and did not clog the cement-mudstone interface. The absence of carbonation allowed diffusion of aqueous species and, thus, for the degradation of the cement paste. The cement material was subjected to decalcification: portlandite dissolution and a CaO/SiO_2 reduction in the C-S-H. Sulphate induced non-destructive ettringite precipitation was found in the largest pores. After 12 months, about 800 μm of cement material was found to be decalcified.

Wang et al. [19] carried out numerical simulations of decalcification due to the Boom Clay pore water via a 1D radial reactive transport model. Their calculations showed that during the first 25,000 years, portlandite is completely dissolved in the last 25 percent of the concrete layer (closer to the Boom Clay interface). After 10^5 years, the zone in which portlandite is still present is about 33 percent of the complete concrete layer. The precipitation of calcite is advanced in the concrete layer up to 30 cm into the concrete from the Boom Clay interface. The calcite precipitation can block the porosity of the concrete, but this is not accounted for in their simulations. As far as the pH is concerned, it remains sufficiently high at 12.5 in the buffer region even after 10^5 years. Note that their calculations make a number of model assumptions, which should be borne in mind whilst interpreting the data for other repository concepts.

In order to assess the effects of mineral reactions on pore clogging of concrete, Liu et al. [20] considered reactions of a full set of mineral phases of a benchmark concrete with Boom clay pore water, in the context of Belgian deep disposal study. Calculations showed clogging at the inlet boundary mainly due to the precipitation of a large amount of calcite. This result was unlike the modeling results from Shao et al. [21], which showed ettringite as the major mineral phase that precipitated, and to a minor extent C-S-H phases in the interaction between hyper-alkaline cement leachate and marl rock at Maqarin natural analogue site. This difference may be due to the 5 times higher sulphate and about 6 times lower bicarbonate concentrations in the marl rock than in the Boom Clay.

2.1.3. Implications on the safety functions of the repository components

In a pure diffusion system and under normal repository evolution condition, decalcification and leaching is generally a very slow process taking thousands of years to degrade the concrete as reported by various studies above. This is also reflected in field studies such as those reported by Bartier et al. [17] and Wang et al. [19]. Since sea water (Boom clay in Netherlands) is low in bicarbonates compared to Boom clay in Mol, clogging due to precipitation is less likely and hence rate of leaching may still be appreciable. Since the concentration of chloride is very high it is possible that portlandite can also be destabilized by high Cl as noted by Shin [14].

As stated above, Perko et al. [15] calculated a decalcification depth of 42 mm in 900 years, which was based on an aggressive water composition with a pH of 4, assuming fully saturated condition. However, typical pH of the Boom Clay pore water is close to 8 and hence the depth of penetration may not be as significant. The decalcification front will commence from the outer surface of the wedge blocks, propagating into the cementitious backfill and then finally into the concrete buffer provided the steel envelope is perforated. During early stages the degree of leaching should be expected to be minimal. Especially during the thermal phase the near field can remain in an unsaturated state for several decades.

It is recommended that specific analysis of decalcification and leaching via the use of a state of the art model (e.g. Jacques et al. [39], see also sections 5.1.1 and 5.2) is carried out to assess a more realistic behaviour of the cementitious components under in situ conditions. Note that the effect of temperature on the leaching rate under buried conditions has not been studied. Table 1 summarizes potential implications on the safety functions of the repository components. This information is largely taken from Wang et al. [19].

Table 1 Potential implications on the safety functions of the repository components related to decalcification and leaching

<i>Post closure safety functions in system containment phase</i>	<i>Component and / or barrier</i>	<i>Implication processes identified in cement degradation</i>		
		Concrete buffer (HLW)/Container backfill (LILW & TE(NORM)) CEM I/CEM III	Concrete Backfill (CEM I+Foam)	Concrete Liner (CEM II)
Limitation of contaminant release	Waste form (dissolution property)	Based on numerical simulations by Wang et al. [19], the pH at the canister/buffer interface may remain sufficiently high for a very long time (10^5 years). High pH is detrimental to the rate of corrosion of the vitrified waste form. Refer to section 1.1 for further details. Note that the high pH helps in minimising the effect of anaerobic steel corrosion of the waste package, which means that it also delays the contact of high pH pore solution with the waste form.		
Limitation of water flow through the system	Boom Clay			
Retardation and spreading in time of contaminant migration	Boom Clay	Laboratory experiments and modelling indicate that an alkaline plume disturbed zone in Boom Clay in Mol would extend about 1-3 m. This range is comparable to conclusions made from studies on similar type of clays considered in France and Switzerland. Laboratory percolation experiments	Similar to concrete liner, but the extent of degradation will be lower because of the distance from the Boom Clay interface. As literature on durability and leaching of foam concrete was not available, the specific implication of	Because portlandite is consumed by fly ash reactivity and transformed into C-S-H phases, concrete state II will be non-existent (in case all fly ash has reacted) or shorter compared to CEM I. The key elements of CEM I are expected to be valid

		on small clay cores demonstrate that an alkaline plume does not have an observable effect on the diffusion of HTO. Bicarbonate is found being retarded in percolation experiment probably due to carbonation reactions. Such retardation is likely to be caused by the formation of secondary calcite rather than by a slower diffusion. Laboratory percolation experiments on small clay cores demonstrate that percolation of Boom Clay with YCW (pH 13.2) increased hydraulic conductivity by a factor of 2 while percolation with ECW (pH around 12.5) caused a decrease in the hydraulic conductivity by about 20%. The observed increase in permeability is likely the result of dissolution of swelling clay (e.g., smectite) and natural organic matter. The decrease of permeability is in line with geochemical modelling predicting a porosity occlusion due to calcite precipitation as a result of clay - ECW interaction. Most of the alteration processes taking place in an alkaline plume disturbed zone of Boom Clay are expected to be in favour of slowing down the migration of	foam on leaching, although expected to be low, is not known.	(disturbance of the clay, changes in permeability and porosity) - although some further modelling or experimental work is needed for confirmation.
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		radionuclides. A possible negative impact of an alkaline plume might be a reduction of sorption for alkaline earth elements. However, such decrease in sorption could be compensated by an enhanced sorption owing to a formation of secondary minerals having a much higher ion exchange capacity. Within the disturbed zone, an alkaline plume will dissolve clay minerals and result in precipitation of C-S-H, zeolites, and calcite phases. In particular, in-house experiments show dissolution of smectite by the cement water with high alkali concentrations and high pH (13.5).		
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2.2. Carbonation

2.2.1. Process description

Carbonation is a process in which the cement components, such as portlandite and the C-S-H phase, react with dissolved carbonate species to form carbonate precipitates such as calcite. The carbonate source may be from the air or from infiltrating water. The dissolved carbonate species in the concrete pore water originate from either the external water in contact with the cementitious materials (carbonation through the aqueous phase) or from exchange of gaseous carbon dioxide with the concrete pore water (carbonation through the gaseous phase). Although both carbonation pathways are essentially the same (interaction of dissolved carbonate species with cement minerals), an important difference is that during carbonation through the gaseous phase, the concrete pore water composition is in relatively close equilibrium with the cement materials and dissolution reactions are small compared to the case of carbonation through the aqueous phase. In the latter, external water may be aggressive to the concrete and can induce dissolution reactions (*e.g.* external water strongly under saturated with respect to portlandite).

In case of carbonation through the gas phase, penetration of gaseous carbon dioxide within concrete and in the presence of water usually initiates a series of reactions with both ions (Ca and C) dissolved in the pore solutions and the hydrated cement paste. Gaseous carbon dioxide first penetrates the material and dissolves in the pore water via a number of chemical reactions. Carbonation through the aqueous phase follows the same pathway, except the first step (dissolution of gaseous carbon dioxide) is not present. The degree of carbonation through the aqueous phase depends on the amount of aggressive CO₂ (Cowie and Glasser [22]).

The main source of CO_{2(g)} is the atmosphere. It is generally stated that the partial pressure of CO_{2(g)} in the atmosphere is 10^{-3.5} atm (Apello and Postma [23]), which corresponds with 316 ppm (or 32 Pa). Another important source of carbon dioxide is (micro)biological activity in soil systems (soil carbon cycle).

A high partial pressure of CO₂ (an external source of CO₂) does not automatically lead to a fast carbonation rate within the cementitious material. The actual carbonation rate depends on a number of other factors. The main ones are related to the fact that the CO₂ ingress in the cementitious material is a diffusion-controlled process. As such, factors controlling the diffusion of CO₂ control also the carbonation rate.

- The water saturation state of the concrete is one of the main factors (Baroghel-Bouny et al. [24]). When the water saturation increases, the pore space filled with air decreases. Because the diffusion of CO₂ is about 4 orders of magnitude faster in the gas than in the aqueous phase, lower water saturation gives higher carbonation rates. In submerged concrete, the rate of carbonation is strongly linked to leaching processes, which are slow processes (Lagerblad [25]). It is important to note that carbonation also decreases when the water saturation of the concrete is too low because the carbonation reactions itself (transformation of portlandite into calcite) takes place in the aqueous phase. The highest carbonation rates occur in the RH range between 50-70 % [4, 24].
- The microstructure of the concrete determines the tortuosity for gas diffusion in the gas phase. For example, the presence of microcracks, total porosity, capillary and gel porosity (associated with the C-S-H phases). Consequently, also the water/cement ratio has an effect. It is observed that carbonation slows down when water/cement ratios are lower (*e.g.* Baroghel-Bouny et al. [24], Kobayashi et al. [26]) because total porosity (and capillary porosity) is lower for lower

water/cement ratios. Similarly, the larger the amount of cement in the concrete, the slower the carbonation front because this also decreases the porosity of the concrete [24]. Also curing influences the carbonation rate [24].

- The outer boundary conditions: it was already mentioned that the environmental relative humidity, and thus also temperature, plays a role.

For a given atmospheric condition, the degree of water saturation and the concrete microstructure are the most influential factors. Because there are only a few well advanced models fit for practical application (Kuhl et al. [27], Grasberger and Meshke [28]), many authors apply simplified laws. Typically, the progress of carbonation in a concrete beam is described by [25]:

$$x(t) = k\sqrt{t} \quad \text{Equation 1}$$

where x [L] is depth of carbonation and t [T] is time. The carbonation rate factor k [M/T^{0.5}] is mostly treated as an empirical parameter dependent on the type of concrete and environmental factors. Lagerblad [25] gave k values for different concrete and environmental classes based on some generalizations. Values for the concrete class representative for the Dessel surface repository (strength class > 35 MPa) are: 2.5, 1, 0.75 and 0.5 mm/year^{0.5} for environmental classes sheltered, exposed, buried and wetted/submerged, respectively. Note that these values are assumed to be representative for concrete subjected to a typical Nordic climate (and are based on empirical data for this, *i.e.* empirical data for Nordic or northern hemisphere conditions). Note also that these values are derived as an average value for different types of concrete, and thus not only for high-quality concrete foreseen in the disposal facility. Although biologically produced CO₂ must be taken into account for buried concrete structures, Lagerblad [25] assumed that diffusion through the soil is a limiting factor in carbonation (important to note that [25] stated that limited diffusion in soil has to be verified). As discussed above, it is possible that diffusion in the soil is not the rate-limiting factor for concrete carbonation. It was anticipated that the expected high relative humidity in soil systems may be an important factor in limiting concrete carbonation in buried systems. Again, similar to [25], it is important to further verify this assumption. Note that for wetted/submerged concrete, water percolation is assumed. With stagnant water, the rate of carbonation will be lower [25].

Because the molar volume of portlandite is smaller than that of calcite, carbonation through the gas phase decreases the porosity of the concrete. In case of carbonation through the aqueous phase, decalcification and leaching processes may counteract porosity decrease by dissolution of primary cement phases. The particular consequence of combined carbonation and leaching on porosity depends on different factors such as concrete properties and boundary conditions (see also section 5.2). Other important consequences of carbonation are that it:

- Enhances the potential for corrosion of embedded steel (see also section 0). Carbonation lowers the pH. At a pH of about 9 [4], the passive film protecting the steel surface is no longer stable. Carbonation results in both uniform corrosion (Naus [29]) and localized corrosion (Nasser *et al.* [30], Miyazato and Otsuki [31]); and
- Affects the chemical immobilisation potential of many radioactive waste species, for example, immobilisation of Cs or Sr, or increase in leaching of Cd, Co, Ca, Pb (see references in [4]).
- Carbonation may influence chloride-induced corrosion (*e.g.* via effect on Friedel's salt equilibrium, Ishida *et al.* [32]).

2.2.2. Specific studies related to deep disposal

In the context of deep disposal in saturated clay systems, carbonation occurs only via the aqueous phase because it is reasonable to assume that the concrete components will resaturate relatively fast. Consequently, in the framework of deep disposal, carbonation cannot be seen independently from leaching and decalcification. Therefore, the discussion in section 2.1.2 is also relevant here. Depending on the clay pore water composition, dissolved inorganic carbon can lead to more or less calcite formation. If calcite formation is more significant than leaching, pore clogging may occur as was illustrated in some numerical studies for Boom Clay - concrete interactions with the pore water concentration in the region around Mol (Belgium) [20, 19]. Similar clogging process was also modeled in case of Opalinus Clay (Kosakowski and Berner [33]). As such, a protective shell could be formed at the interface. Note however that the clogging is not always due to calcite but could be the consequence of other phases, which strongly depends on the clay pore water composition. On the other hand, when the leaching is more significant, carbonation and calcite precipitation could not lead to clogging. In this case, calcite is one of the many solid phases controlling concrete pore water composition, pH and the leaching fronts in the concrete. The thin line between clogging/leaching through differences in pore water composition was illustrated in [15] although the application domain was not deep disposal in that study.

2.2.3. Implications on the safety functions of the repository components

Table 2 summarizes potential implications on the safety functions of the repository components.

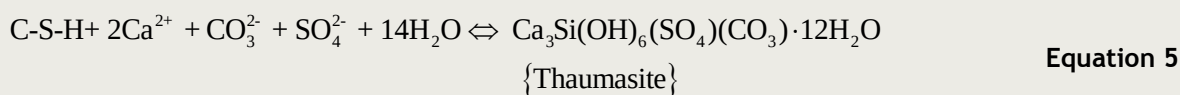
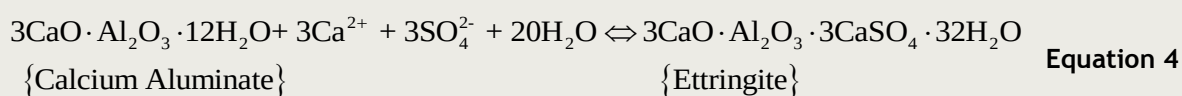
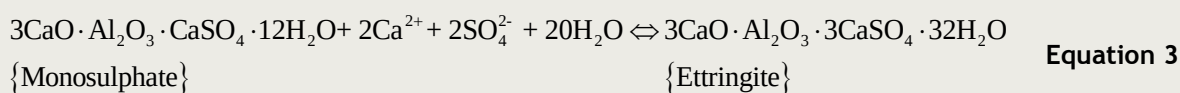
Table 2 **Potential implications on the safety functions of the repository components related to carbonation**

<i>Post closure safety functions in system containment phase</i>	<i>Component and / or barrier</i>	<i>Implication processes identified in cement degradation</i>		
		Concrete buffer (HLW)/Container backfill (LILW & TE(NORM)) CEM I/CEM III	Concrete Backfill (CEM I+Foam)	Concrete Liner (CEM II)
Limitation of contaminant release	Waste form (dissolution property)	The potential lowering of the pH is likely to lower the dissolution rate of certain waste forms. Hence, can be seen as beneficial.	No direct contact with the waste form.	No direct contact with the waste form.
Limitation of water flow through the system	Boom Clay			
Retardation and spreading in time of contaminant migration	Boom Clay	Pore clogging is likely to minimize the rate of alkaline plume thus having limited impact on the sorption property of the Boom Clay and also limiting transport of deleterious substances towards the overpack.		

2.3. Sulphate attack

2.3.1. Process description

Sulphate attack is the geochemical process in which dissolved sulphate species reacts with cement components with the precipitation of sulphate minerals as gypsum, ettringite and thaumasite (Pabalan et al. [4]):

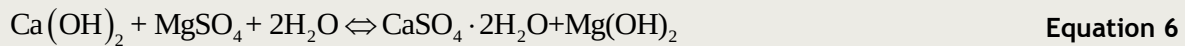


The molar volumes of the S-phases differ significantly from those of the original constituent phases. This may lead to the build-up of internal stress causing cracking. Depending on the source of the sulphate, there is a distinction between internal and external sulphate attack:

- *Internal sulphate attack*, also called delayed ettringite formation (DEF or delayed sulphate attack), is the formation of ettringite after hydration of the cement from the sulphate present in cement. This form of sulphate attack can be limited by an appropriate choice of the cement (ettringite formation is controlled by limiting the SO_3 content of the cement used ($\text{SO}_3 \leq 3.5\%$) (Gens [34]), limiting C_3A content).
- *External sulphate attack*, in which sulphate penetrates from the surrounding environment into the concrete. Two forms of external sulphate attack in concretes and mortar are distinguished: the ettringite sulphate attack (ESA) and thaumasite form of sulphate attack (TSA). ESA can be limited by an appropriate choice of the cement. A sulphate resisting Portland cement contains a limited amount of C_3A (up to 3%) which avoids ettringite formation. TSA is not necessarily prevented by a low C_3A content [35]. As discussed in Jacques et al. [36], factors favourable for thaumasite formation are sources of SO_4^{2-} ions, SiO_3 (internally from the C-S-H phases), CO_3^{2-} (from the aggregates), ground water, and low temperatures (thaumasite preferentially forms at low temperatures below 15°C , but can be present at higher temperatures also) (Schmidt et al. [37]). Note that in the long term, i.e. after the thermal phase, the temperature in Boom clay at Mol will be typically around 16°C .

Note that the cation associated with the sulphate (the negative charge of the sulphate must be balanced by cations (Glasser et al. [5])) also determines the aggressiveness of the sulphate rich water (Adenot [10]). Protons will dissolve calcium containing cement hydrates (Glasser et al. [5]). Sodium and potassium have an effect on the pH. Especially magnesium sulphates will have a detrimental effect (both magnesium and sulphate ions

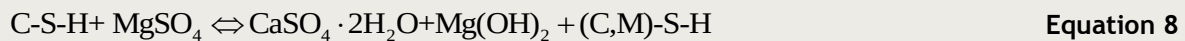
participate in the chemical concrete degradation) with the formation of brucite (Adenot [10]), e.g. attack of magnesium sulphate on portlandite gives gypsum and brucite:



Gypsum may react with C₃A to form ettringite:



Also C-S-H phases are altered by magnesium sulphate resulting in decalcification of the C-S-H and formation of gypsum and brucite:



where (C,M)-S-H is a (poorly-crystalline) calcium-magnesium silica hydrate (Adenot [10]). Also hydrotalcite might form in the presence of magnesium (Jacques [38]; Jacques et al. [39]). The very detrimental effect of magnesium sulphate is obvious when sea water interacts with the concrete (Jacques et al. [39]; Adenot [10]).

Lee et al. [40] carried out an experimental study on the sulfate attack of mortar specimens with or without silica fume exposed to sulfate and sulfate-chloride solutions (with the same concentration of SO_4^{2-} ions) up to 510 days. The overall aim of the study was to investigate the beneficial effect of chloride ions on sulfate attack. Results indicated that the presence of chloride ions in sulphate environments mitigated the deterioration of ordinary Portland cement mortar specimens, especially with higher water to binder ratio, due to sulphate attack. It seems that the mitigating effect of chloride ions on sulphate attack is attributable to the increased solubility of sulphate products in the chloride-bearing sulphate solution, and the chemical binding of the ions to form Friedel's salt.

2.3.2. Specific studies related to deep disposal

In a French study concerning intermediate level waste disposal, the internal sulphate attack was considered to be probably a secondary phenomenon, particularly considering the choice of the composition of the concretes used in the structures. However, based on the quantities of sulphates brought in by the argillite water (Altmann & Jacquot, [41]), a sulphate attack may occur on their interface. According to Bourbon [42], this phenomenon is likely to affect only about 10 centimetres of concrete in 10,000 years. Also, this phenomenon will only have a minor effect on the consumption of portlandite, which controls the pH of concrete. Waste packages whose contents are likely to release some species which may be aggressive to concrete are essentially bituminized sludge B2 reference packages. These release organic acids and sulphates. A balance performed over all the acids likely to be released by the bituminized sludges, independently of any kinetics, leads to a degradation of the concrete of the disposal packages only. Coating and filling concretes are unaffected (Bourbon [42]). The sulphate release kinetics (10^{-4} per year) leads to a sulphate attack in the disposal package and does not massively affect the cell.

Pyrite or iron sulphide (FeS_2) is almost always present in marine clays. The oxidation of pyrite results in the production of protons (acidification) and sulphate ions, both of which may participate in detrimental reactions affecting concrete durability. The acidification itself can be buffered by the presence of carbonates such as calcite (Waite et al. [43]). When the clay is saturated, oxygen diffusion in the clay is slow and hence the pyrite oxidation rate is also slow. Importantly, calcite which is also present in pyrite-rich clays (during pyritization, bicarbonate is formed leading to CaCO_3 precipitation (Baeyens et al. [44])) buffers the acidity (by dissolution of calcite) and sulphate concentration (e.g. by

gypsum precipitation (Molson et al. [45]), both generated by the pyrite oxidation. In this context, results from a recent geochemical study by De Craen et al. [46] on the oxidation behaviour of Boom Clay in the HADES URF suggest that the level of sulphates remain relatively high in the near field even 25 years after the excavation. This points to the fact that the sulphates are not easily reducible in the course of the open drift phase. The concentrations of thiosulphates found are generally low, and hence no negative impact can be expected towards the metal corrosion directly related to the pyrite oxidation and the associated sulphate-reduced species. However, they stated that high sulphates present a potential risk for the stability of the concrete lining (Planel et al. [47], Lothenbach et al. [48]). This is important if the option to retrieve the waste from the repository after a certain period of time is to be considered.

Sulphur species (sulphide, sulphate and thiosulphate) can also cause localized corrosion of steel. Govaerts and Weetjens [67] carried out a scoping study to examine the peak concentrations of sulphide, sulphate and thiosulphate species at the overpack testing different concentrations in the clay and assuming no reactivity with concrete. They demonstrated through simplified calculations that the peak concentration of sulphides at the overpack does not exceed 0.26 mol/l. The actual concentration at the overpack can be expected to be much lower, as it is not likely that all pyrite will ultimately end up as sulphides. In fact, using best estimates of the model parameters, the results suggest a peak concentration not exceeding 0.13 mol/l after about 1000 years. As far as the sulphate and thiosulphate species are concerned, their calculations showed that the peak concentration at the overpack does not exceed 91.7 and 4.1 mmol/l, assuming EDZ concentrations are 215 mmol/l and 9.5 mmol/l, respectively. When using best estimates of the model parameters, their results suggest peak concentrations not exceeding 53.9 mmol/l and 2.4 mmol/l after about 1000 years. Note that no reactions of the aggressive species with concrete components were included in their calculations as the Boom Clay pore water in Mol is low in sulphates and chlorides. A study similar to the above is being finalised for the OPERA concept within the GEPETO framework by SCK-CEN (refer to WP 5.1.3 deliverables).

2.3.3. Implications on the safety functions of the repository components

For the disposal facility, two sources of sulphate exist: (i) from the oxidation of pyrite, which is present in the Boom clay and (ii) the composition of the native pore water, which is similar to sea water in the current study.

During the construction phase, sulphate attack (originating from both pyrite oxidation and the native Boom Clay water) on concrete liners remain an important concern. After repository closure, there is no supply of oxygen and hence sulphate attack is only possible due to the native Boom Clay water, which is rich in sulphates. However, note that based on the results of Lee et al. [40], the presence of high chloride (>20,000 ppm) may counter the sulphate attack due to the formation of Friedel's salt (further discussed in the preliminary analysis presented in section 5.1.1).

The external sulphate attack is mainly controlled by transport processes under a concentration gradient (diffusion). Also factors influencing geochemical reactions and thermodynamic equilibrium influence the degree of sulphate attack. As such, composition of the ground water, concrete microstructure (e.g. defined by the water/cement ratio of the concrete), transport properties (related to microstructure), temperature, water saturation of concrete, replenishment of sulphate in concrete pore water, composition of the concrete are all important parameters. Therefore, after the repository closure, and after resaturation of the concrete barriers, sulphate attack is diffusion driven and it will take a very long time for sulphate species to diffuse through the backfill and then to the concrete buffer. Note that initially sulphate can also advect towards the cementitious

components with the resaturation water and the time scale depends on the capillary properties of the material.

From a recent assessment by Liu et al. [20], ettringite formation was seen as less likely in the case of Boom clay in Mol due to a very low sulphate in ground water. But this is not the case in the Netherlands Boom Clay where the ground water composition is similar to sea water with elevated concentrations of sulphate ions (upper bound value = 0.02 mol/l).

Table 3 summarizes potential implications on the safety functions of the repository components.

Table 3 Potential implications on the safety functions of the repository components related to sulphate attack

<i>Post closure safety functions in system containment phase</i>	<i>Component and / or barrier</i>	<i>Implication processes identified in cement degradation</i>		
		Concrete buffer (HLW)/Container backfill (LILW & TE(NORM)) CEM I/CEM III	Concrete Backfill (CEM I+Foam)	Concrete Liner (CEM II)
Limitation of contaminant release	Waste form (dissolution property)	No quantitative information available, but cracking of the cementitious components may occur if ettringite or gypsum precipitates. This may lower the pH thus promoting anaerobic corrosion of steel, which in turn will have an influence on the waste form dissolution. However, note that waste form is stable at lower pH. The potential for sulphate cracking requires site specific quantitative data.	Not known.	Same as concrete buffer; sulphate resistance plays only a role in ettringite formation, gypsum can still potentially form. Given the uncertainty of the water composition, quantitative assessment is difficult at this stage.
Limitation of water flow through the system	Boom Clay			
Retardation and spreading in time of contaminant migration	Boom Clay	The cracking in general can lead to preferential transport of high pH pore water from the cementitious barriers into the clay. High pH can affect radionuclide sorption of the clay, positively or negatively depending on the radionuclide.	Not known.	

2.4. Chloride ingress

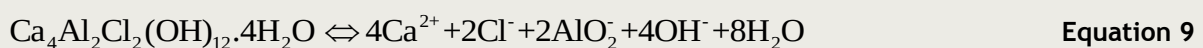
2.4.1. Process description

Chloride ingress is the penetration and redistribution of chloride in concrete. As such, chloride ingress is not a chemical degradation process, but it gives rise to some chemical degradation mechanisms. Most importantly, high chloride concentrations initiates corrosion of steel and at very high levels may alter the solid phase. Diffusion is the main transport mechanism in water-saturated intact concrete in absence of a pressure gradient.

Chloride is present in the cementitious material as chloride associated with the concrete production itself. Background chloride concentration in cement pore water is generally low. Stable chloride is present in commercial cements up to 0.01 wt%. Chloride concentrations up to 0.4% (by weight of cement) can be taken as a conservative value below which steel corrosion will not be significantly altered (Alonso et al. [49]; Izquierdo et al. [50]). Only part of total chloride in cement remains in the pore water under soluble form because of sorption and/or formation of a solid-solution (Nielsen et al. [51]). The pore water concentration of chlorine originating from cement itself is in a range of millimolal to a few tenths of millimolal. Friedel's salt ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$) may be formed as a solid-solution if the pore water chloride concentration increases above a few millimolal (Bothe et al. [52]).

Two external sources of chloride are possible: one originating from the waste matrix and the other originates from the ground water which mixes (through diffusion) with concrete pore water.

Two main chloride binding mechanisms are possible (Yuan et al. [53]): (i) physical sorption of chloride to C-S-H gels (Hirao et al. [54], Henocq et al. [55]), Beaudoin et al. [56]) and (ii) chemical reaction with AFm phases. AFm serves as an important sink for chloride by forming Friedel's salt (Birnin-Yauri and Glasser [57], Bothe and Brown [58], Nielsen et al. [59], Balonis et al. [60]). The dissolution reaction of Friedel's salt is, ideally:



with solubility constants of -27.69 [60], -24.79 to -27.1 [57], -28.8 to -27.6 [58] and -27.57 (Hobbs [61]). There is no agreement in literature which of the two binding mechanisms is dominant in cementitious systems, physical sorption (Tang and Nilsson [62]) or the chemical reaction (Henocq et al. [55]). This is because chloride binding depends on many factors such as chloride concentration, cement composition, supplementary cementitious additions, hydroxyl ion concentration, cation of chloride salt, temperature, carbonation, sulfate ion and electrical field (Yuan et al. [53]). Friedel's salt, a chloride-containing calcium aluminate hydrate, is known to play an important role as a diffusion barrier against chloride migration (Balonis et al. [60]).

Interaction of chloride with the cement phases is discussed in Ochs et al. [63]. It is important to note that the impact of the chloride cannot be evaluated without considering the impact of the associated cation. For instance, in a NaOH environment, the solubilities of portlandite and C-S-H increases with increasing NaOH concentrations up to NaOH concentrations of 0.5 mol/ℓ, but thereafter little change is found up to 1.5 mol/ℓ (Glasser et al. [64]). At low NaOH concentrations, chloride weakly sorbs as discussed above (low sorption values were reported in Wang et al. [65]).

When Cl exceeds a few millimolar, chloride is increasingly bound by an ion exchange mechanism. As chloride concentrations increase into the range of approximately 2-20

millimolal chloride, the normal sorption will be supplemented by a “spike” of chloride uptake as Cl increasingly replaces other anions (mainly OH) in the structure of the AFm - type phase. This “spike” will extend over a range of compositions because of (i) the gradual nature of the replacement, involving some re-organization of the layers (ii) the complex anion chemistry of AFm (besides chloride and sulphate, also carbonate determines the anion partition coefficient), and (iii) the presence of soluble alkalis, Na and K, which affect the equilibrium displacement processes. As mentioned above, the AFm phase is converted into a Cl-AFm phase, namely Friedel’s salt, by ion exchange reactions or precipitation/dissolution reactions (Jones et al. [66]). The formation of Friedel’s salt thus buffers the cement pore water against high Cl concentrations. However, when the buffer capacity (and sorption capacity) is depleted, Cl concentrations can go up again to several molars and new processes are anticipated. The solubility limit of NaCl can be reached with other ions influencing this limit. Most typically, solubility of NaCl decreases in presence of other ions, a phenomenon known as salting out. Also cement solid phases will be attacked by chloride (e.g. portlandite may form so-called basic halide). However, knowledge of cement behaviour (both chemically and physically) at chloride concentration at level of several molars is lacking. At these high concentrations, sodium will also react with the cement phases.

The high Cl concentration can have an effect on the sorption of radionuclides. Highly stable chloride concentrations lower the sorption of radioactive chloride (^{36}Cl [65]). Ochs et al. [63] also reported a high effect of chloride on Ag, Pb and Pd on sorption and solubility values due to stable aqueous complexes between these cations and chloride. Wang et al. [65] identified high impact on sorption of Cs, Sr and Ra due to competition with Na and effects of higher ionic strength.

2.4.2. Specific studies related to deep disposal

A large number of literatures exist concerning chloride effect on steel corrosion. However, there are fewer literatures concerning concrete degradation due to chloride in the context of deep disposal studies. Only a qualitative discussion is presented by Hoglund et al. [16], who stated that chloride can attack calcium aluminates forming calcium aluminate chlorohydrates, which 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.

They also discussed the importance of combined sulphate and chloride attack. The first attack comprises a formation of monochloro-aluminates which crystallize in the pores. If, thereafter, sulphate penetrates the concrete, the monochloro-aluminates will react with the sulphate, forming expanding ettringite. Therefore, they claimed that the 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.

Govaerts and Weetjens [67] calculations showed that peak concentrations of chloride at the overpack would not exceed 4.9 mmol/l. This is for the case where it is conservatively assumed that transport parameters for chloride through Boom Clay and the cementitious EBS are similar, and its concentration in the EDZ is set to 12 mmol/l. When they used best estimates of the model parameters, the results showed peak concentrations not exceeding 2.9 mmol/l. They additionally carried out thermodiffusion analysis of chloride and concluded that the impact of thermodiffusion is, even in the presence of severe thermal gradients, quite limited. Also it is likely that thermodiffusion could even decrease

concentrations at the overpack. Thermal osmosis, which they did not consider, will likely counteract the effect of thermodiffusion. No reactions of the aggressive species with concrete components were included in the calculations. Note however that the pore water concentration in Boom clay in Netherlands would be in the region of 540 mmol/l. Thus similar calculations would be needed to estimate the concentration of chloride for this 540 mmol/l. Such a work is currently ongoing at SCK-CEN within the GEPETO project.

2.4.3. Implications on the safety functions of the repository components

Chloride has an impact on concrete and its safety functions in three ways: (i) interaction with the cement phases, (ii) sorption of radionuclides, and (iii) initiation of corrosion. The corrosion of steel (envelope, overpack and canister) is the most critical impact. Note that Friedel's salt is similar in appearance to ettringite but do not cause any expansion (Santhanam, [68]) (refers to work of Verbeck [69]). However, a quantitative understanding of the effect of chloride on calcium aluminates warrants further study.

The impact of chloride cannot be fully assessed without also taking into account the cation associated with chloride (Wang et al. [65]). Overwhelmingly, this will be sodium. Sodium is already present in the cement before ingress of any NaCl from the surrounding and that the cement solids are saturated with respect to sodium, most of which are dissolved in the pore fluid. In its intrinsic fresh state, the cement is virtually chloride free. It does however have significant capacity to react with and combine chloride. But to maintain charge balance when NaCl becomes available, the cement replaces the chloride removed into phases such as Friedel's salt by contributing OH (hydroxide) to the aqueous phase, with the result that the pore fluid pH raises. Thus notwithstanding the fact that aqueous solutions of NaCl are neutral, in the presence of cement solids NaCl elevates the pH. This has in general the effect of prolonging the State I (dominated by Na and K release) conditions and delaying the passage of the cement to State II (portlandite dissolution phase). It also (i) has the impact of somewhat mitigating chloride complexation because of increased competition from [OH], (ii) of altering the solubility of other cement components, for example, sulphate, which may affect sorption and finally (iii) by changing the ionic strength of the solution and hence species solubility. Of course these effects do not occur singly, nor can they necessarily be isolated for separate study even in the laboratory. At present there is insufficient knowledge to decide how these effects couple.

Table 4 summarizes potential implications on the safety functions of the repository components.

Table 4 **Potential implications on the safety functions of the repository components related to chloride ingress**

<i>Post closure safety functions in system containment phase</i>	<i>Component and / or barrier</i>	<i>Implication processes identified in cement degradation</i>		
		Concrete buffer (HLW)/Container backfill (LILW & TE(NORM)) CEM I/CEM III	Concrete Backfill (CEM I+Foam)	Concrete Liner (CEM II)
Limitation of contaminant release	Waste form (dissolution property)	Cl does not give rise to any cement degradation product that affects the safety function. It only affects the corrosion rate of the waste package, which in turn allows high pH pore fluid to come in contact with the waste form thus making it unstable.		
Limitation of water flow through the system	Boom Clay			
Retardation and spreading in time of contaminant migration	Boom Clay			

2.5. Interaction with waste form

2.5.1. Process description

Concrete degradation may also occur due to the interaction with corrosion products from the waste form itself. The alteration of (nuclear waste) glass in contact with water involves several serial and parallel processes. The most important processes are the following (e.g. Gin [70]):

- Selective release of the soluble glass components (water diffusion, ion exchange)
- Hydrolysis of the glass matrix
- Gel formation and evolution
- Silica saturation of the solution
- Precipitation of secondary phases
- Retention of radionuclides in gel and secondary phases
- Removal of Si from the solution by advection, diffusion or sorption

At neutral pH, these processes cause fast initial dissolution, followed by the formation of a protective alteration layer and a strong decrease of the dissolution rate, as shown in Figure 2-1.

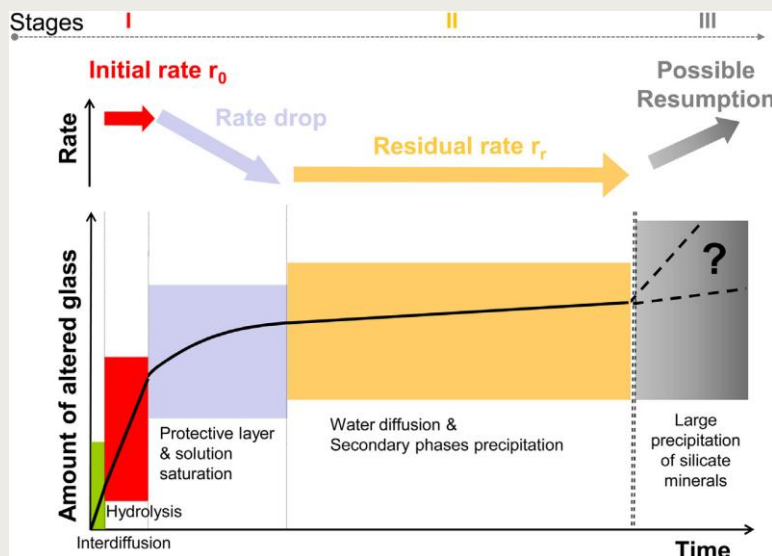


Figure 2-1 Stages of nuclear glass corrosion and related potential rate-limiting mechanisms. The duration of each stage depends on glass composition and leaching conditions (temperature, pH, composition, renewal rate of the solution, etc.) (Gin [70]).

All of these processes are influenced by the high pH and typical cement pore water composition. Selective leaching tends to become relatively less important at high pH (Ojovan [71], Chave [72]). The hydrolysis of the silica network is accelerated by the high pH (Iler [73], Boksay [74], Ferrand [75]). The gel tends to be less dense and less protective than at lower pH (Gin [76], Ferrand [77]). The glass solubility increases at high pH because of the changing silica speciation (e.g. Utton [78]). The high pH allows the precipitation of secondary phases that are not stable at lower pH, and that triggers the glass dissolution (e.g. Fournier [79]).

In a system with little transport limitations between the pristine glass surface and the concrete, the glass dissolution will be triggered mainly by the reaction of the glass with the concrete phases (Ferrand [77]). The main mechanisms according to which the glass

interacts with the cement are (i) the reaction of Si released from the glass with portlandite to form C-S-H (pozzolanic reaction) (Atkins [80]; Taylor [81]), (ii) the reaction of the Al released from the glass with the C-S-H phases to form C-A-S-H phases (e.g. Blanc [82]), (iii) the further enrichment of the C-S-H phases with Si (e.g. Hou [83]), and (iv) the formation of an A-S-R gel (Hou [83]).

These mechanisms can temporarily trigger the glass dissolution at a rate close to the maximum initial rate (Stage I in Figure 2-1). As a result of the formation of alteration layers at the interface between the glass and concrete, the distance between the pristine glass surface and the unreacted concrete will increase, and this is expected to decrease the dissolution rate. As long as the pH remains higher than about 11.5 (depending on the temperature) (Gin [76]), the dissolution rate will remain relatively high or there is a risk for a corrosion resumption, even after a (temporary) rate decrease (stage III in Figure 2-1).

The glass dissolution itself will, however, lead to a local pH decrease. This may finally lower the glass alteration layer. The high Ca concentrations in portlandite cement water may have a favorable role by forming a passivating layer, but an unfavorable role when the continued Ca supply triggers the pozzolanic reaction (Mercado-Depierre [84]). The net effect depends on the glass surface to volume ratio and hence the relative supply in Ca and Si. The precise effects of the high pH cement water or concrete on the glass alteration depends on the glass composition, so it cannot be generalized from one glass to another.

2.5.2. Specific studies related to deep disposal

One can also expect that the C-S-H formation will decrease the porosity of the concrete close to the glass, but these effects need to be confirmed experimentally. Such an exercise is currently ongoing at SCK-CEN.

2.5.3. Implications on the safety functions of the repository components

The aforementioned reactions (section 2.5.1) of the glass with the concrete will accelerate the evolution of the concrete from 'young' to 'old' concrete, because the pozzolanic reaction transforms portlandite into C-S-H phases, and the alkalines in solution (K, Na) are extracted from the solution by the formation of secondary phases. So it can be expected that the pH of the reacting concrete buffer will decrease faster than it would without the reaction with the glass.

Table 5 summarizes potential implications on the safety functions of the repository components.

Table 5 **Potential implications on the safety functions of the repository components related to waste form**

<i>Post closure safety functions in system containment phase</i>	<i>Component and / or barrier</i>	<i>Implication processes identified in cement degradation</i>		
		Concrete buffer (HLW)/Container backfill (LILW & TE(NORM)) CEM I/CEM III	Concrete Backfill (CEM I+Foam)	Concrete Liner (CEM II)
Limitation of contaminant release	Waste form (dissolution property)	High pH will negatively affect the rate of dissolution of waste form as detailed in section 2.5.1, i.e. the seven processes listed. Note that high pH state itself is not a cement degradation process as it is a design requirement.		
Limitation of water flow through the system	Boom Clay	Not known.		
Retardation and spreading in time of contaminant migration	Boom Clay	Not known.		

3. Mechanical degradation processes of the cementitious EBS components and their implications on safety functions

In general, mechanical degradation of concrete results in loss of strength and cracking, thus affecting its service life. The main impact being loss of physical containment, thus forming preferential pathways for water flow and chemical transport. It is well acknowledged that physical, chemical, thermal and structural factors are the principal causes of mechanical degradation.

In the context of deep geological disposal, there is limited data on the mechanical behaviour of concrete. Only some numerical estimates due to restraints and imposed loads can be found in the work related to UK Nirex Reference Vault Backfill (NRVB) for low and intermediate level waste (Swift et al. [85]). However, the design of the NRVB is entirely different from that of the OPERA disposal concept, although the processes causing cracking should be similar.

In fact, there is not much data either on the long term behaviour of deeply buried concrete in general. Nevertheless, an attempt is made here to describe the potential mechanical degradation processes relevant to deep geological conditions and their possible implications to the safety functions of the repository components. Note that the concrete components are fully confined and subjected to a confining pressure equal to the overburden pressure of the host rock (appx. 10 MPa at 500 m depth [3]). This essentially means that there will be no free expansion of concrete components unless there are voids created during the construction process.

It is to be borne in mind that OPERA safety concept does not attribute any mechanical safety functions to the cementitious barriers for the post-closure safety. Thus the main purpose of the literature review presented in this section is to examine the potential consequences of mechanical degradation of cementitious components on the safety functions of other components of the repository.

Mechanical degradation occurs before and after hardening, all of which can lead to cracking. The aim of this report is to particularly capture the long term mechanical degradation processes, i.e. mainly the behaviour under in situ conditions. Thus, the following degradation processes are seen as relevant to the deep geological disposal:

- f) Decalcification and leaching
- g) Carbonation
- h) Sulphate attack
- i) Corrosion induced cracking
- j) Freeze-thaw
- k) Long term temperature variation
- l) Creep

Whilst processes such as decalcification or carbonation will lead to loss or gain in compressive strength, respectively, processes such as sulphate attack, corrosion, freeze-thaw, etc. may lead to cracking due to tensile stresses exceeding the tensile strength of the cementitious components.

3.1. Mechanical consequences of decalcification and leaching

3.1.1. Process description

Decalcification leads to a loss of material, increase in porosity and consequently a decrease in Young's modulus and compressive strength of the material, in addition to change in stress-strain behaviour compared to a sound material. It can also initiate decalcification shrinkage leading to microcracks.

As elucidated by Mehta and Monteiro [86], in general, there exists a fundamental inverse relationship between porosity and strength of solids and can be typically related through a power function. Whereas in hardened cement paste or mortar the porosity can be related to strength, with concrete the situation is not simple. The presence of microcracks in the interfacial transition zone (ITZ) between the coarse aggregate and the matrix makes concrete a complex material for prediction of strength by precise strength porosity relations.

Huang and Qian [87] obtained experimental mean compressive stress - mean axial strain curves of a leached concrete with different degradation degrees. The leaching showed a remarkable effect on the stress-strain behaviour with decrease in modulus and peak strength as the degree of leaching increases.

Xie et al. [88] similarly found that mechanical responses are strongly affected by leaching degradation, in particular, the failure stress, the plastic yield stress in deviatoric shearing and the pore collapse yield stress are drastically reduced in a completely degraded cement paste (based on an uncoupled chemical and mechanical test).

Heukamp et al. [89] demonstrated through triaxial tests of leached mortar specimens that leaching leads to a global strength loss due to chemical decohesion along with an important loss of frictional performance. Environmental scanning electron microscope (ESEM) pictures of both leached and unleached material suggested that this loss of frictional performance can be associated with a highly eroded microstructure due to the leaching. In addition, the frictional behavior of leached cement pastes is found to be strongly dependent on the drainage conditions of the material and thus, on the interstitial pore pressure. Through a poromechanical analysis, it was shown that this high pore pressure sensitivity of leached cement paste can be attributed to the low skeleton-to-fluid bulk modulus ratio of the degraded material, which, together with the increase in porosity, leads to the high compressibility of calcium-leached materials. This low ratio is the consequence of an intrinsic chemical damage of the solid skeleton, which occurs during calcium leaching. Heukamp et al. [89] highlighted that this pressure sensitivity should be considered in design and operation of cementitious components in nuclear waste storage, as many possible stress situations may occur under almost undrained conditions.

In yet another related study, Heukamp et al. [90] demonstrate that low C/S ratio caused by leaching of cement paste leads to high plastic deformation and reduced cohesion. In the case of mortars, a competition between plastic behaviour and porosity controlled structural deformation takes place.

Experimental work of Phung [91], Rougelot et al. [92] and Chen et al. [93] have evidenced the existence of decalcification shrinkage leading to microcracking particularly around rigid aggregates. Chen et al. [93] propose that leaching of C-S-H essentially induces polymerization shrinkage, especially in the region where Ca/Si ratio is lower than 1.2. Because leaching also induces a significant loss of mechanical properties, the decalcification shrinkage could generate tensile stresses surrounding rigid particles (e.g.

limestone fillers, unhydrated cements), which results in cracking. According to [93] and [91], the decalcification shrinkage also can generate differential stresses in the region where there exists a gradient of Ca/Si ratio. Rougelot et al. [92] showed through numerical simulations the occurrences of high plastic strains around rounded glass aggregates, which prevented free strains of the matrix, due to the shrinkage. According to [91], the leaching of Ca and other leachable elements creates connected pathways, which can increase the percolation of the pore system and as a result, transport properties can be enhanced.

A number of complex chemo-mechanical models exist that can be used to evaluate the mechanical stability of cementitious components (e.g. Gerard et al. [94]; Bary [95]; Heukamp et al. [89]). The simplest approach is that taken by Walton et al. [96] who incorporated the effect of leaching by assuming that the concrete loses half its strength when 33% of calcium hydroxide has been depleted based on Lea [97]. Atkinson and Hearne [98] simply assume the concrete fails when one third of the calcium (not calcium hydroxide) in a layer is depleted.

3.1.2. Specific studies related to deep disposal

ANDRA, the French waste management agency considered possible scenarios under which deep disposal concrete tunnels (at 500 m underground in Callovo Oxfordian clay) stability had to be demonstrated. These scenarios combine water saturation of the tunnel, leaching of the concrete structure and ground convergence towards the tunnel (Sellier et al. [99]). Sellier et al. [99] studied via numerical modelling the effect of simultaneous leaching and ground convergence. Calculations showed that the leached concrete was able to absorb the ground displacement without too much damage. They attributed this to the leached concrete having a large volumetric strain capability due to its increased porosity, so it can absorb a large part of the ground movement and consequently avoid the sound concrete being overloaded. This beneficial effect of leaching is temporary; when the leached zone reaches the internal surface of the tunnel between 75,000 and 103,000 years damage appears in this zone. They concluded on the basis of the first simulations, the high performance concrete disposal structures present good stability for several thousand years.

3.1.3. Implications on the safety functions of the repository components

As stated in section 2.1, decalcification and leaching by pure diffusion is a very slow process controlled by low permeability and diffusivity of cementitious components and the host clay. As such this process cannot be avoided. The design choice to have cementitious backfilling around the steel envelope serves to minimize convergence due to creep, in addition to the ability of leached concrete to absorb creep convergence. Moreover, it is to be borne in mind that the disposal system is completely confined unlike tunnels which are exposed on the interior surface.

It is recommended that leaching-damage study is undertaken similar to the work of Sellier et al. [99] for the OPERA concept. Table 6 summarizes potential implications on the safety functions of the repository components.

Table 6 Potential implications on the safety functions of the repository components related to mechanical consequences of decalcification and leaching

<i>Post closure safety functions in system containment phase</i>	<i>Component and / or barrier</i>	<i>Implication processes identified in cement degradation</i>		
		Concrete buffer (HLW)/Container backfill (LILW & TE(NORM)) CEM I/CEM III	Concrete Backfill (CEM I+Foam)	Concrete Liner (CEM II)
Limitation of contaminant release	Waste form (dissolution property)	Loss of compressive strength due to leaching resulting in possibly some cracking and thus preferential flow paths that may affect the dissolution rate of waste forms. Very long term process (>> 10,000 years) because of slow dissolution of cement. In HLW, this will accelerate the transport of chlorides and sulphates towards the overpack, which can accelerate corrosion of the overpack and thus expose the vitrified waste form to a high pH environment (detrimental).		
Limitation of water flow through the system	Boom Clay			
Retardation and spreading in time of contaminant migration	Boom Clay	Same as above, but will accelerate the transport of cementitious pore water from the EBS towards the clay. However, the effect is limited to the nearfield thus affecting sorption in the nearfield - positive or negative is radionuclide specific. Self-sealing capacity of the Boom Clay may be affected due to mineralogical transformation. However, the radial extent of the perturbed zone will be limited and in fact governed by the extent of calcium ingress into the Boom Clay.		

3.2. Mechanical consequences of carbonation

3.2.1. Process description

Carbonation leads to an increase of density, compressive strength, modulus of elasticity and shrinkage (e.g. Chang et al. [100]; Jerga [101]). In general, about 5 to 10% increase in the compressive strength was found for atmospheric CO₂ concentration (Jerga [101]). Jerga [101] also found that carbonation not only led to an increase of strength, strain of the peak compressive stress and the initial tangent modulus of elasticity, but also on the shape of the stress-strain diagram. The ascending branch of the stress-strain diagram could be characterized by brittleness and plasticity coefficients. The descending branch of the stress-strain diagram indicated the potential brittle failure of carbonated concrete. Because of restraints preventing the concrete from contracting freely, surface cracking would be developed as a result of the shrinkage.

3.2.2. Specific studies related to deep disposal

As such there are no data available for the mechanical consequences of carbonation under saturated conditions. However, data relevant to atmospheric carbonation for exposed concrete under deep geological conditions are available. This is relevant for concrete wedge blocks (liners) and other components exposed during the operational phase.

In the context of French management of Intermediate-Level Long-lived radioactive Waste (ILLW), Thouvenot et al. [102] carried out simulations of atmospheric carbonation of ILLW concrete packages having a wall thickness of 11 cm. The calculations showed that the wall fully equilibrated with the ambient conditions (40% relative humidity (RH)) within 2 to 10 years. However, a carbonation depth of only 2 cm was predicted for 100 years. The initial degree of saturation of concrete was assumed to be 0.8.

Swift et al. [85] reported a difference of about 600 microstrain between carbonated and non carbonated samples. The experiments they cited were based on simultaneous drying and carbonation, compared with the shrinkage of non-carbonated samples. This was stated to be rather conservative because 4% concentration of CO₂ was used in their experiments, which is too high to be applicable at larger depths. They commented that at the top surface of the backfill carbonation would not be expected to exceed about 10 mm in the first 50 years of exposure, and at higher humidity the rate of carbonation would be much less. They suggest that carbonation is not expected to contribute to the development of cracking in a vault with a 16 × 16 m cross section, as the period of drying before resaturation is expected to be relatively short and any effect will only occur close to the exposed surface.

3.2.3. Implications on the safety functions of the repository components

The depth of atmospheric carbonation depends upon various factors such as RH, initial moisture conditions and properties of concrete. For instance, in Mol HADES laboratory, recent RH data shows an average of 30%. Even if the exposed concrete components completely equilibrate with this RH during the operational phase, atmospheric carbonation would still be low because of low water content available at such RH. The critical range of RH for carbonation is between 50 and 65%. If carbonation cracks are formed on the exposed surfaces of concrete liners, then the depth of penetration could be higher.

Once the repository is closed and the system resaturates, carbonation is still possible but likely to be slower than atmospheric carbonation. Therefore, the initial mechanical properties of concrete are less likely to evolve significantly in the long term. Note that under saturated conditions, carbonation is triggered mainly by the carbon content in the Boom Clay pore water. Once the process triggers at the concrete/clay interface, the

porosity is likely to reduce, probably leading to pore clogging. If this happens, the carbonation front is retarded. Note that complete pore clogging may not happen under in situ conditions because of spatial heterogeneity.

Table 7 summarizes potential implications on the safety functions of the repository components.

Table 7 **Potential implications on the safety functions of the repository components related to mechanical consequences of carbonation**

<i>Post closure safety functions in system containment phase</i>	<i>Component and / or barrier</i>	<i>Implication processes identified in cement degradation</i>		
		Concrete buffer (HLW)/Container backfill (LILW & TE(NORM)) CEM I/CEM III	Concrete Backfill (CEM I+Foam)	Concrete Liner (CEM II)
Limitation of contaminant release	Waste form (dissolution property)	Embrittlement and increase in strength up to carbonation depth, but carbonation rate is hindered because of pore clogging limiting the transport of carbonated water under saturated conditions. Beneficial for minimizing corrosion of steel, thus limited contact with the HLW waste form.	Not known.	Same as concrete buffer/container backfill.
Limitation of water flow through the system	Boom Clay			
Retardation and spreading in time of contaminant migration	Boom Clay			

3.3. Mechanical consequences of sulphate attack

3.3.1. Process description

As described in section 0, three types of sulphate attack (DEF, ESA, TSA) are identified all of which will result in expansive forces due to the formation of ettringite or thaumasite. The expansive forces could be directly caused due to anisotropic growth of crystals or indirectly by increasing the pore water pressure giving rise to internal stresses that might ultimately, in specific instances, destroy the concrete or mortar [103]. It is found that the stresses caused by thaumasite formation are not significant, however, thaumasite is a non-binder (which replaces part of the C-S-H binder), which is even more critical than the stresses generated. The stresses and debonding can both result in the formation of macrocracks. Experimental evidences from samples exposed to sulphate suggest a random crack pattern with visible macrocracks and almost disintegrated specimens.

3.3.2. Specific studies related to deep disposal

There is only one study concerning Nirex Reference Vault Backfill (NRVB) that addresses the issue of sulphate attack in the context of deep disposal. Exposure of two well-aged NRVB samples to a 0.1 mol/dm^3 solution of sodium sulphate produced a 1% weight gain over a period of five months (Crossland [104]). Both specimens (25 mm cross-section) remained intact. The increase in the dimensions of the two samples was variable: one produced a volume increase of 0.19% and the other 0.02% (620 and 80 linear microstrain, respectively). It is suggested that the additional volume of new mineral phases had been accommodated within the NRVB porosity. A sulphate concentration of 0.1 mol/dm^3 is significantly higher than levels commonly found in groundwater so it was argued that the internal strain produced by sulphate attack within the NRVB is low enough to avoid cracking. This is probably because its high porosity provides voidage into which the new minerals can expand; a likely consequence of this is that sulphate reactions with the NRVB will probably lead to a reduction in permeability. However, note that Foam concrete has been the suggested material for OPERA backfill material, which is CEM I based and with a much higher porosity (0.43-45) compared to NRVB (0.2-0.3).

3.3.3. Implications on the safety functions of the repository components

Table 8 summarizes potential implications on the safety functions of the repository components.

Table 8 Potential implications on the safety functions of the repository components related to mechanical consequences of sulphate attack

<i>Post closure safety functions in system containment phase</i>	<i>Component and / or barrier</i>	<i>Implication processes identified in cement degradation</i>		
		Concrete buffer (HLW)/Container backfill (LILW & TE(NORM)) CEM I/CEM III	Concrete Backfill (CEM I+Foam)	Concrete Liner (CEM II)
Limitation of contaminant release	Waste form (dissolution property)	No quantitative information available, but cracking may occur if sulphates that reach the buffer/backfill via the pores or preferential pathways react to form ettringite or gypsum. Requires site specific quantitative study to confirm. Note that this will be a very long term process as the transport of sulphates is diffusion driven, except for the fraction that may ingress with the resaturation water soon after backfilling. The effect on the waste form is indirect in the sense that sulphate induced corrosion of overpack will expose the vitrified waste to high pH environment. For cemented wastes, dissolution rate may also be affected due to the diffusion of deleterious substances from the Boom Clay.	No information is available.	See Table 3.
Limitation of water flow through the system	Boom Clay			
Retardation and spreading in time of contaminant migration	Boom Clay	Sulphate cracking can enhance transport of cementitious water into the clay affecting its sorption capacity, but limited in diffusive system.		

3.4. Corrosion induced cracking (mainly for supercontainers)

3.4.1. Process description

Concrete provides a highly alkaline chemical environment that leads to the formation of a thin but dense and impenetrable oxide/hydroxide layer (the so-called 'passive' film) on the surface of the steel that will protect the underlying metal, which in turn will result in very low and almost negligible uniform corrosion rates (i.e. passive dissolution).

If local breakdown of the passive film occurs (by e.g. carbonation, ingress of aggressive species such as Cl^- , etc.), corrosion products may form at the steel/concrete interface. Because corrosion products occupy a higher volume than the original steel (Broomfield [105]), they will induce mechanical forces (expansive stresses) on to the surrounding concrete, which, eventually, can result in cracking of the concrete layer. These cracks in turn provide a pathway for the rapid ingress of aggressive agents to the steel surface, which can accelerate the corrosion process.

The formation of a thick layer of expansive corrosion products that could pose a potential threat to the mechanical integrity of the concrete buffer is linked to the corrosion of the carbon steel overpack under active conditions (availability of O_2 , CO_2 , etc.). However, in a repository facility constructed in a deep geological clay formation, the environmental conditions are expected to evolve rather rapidly to anaerobic conditions. Under these reducing conditions, corrosion rates are predicted to be very low ($\leq 0.1 \mu\text{m}/\text{year}$) (Kurstien et al. [106]) and the formation of corrosion products will be rather limited.

Another serious consequence of corrosion is the release of hydrogen gas because of corrosion of the metallic waste, which is in large volume. If the (expansive) gas pressure exceeds the tensile strength of the surrounding concrete under the confining (overburden) pressure, local cracks can develop. Whether or not the resultant cracks form continuous or discrete pathways depends upon the existing cracks and involves great deal of complexity.

3.4.2. Specific studies related to deep disposal

In the Belgian disposal programme, experimental and modelling studies are currently ongoing, under the supervision of NIRAS/ONDRAF, to estimate the long-term build-up of these corrosion products (over a timescale of 100,000 years). The results of this study will become available in due course of time.

Li and Weetjens [107] performed exploratory calculations to evaluate whether the diffusive removal capacity of gas through Boom Clay would be sufficient or not to evacuate the gas generated by different waste classes and engineered barrier system (EBS) materials. Results show that diffusive removal is expected to be sufficient to evacuate all the gas produced in vitrified HLW and spent fuel (SF) disposal galleries, while the occurrence of a pressurized gas phase in the repository cannot be ruled out for Eurobitum and CSD-C. As the formation of a free gas phase in the near field cannot entirely be ruled out for B-wastes, they argue that the possible gas-induced perturbations should be evaluated and the potential for significant effects on the functioning and performance of the disposal system should be assessed. The main concern from the point of view of mechanical degradation of cementitious components is whether or not the resultant gas pressures are high enough to exceed the tensile strength of the material, and thus form preferential pathways for RNs transport given that there is also an overburden pressure of 10 MPa.

3.4.3. Implications on the safety functions of the repository components

It appears that corrosion induced cracking of the concrete buffer cannot be ruled out during the life time of the repository. However, for the aggressive substance to reach the

overpack, first of all the steel envelope should become perforated (also via corrosion), followed by a slow diffusion of the substance from the Boom Clay towards the overpack after negotiating through the concrete liner, backfill and buffer. And once in contact, the corrosion rate itself anticipated to be too low, the physical impact (i.e. cracking) on the concrete buffer would be a very long term process. Site specific quantitative assessment is needed to quantify the time and extent of impact.

Note that the 6 mm steel envelope is mainly prone to pitting corrosion and the volume of corrosion products would not be sufficient to cause cracking through the entire thickness of the backfill. There may be some local cracking at the envelope/backfill interface. The cementitious backfill is designed porous enough for gas migration; there exist gaps between the wedge blocks in the concrete liner, which allow gas to dissipate.

Therefore, the main consequence of the cracked buffer is that it may allow faster travel of deleterious substances that may promote increase in corrosion rate, which in turn may expose the waste form to the high pH environment. Table 9 summarizes potential implications on the safety functions of the repository components.

Table 9 Potential implications on the safety functions of the repository components related to related to mechanical consequences of corrosion induced cracking (mainly for supercontainers)

<i>Post closure safety functions in system containment phase</i>	<i>Component and / or barrier</i>	<i>Implication processes identified in cement degradation</i>		
		Concrete buffer (HLW)/Container backfill (LILW & TE(NORM)) CEM I/CEM III	Concrete Backfill (CEM I+Foam)	Concrete Liner (CEM II)
Limitation of contaminant release	Waste form (dissolution property)	Cracked buffer allows faster travel of deleterious substances that may promote increase in corrosion rate, which in turn may expose the vitrified waste to the high pH environment.		
Limitation of water flow through the system	Boom Clay			
Retardation and spreading in time of contaminant migration	Boom Clay			

3.5. Mechanical consequences of freeze-thaw process

3.5.1. Process description

Under freezing conditions, a portion of pore water in the cementitious matrix or the moisture in absorbent aggregates may cause deleterious expansion (Page and Page [103]). This is due to ice formation process, during which water expands by approximately 9% of its volume (Kaufman [108]). Expansion that can be accommodated is not a problem but restraint of movement will give rise to tensile stresses. The induced stresses may exceed the material's tensile capacity leading to cracking (Page and Page [103]).

Several factors influence the mechanical behaviour of the matrix: (i) the number of temperature cycles (climatic conditions) is more significant than the absolute lowest temperature (Fagerlund [109]), (ii) higher the w/c ratio, higher the tendency for cracking due to higher amount of water available to expand (Fagerlund [109]), (iii) unsaturated matrix has lesser tendency for cracking as air pockets serve to absorb expansion of water (Litvan [110]), (iv) greater the freezing rate greater is the tendency for cracking, especially when the material is saturated and also when spacing factor of air voids and porosity are higher.

Other important factors that govern the deleterious freeze-thaw process are permeability, aggregate characteristics, amount of entrained air and pore salinity (higher the salinity higher the excess pore pressure due to counter osmotic force).

The data reported in the literature indicate that most, if not all, types of cement commonly used do not behave differently with respect to freeze/thaw phenomena (for the same concrete quality) (Neville [111]). Frost action is therefore not a determining factor in the choice of the cement. However, the resistance of the concrete to freeze-thaw cycling should be tested for the specific concrete to be used.

An approach to evaluate durability indicator exists which is based on ASTM test methods, however, they are more intended to compare the behaviour of different types of concrete (Walton et al. [96]). Note that it is not straightforward to extrapolate laboratory test results to field conditions as the conditions of the tests are not the same as in reality, e.g. laboratory tests are typically carried out in fully saturated conditions whereas during fabrication, installation and long term operation the material can remain in partially saturated state. Also there are several empirical and numerical models to predict cracking tendency as discussed in Walton et al. [96].

3.5.2. Specific studies related to deep disposal

There are fewer literatures that specifically address freeze-thaw effects under deep disposal conditions. A study by Luping et al. [112] on the Swedish final repository for short-lived low and intermediate level radioactive waste suggested that it is hardly possible that there will be a structural collapse due to the reduction in tensile strength in concrete containers filled inside with grout after filling of nuclear waste, unless the steel reinforcement in the reinforced concrete structure is designed with significantly less amount of steel bars and there exists large unfilled volume under the concrete roof. This was based on freeze-thaw calculations in the temperature range 0 to -10°C.

3.5.3. Implications on the safety functions of the repository components

It is reasonable to state that the freeze-thaw effect is more relevant during construction and storage of concrete wedge blocks above ground as strong seasonal variations in temperature would exist. Thus through proper choice of materials and construction and

storage conditions the effect could be minimised. As far as in situ conditions are concerned, based on a recent work by Govaerts et al. [113] for the Mol region, the permafrost front hardly reaches a depth of 200 m for the next realistic glacial cycle (Weichselian glaciations). Therefore, cracking may be less likely, more so under confined condition.

Table 10 summarizes potential implications on the safety functions of the repository components.

Table 10 **Potential implications on the safety functions of the repository components related to mechanical consequences of freeze-thaw process**

<i>Post closure safety functions in system containment phase</i>	<i>Component and / or barrier</i>	<i>Implication processes identified in cement degradation</i>		
		Concrete buffer (HLW)/Container backfill (LILW & TE(NORM)) CEM I/CEM III	Concrete Backfill (CEM I+Foam)	Concrete Liner (CEM II)
Limitation of contaminant release	Waste form (dissolution property)	Usually, severe freeze-thaw cycles will not occur below ground. Therefore, cracking due to this process is less likely at such depths, even during construction phase. After construction, only unusual climatic conditions such as permafrost can influence cracking due to freezing. If cracking is possible, then it may bring deleterious substances in contact with the overpack promoting corrosion and in turn exposing vitrified waste to the high pH environment. For cemented wastes, dissolution rate may also be affected due to the diffusion of deleterious substances from the Boom Clay.		
Limitation of water flow through the system	Boom Clay			
Retardation and spreading in time of contaminant migration	Boom Clay	Same as above, except that in the event of cracking the rate of alkaline plume through the clay may slightly increase due to additional contact of Boom Clay pore water with the cracked cementitious material. The alkalinity of the clay will affect sorption of radionuclides.		

3.6. Mechanical consequences of long term temperature variation

3.6.1. Process description

Variations in the ambient conditions at the outer surface of cementitious components are inevitable and bring about changes in temperature as well as humidity. This is mainly the case during the construction phase and has the same effect as drying shrinkage. On the other hand, after emplacement the concrete is exposed to heat released from the waste package. This will give rise to thermo-hydraulic gradients in the EBS components and there may be a temporary phase of desaturation adjacent to the overpack, i.e. in the backfill. Especially, in the concrete buffer, any rise in temperature can lead to thermal expansion of water creating expansive forces within the envelope.

3.6.2. Specific studies related to deep disposal

Currently, no information is available concerning the stress evolution in the buffer due to thermo-hydraulic gradient to assess the cracking tendency of the cementitious components.

There is one study in the context of UK NRVB (Swift et al. [85]) that pertain to long term thermal contraction of the backfill. In their study, the thermal phase is mainly associated with heat of hydration and not heat emitting waste. They calculated a free contraction of 95 microstrain at an average rate of only two microstrain per year based on the coefficient of thermal expansion of the backfill material and calculated temperature drop after waste emplacement. They suggested that this magnitude of contraction would be unlikely to cause cracking if there were no other strains. Moreover, they argued that the backfill will creep, and over a long period as much as 60% of the restrained strain may be relieved by creep. In addition, the waste packages adjacent to the backfill will also be contracting and hence this additional strain was also considered in their calculations, which suggested that the restrained-strain will approach, but not exceed, the strain capacity of the backfill over the initial 50 years from backfilling. They therefore concluded that the long-term thermal contraction of the backfill is considered to be minimal. However, due to uncertainties they expect a very small risk of a gap opening of 0.1 mm.

3.6.3. Implications on the safety functions of the repository components

Recall that according to the OPERA safety concept the buffer has no safety function but provides confidence in the prediction of post-closure safety by design criteria.

Impact of cold environment is discussed in section 0. As far high temperature effects are concerned, calculations specific to OPERA concept and material is necessary to predict the magnitude of tensile stresses in the cementitious components during the thermal (both heating and cooling) phase and hence to comment on its implication. Such calculations have been performed within the framework of GEPETO by SCK-CEN (see WP 5.1.3 deliverables for temperature data) Appreciable tensile stresses within the cementitious components cannot be ruled out.

Table 11 summarizes the potential implications on the safety functions of the repository components.

Table 11 Potential implications on the safety functions of the repository components related to mechanical consequences of long term temperature variation

<i>Post closure safety functions in system containment phase</i>	<i>Component and / or barrier</i>	<i>Implication processes identified in cement degradation</i>		
		Concrete buffer (HLW)/Container backfill (LILW & TE(NORM)) CEM I/CEM III	Concrete Backfill (CEM I+Foam)	Concrete Liner (CEM II)
Limitation of contaminant release	Waste form (dissolution property)	Potential for tensile cracking during the thermal phase. This may potentially enhance corrosion of the overpack, which in turn may expose vitrified waste to the high pH environment.		
Limitation of water flow through the system	Boom Clay			
Retardation and spreading in time of contaminant migration	Boom Clay	Same as above, except that in the event of cracking the rate of alkaline plume through the clay may slightly increase due to additional contact of Boom Clay pore water with the cracked cementitious material. The alkalinity of the clay will affect sorption of radionuclides.		

3.7. Mechanical consequences of long term creep

3.7.1. Process description

In general, creep affects strains and deflections and often also stress distribution. Creep reduces internal stresses due to non-uniform shrinkage, so that there is a reduction in cracking. Thus the effect is beneficial. In mass concrete, creep in itself may be a cause of cracking when a restrained concrete mass undergoes a cycle of temperature change due to the development of the heat of hydration and subsequent cooling. Concrete can suffer a time-dependent failure, which is known as creep rupture or static fatigue (Page and Page [103]). Al-Kubaisy and Young [114] performed a series of tests under sustained tension at high stress-strength ratio (from 0.6 to 0.95). They observed that cracks grow in cement matrix with time and eventually macroscopic cracks are formed which bridge the interfacial cracks and produce failure. In the case of concrete, the stress needs to exceed approximately 0.6 to 0.8 of the short term strength for creep rupture to occur in either compression or tension. However, considering the OPERA concept, the maximum overburden pressure (10 MPa), which will be experienced by the cementitious components at 400 m depth is not more than 20% of the short term strength of concrete.

Creep is generally thought to approach a limiting value as the time after first loading approaches infinity. About 50 per cent of the final creep develops in the first 2-3 months and about 90 per cent after 2-3 years. After several years under load, the rate of change of creep with time is very small (Gilbert and Ranzi [115]). Therefore, the influence of creep (coupled with shrinkage) on cracking during the early stages of material evolution is important.

Although it is found that the change of creep with time becomes very small, the long term chemical degradation of concrete, specifically leaching, also influences the creep behaviour because of the reduced strength of concrete. According to Torrenti et al. [116] and Larrard et al. [117], under high stress levels, tertiary creep can develop leading to creep ruptures.

3.7.2. Specific studies related to deep disposal

To the author's knowledge, there are no studies available.

3.7.3. Implications on the safety functions of the repository components

Leaching is a very slow process taking several tens of thousands of years for it to penetrate several centimeters, assuming there are no preferential pathways. Moreover, as stated earlier, the applied stress levels on the cementitious components are not that high (10 MPa). Table 12 summarizes potential implications on the safety functions of the repository components.

Table 12 **Potential implications on the safety functions of the repository components related to mechanical consequences of long term creep**

<i>Post closure safety functions in system containment phase</i>	<i>Component and / or barrier</i>	<i>Implication processes identified in cement degradation</i>		
		Concrete buffer (HLW)/Container backfill (LILW & TE(NORM)) CEM I/CEM III	Concrete Backfill (CEM I+Foam)	Concrete Liner (CEM II)
Limitation of contaminant release	Waste form (dissolution property)	No data available to comment. Very long term process.		
Limitation of water flow through the system	Boom Clay			
Retardation and spreading in time of contaminant migration	Boom Clay			

4. Retrievability

With the exception of sulphate attack and atmospheric carbonation, most of the processes discussed within this report are very long term processes and may not have any adverse impact in the time frame considered for retrievability. Sulphate attack of concrete liners is suggested as being a potential concern mainly because of high sulphate content in the native pore water and due to the sulphate that may be released from pyrite oxidation, especially before backfilling due to the availability of oxygen. The potential for ettringite or gypsum formation under the given geochemical conditions of the repository needs to be closely examined. In this respect, Chapter 5 briefly touches upon the role of sulphate content based on some preliminary geochemical calculations. Note that atmospheric carbonation can lead to carbonation shrinkage cracking but mainly on the outer surface. The coupled impact of sulphate attack and carbonation is not known.

5. Models for major cement degradation processes

This chapter mainly presents a geochemical modelling approach to explore the concrete chemistry under deep geological conditions. Though not within the scope of this work package, an additional step is taken in carrying out preliminary geochemical calculations, including pertinent uncertainty analyses to gain a first level understanding of the chemical degradation processes of concrete. Also included are some simplified mathematical models, which are capable of exploring the chemo-mechanical behaviour associated with decalcification and sulphate attack.

5.1. Geochemical model for decalcification and leaching, carbonation and sulphate attack

The most advanced approach for modelling the decalcification of cementitious materials is within the framework of a thermodynamic geochemical modelling. This approach is based on calculating thermodynamic equilibrium between aquatic species and cement hydrates. For example, refer to Lothenbach [118] for a description of the approach and Jacques et al. [119] for applications in the context of long term safety assessment for near surface disposal. Following an approach in which cement-equilibrated pore water is sequentially replenished with a new amount of fresh-environmental water but keeping track of the changed cement solid phases. With this, the change in both the aqueous and solid phases during leaching of the cement phase is calculated (e.g. Jacques et al. [13]). This helps in understanding, on a chemical level, the consequences of various factors such as cement/concrete composition, environmental solution composition or temperature on the composition and evolution of the pore water and cement phases. However, this approach is insufficient if spatio-temporal evolution of the pore water and cement phase composition is desired. For this, typically, reactive transport models are used, which integrate transport solvers with geochemical solvers (Steeffel et al. [120]). Such models can capture many coupled processes:

- Geochemical disequilibrium induced by transport of ions, gases or moisture into or out of the cementitious materials from or towards the far field (Boom Clay) as a boundary condition. The transport is affected by physical material properties such as porosity, tortuosity, permeability etc.
- Transport of ions and gases within the cementitious materials are governed by interactions with the solid phase through processes such as precipitation/dissolution and sorption.
- The change in transport properties due to microstructural changes during dissolution/precipitation processes.

Based on the type of boundary condition, reactive transport models may be focussed on the geochemical changes within the cementitious materials itself by defining a constant boundary solution (typically the environmental solution composition) (e.g. Perko et al. [15], Jacques et al. [121], Liu et al. [122], Perko et al. [123]) or on the interaction of the cementitious material with the host matrix (e.g. De Windt et al. [124], Wang et al. [19], Marty et al. [125]).

5.1.1. Geochemical calculations

A first prerequisite for thermodynamic modelling of cementitious materials is the knowledge of thermodynamic data for all aqueous species and cement hydrates. The quality and completeness of the thermodynamic dataset determines the quality of the modelling results [118]. Recently, some highly qualitative and consistent thermodynamic data sets for cementitious materials have been compiled. Two examples are:

- The CEMDATA07 database documented in Matschei et al. [126], Lothenbach et al. [127], and Schmidt et al. [128]. Thermodynamic data was originally published under the form of Gibbs free energy, enthalpy, entropy, heat capacity and molecular volume to be used in a Gibbs minimization geochemical solver (GEMS, Kulik [129]). Jacques [38] converted the database to a format suitable in geochemical solvers based on mass action laws. To be representative for conditions of Boom Clay pore water, two Cl-phases (Friedel's salt and Kunzel salt) were added to the database (based on Balonis et al. [130]).
- Thermodynamic data for cementitious materials consistent with the Thermochimie [131] and Thermoddem [132] databases presented in the work of Blanc et al. [133,134].

As an example, the consistent geochemical database CEMDATA07 under the format of PHREEQC (Parkhurst and Appelo [135]) is reported in Appendix 1 (based on [38]). It is used to calculate the geochemical changes during leaching following the approach described in [13].

5.1.1.1. CEM I (sulphate resistant)

As it is just to illustrate the approach, the concrete composition for the containment of high level waste is taken from Table 5.1 in [3], which has a CEM I cement type and a water/cement ratio of 0.5 (per m³ there is 350 kg of cement and 175 kg of water). As the CEM I is defined as a sulphate resistant cement type (C₃A at most 5% according to EN 197-1:2011), the cement oxide composition is taken from [127] (Table 1, composition for SRPC (CEM I 42.5 N HTS)). A representative (“reference”) pore water composition of Boom Clay at the envisaged depth is not available. Concentrations of some elements are given in Table 4.1 of [136]. However, some key elements are missing (C, Si, and Al) and the pH of some samples is lower than expected. This composition is not discussed here further; the simulations presented here should therefore be interpreted as an illustration of how geochemical modelling can help in identifying processes and related uncertainty.

Here, it is simply assumed that the pH should be closer to seawater (7.5 at the lower end of the range given for seawater in that report and 6.7 for sample 103), C is in equilibrium with calcite, Si is in equilibrium with quartz and Al is in equilibrium with kaolinite (identified as case 1). To partially address uncertainty, case 1 is compared with alternative cases having a different pH and a different composition (sample 104 and sample 103). Note also that PHREEQC calculations indicated that the solution of sample 104 is oversaturated with respect to gypsum. This will result in continuous gypsum precipitation during cement leaching. Therefore, two cases are considered, which examine the effect of neglecting gypsum precipitation (case 3 and 4). In addition, some small variations in the geochemical model are allowed with respect to the Cl-form. These cases are summarized below:

- Sample 104, pH 7.5, Kuzel salt (case 1)
- Sample 104, pH 6.7, Kuzel salt (case 2)
- Sample 104, pH 7.5, Kuzel salt, no gypsum (case 3)
- Sample 104, pH 7.5, Friedel's salt, no gypsum (case 4)
- Sample 103, pH 6.7, Friedel's salt (case 5)

Figure 5-1 summarizes the result for case 1 (an example PHREEQC input file is given in Appendix 2). The area of the graph is shaded by three different shades of orange along the x-axis. These three colors indicate different major phases in the cement composition evolution: the dark orange color is for the phase in which portlandite is present, the medium orange color is when the C-S-H phases are still present, and the lightest color is when most cement phases are dissolved. Contrary to less aggressive water (such as rain

water) in which only portlandite is reactive during the portlandite phase, cement minerals already dissolve. For example, during leaching, a sequence of monocarboaluminate, hydrotalcite and ettringite are dissolving to provide Al (and S) for the formation of Kuzelsalt. The formation of Kuzel salt buffers the Cl concentrations to low values. However, when monocarboaluminate, hydrotalcite and ettringite are depleted, no additional Kuzel salt is formed and Cl concentrations are no longer buffered. Note also that brucite is formed when Mg is no longer buffered by hydrotalcite. The significant gypsum precipitation is due to the oversaturation of it in the 'Boom Clay pore water' and might be somewhat artificial. After mixing the cement with about 20 liters of water, all portlandite is dissolved (dark orange area of the graph). Subsequently, the calcium silicate hydrates (C-S-H) gradually dissolve inducing a decrease in the pH. The effect of uncertainty on the pH of the external water is illustrated in case 2 in which a lower pH gives a higher partial pressure of CO₂ by the imposed equilibrium with calcite in the Boom Clay pore water calculations. The effect on the portlandite-phase is small, but a smaller amount of water (250 l as opposed to 400 l) is needed to dissolve all C-S-H phases (Figure 5-2). The lower pH of the external water also leads to more calcite precipitation.

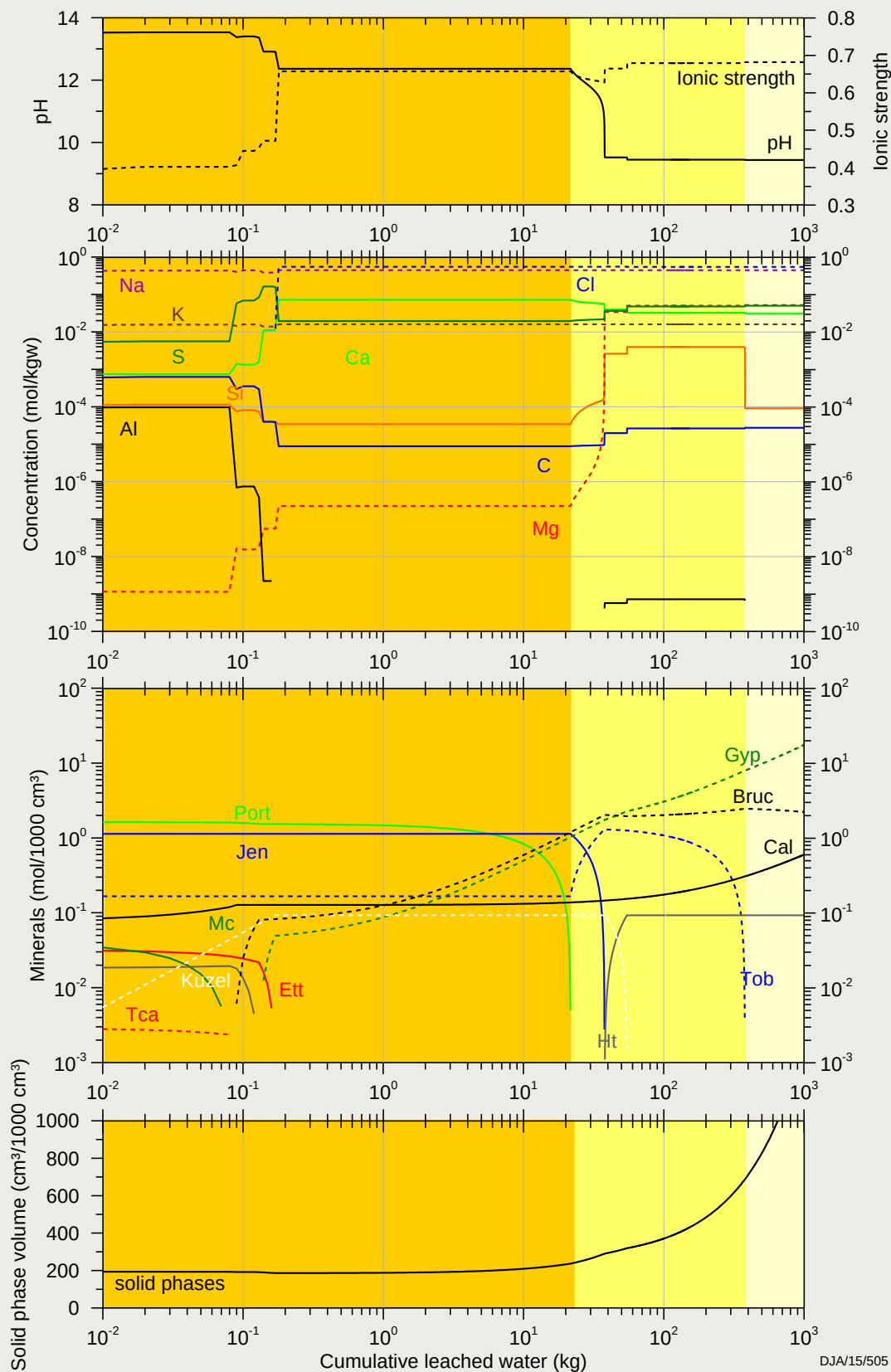


Figure 5-1 Geochemical evolution of concrete in contact with Boom Clay water (case 1; sample 104 in [136] with a pH of 7.5). Minerals are: Por: portlandite, Jen: jennite, Cal: calcite, Mc: monocarboaluminate, Kuzel: Kuzels Salt, Tca: tricarboaluminate, Ett: Ettringite, Ht: hydrotalcite, Tob: tobermorite, Bruc: brucite, Gyp: gypsum.

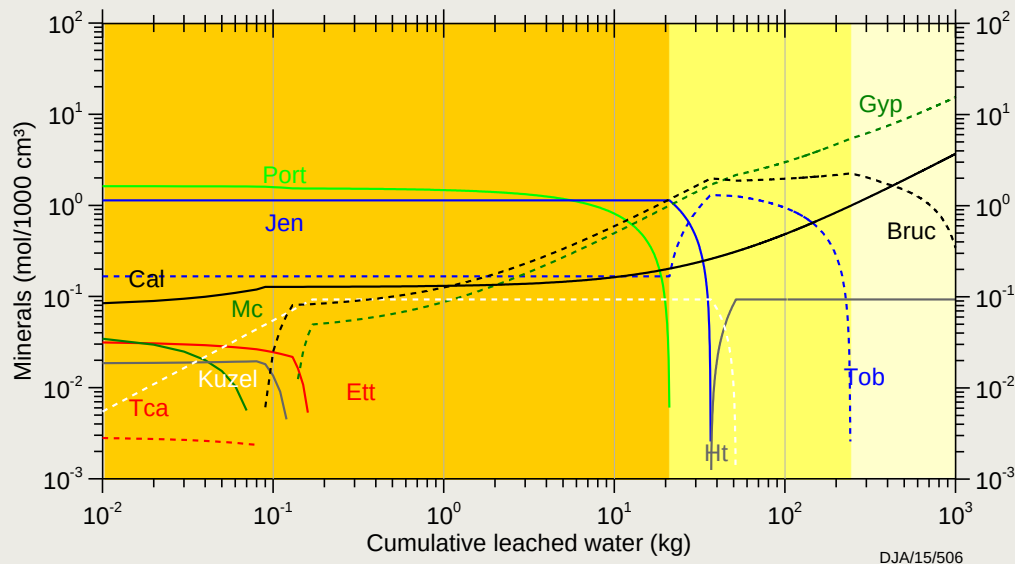


Figure 5-2 Geochemical evolution of concrete in contact with Boom Clay water (case 2; sample 104 in [136] with a pH of 6.7). Minerals are: Por: portlandite, Jen: jennite, Cal: calcite, Mc: monocarboaluminate, Kuzel: Kuzels Salt, Tca: tricarboaluminate, Ett: Ettringite, Ht: hydrotalcite, Tob: tobermorite, Bruc: brucite, Gyp: gypsum.

As it is expected that Boom Clay water will not be oversaturated with gypsum, the third case does not allow for gypsum precipitation (Figure 5-3). Again, the geochemical changes during the portlandite phase are unaffected. Leaching is slightly less aggressive during the C-S-H phase (i.e. slightly more water is needed to dissolve all C-S-H phases). The most important observation is that there are now only changes in solid phase volume after the C-S-H phase.

A fourth case considers the influence of the choice of the Cl-bearing mineral. Figure 5-4 shows the evolution when Friedel's salt is chosen. Cl concentrations are buffered to slightly higher values when Friedel's salt is forming at the expense of monocarboaluminate and hydrotalcite. Note also the ettringite precipitation during the portlandite phase and subsequent dissolution during the C-S-H phase. Note that the maximum amount of ettringite formed is lower than it should be in the case of regular CEM I (results not shown). The choice of the Cl-bearing phase does not influence the aggressiveness of the system in terms of the amount of water needed to dissolve portlandite and C-S-H.

In a final case, a different water composition is selected (sample 103 in [136]). The sample, with the restrictions defined above, is not supersaturated with gypsum. Compared to sample 104, the amount of water needed to dissolve all portlandite is about the same (Figure 5-5). It seems that water sample 103 is slightly less aggressive because more water (about 500 l) is needed to end the C-S-H phase. Note that somewhat more Friedel's salt is formed compared to case 4, but less ettringite.

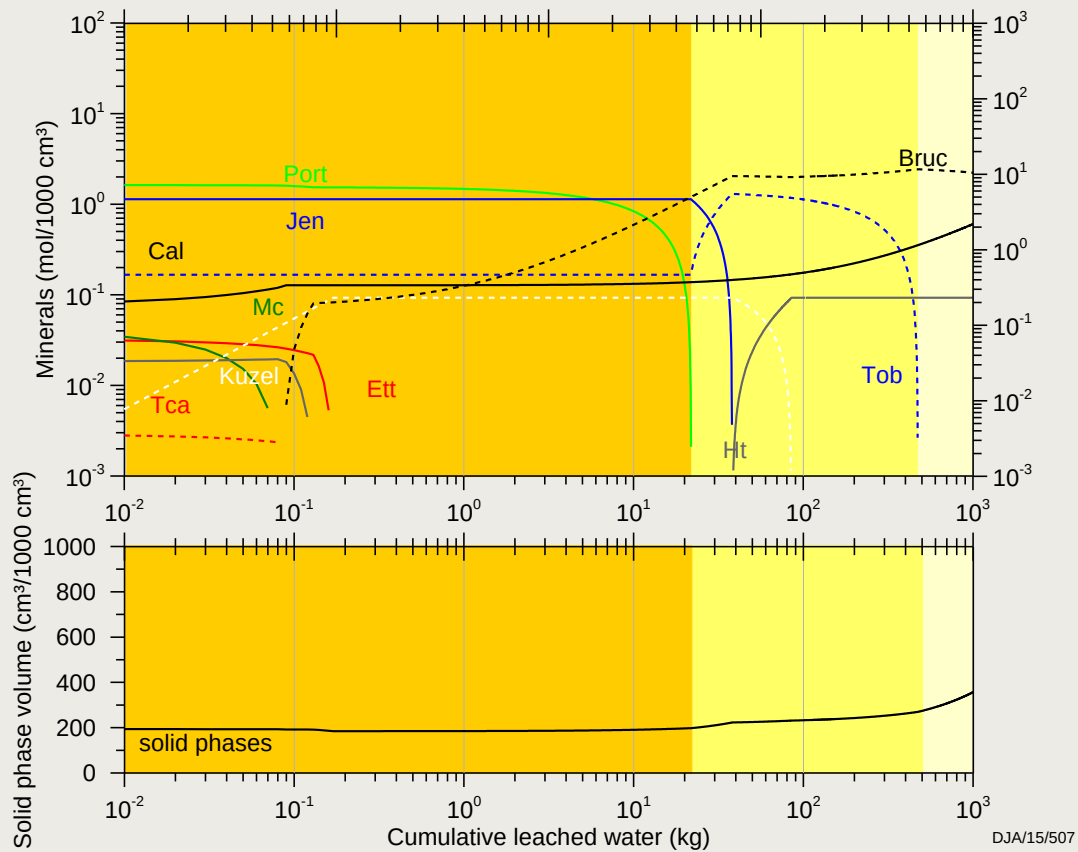
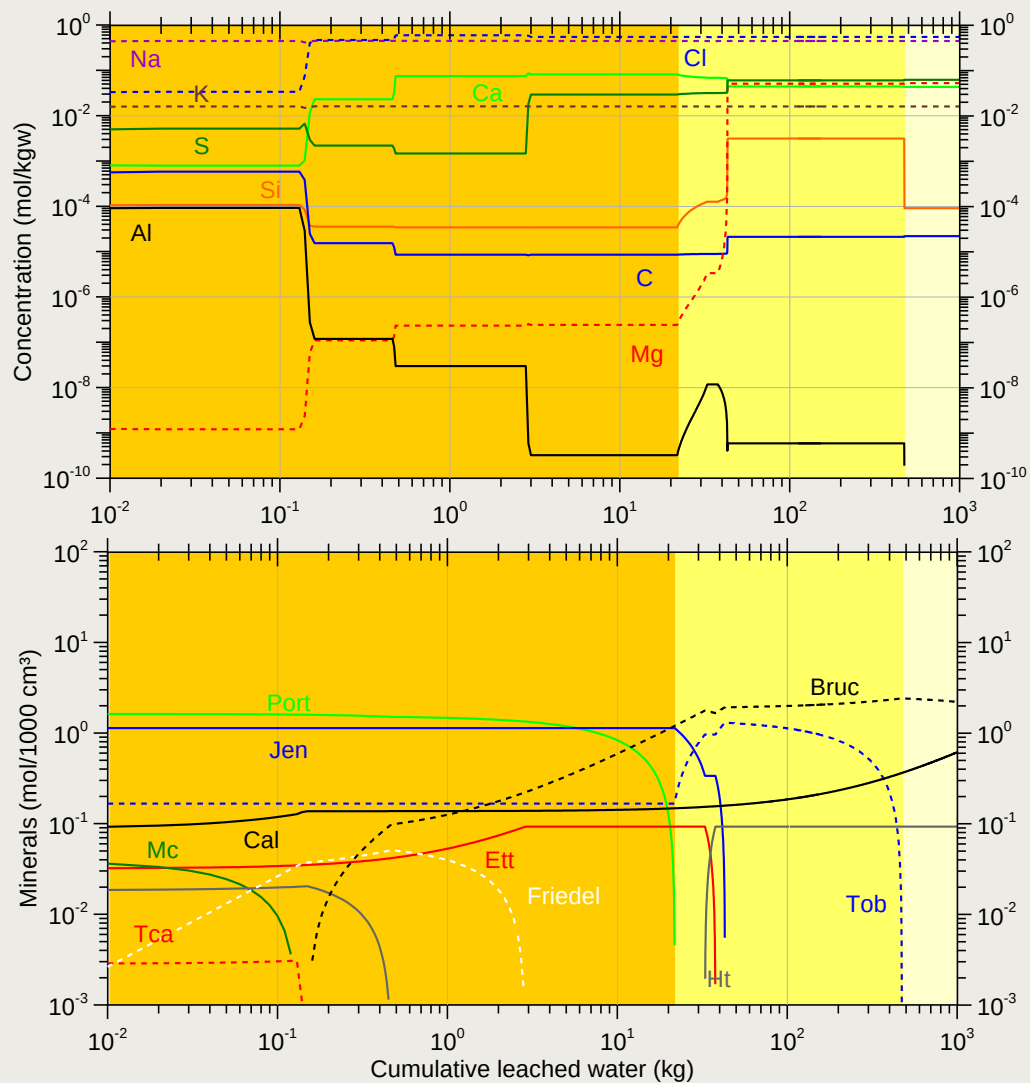


Figure 5-3 Geochemical evolution of concrete in contact with Boom Clay water (case 3; sample 104 in [136] with a pH of 7.5, no gypsum precipitation). Minerals are: Por: portlandite, Jen: jennite, Cal: calcite, Mc: monocarboaluminate, Kuzel: Kuzels Salt, Tca: tricarboaluminate, Ett: Ettringite, Ht: hydrotalcite, Tob: tobermorite, Bruc: brucite.



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Figure 5-4 Geochemical evolution of concrete in contact with Boom Clay water (case 4; sample 104 in [136] with a pH of 7.5, no gypsum precipitation). Minerals are: Por: portlandite, Jen: jennite, Cal: calcite, Mc: monocarboaluminate, Friedel: Friedel's Salt, Tca: tricarboaluminate, Ett: Ettringite, Ht: hydrotalcite, Tob: tobermorite, Bruc: brucite, Gyp: gypsum.

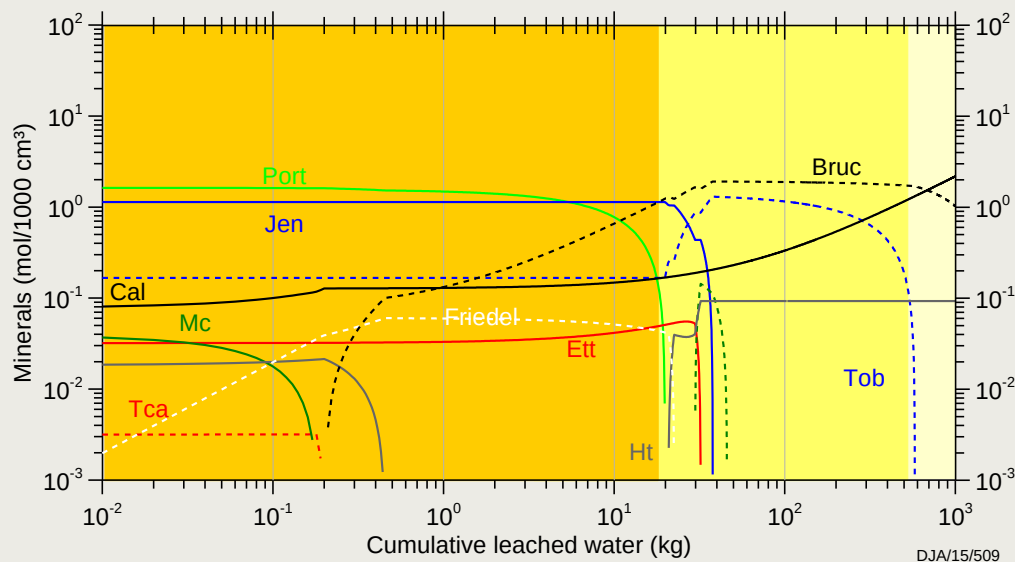


Figure 5-5 Geochemical evolution of concrete in contact with Boom Clay water (case 5; sample 103 in [136] with a pH of 6.7). Minerals are: Minerals are: Por: portlandite, Jen: jennite, Cal: calcite, Mc: monocarboaluminate, Friedel: Friedel's Salt, Tca: tricarboaluminate, Ett: Ettringite, Ht: hydrotalcite, Tob: tobermorite, Bruc: brucite, Gyp: gypsum.

The following main conclusions can be drawn:

- Cl is only buffered during precipitation of Friedel's salt or Kunzel salt, the latter being less soluble and resulting in smaller Cl concentrations for small amounts of leached water;
- The uncertainties related to the pore water composition (element concentrations, pH) do not influence significantly the dissolution of portlandite.
- The pH is of particular interest because it determines the amount of calcite formed (assuming the Boom Clay pore water is in equilibrium with calcite).
- However, the uncertainties do have an effect on the amount of water needed to leach the C-S-H phases, which is linked to a pH decrease. Note that there is also uncertainty with respect to the geochemical model for the C-S-H, which increases or decreases the amount of water for the C-S-H by approximately a factor of two (see [39] and [137]).
- Ettringite formation is not seen as sulphate is being used in the formation of Friedel's salt.

5.1.1.2. CEM II (with fly-ash)

The concrete used as mechanical support is of type CEM II with fly-ash additions. As the fly ash contribution are between 19 to 23% of CEM I, type CEM II/A or CEM II/B V are considered in this study (section 3.2 in [Fout! Bladwijzer niet gedefinieerd.]). De Weerd et al. [138] studied the hydration of CEM II with 35 % fly ash. Similarly, in this study, the clinker and fly-ash composition is used to simulate the initial composition for a blended cement of 80 % CEM I and 20 % fly ash (mixing 386 kg cement with 125 kg of water, Table 3-1 in [Fout! Bladwijzer niet gedefinieerd.]). As noted in [138], Al is incorporated in the C-S-H but C-(A)-S-H phases are not available in the thermodynamic database.

For the assumption of full hydration of cement clinkers and fly-ash, the model predicts no portlandite. Monosulphaluminate is predicted with only trace amounts of ettringite and the pH is about 12.5. This is in qualitative agreement with the simulations of [138] (simulation up to 200 d with kinetic hydration of cement clinkers and fly ash): ettringite is replaced by

monosulphoaluminate, a decreasing pH with time and a decreasing amount of portlandite (note that after 200 d, approximately 90 % of the clinkers are hydrated, but only 35 % of the fly ash has reacted). As fly ash reacts slower than the cement clinkers, portlandite (formed via the hydration of the clinkers) will react with the silicates from the fly ash to form additional C-S-H with alumina partly incorporated within the C-S-H and AFm and AFt phases. A scoping calculation for leaching with case I assumptions was performed with the following simplified assumptions:

- starting from complete cement clinker and fly ash reactivity (uncertain how much fly ash remains unreactive in the long term),
- no Al incorporation in C-S-H ([138], changed Al/Si in C-S-H to 0.13, but this was also a simplification), and
- no solid solution with ettringite (simulations become numerically unstable).

Note that the simplifications used here are a source of uncertainty, which can be decreased by further studies.

As in the previous examples, simulation is carried out for up to 1000 kg of cumulative leached water as shown in Figure 5-6. Note that the initial amount of tobermorite (assuming complete reactivity of cement clinkers and fly-ash) is higher compared to the amount of CEM I-SR and the absence of portlandite. It is also clear that the concrete is still in state III, which indicates some increased stability. Mechanical stability will be also linked to the amount of gypsum formed, and the change in the volume of the solid phases.

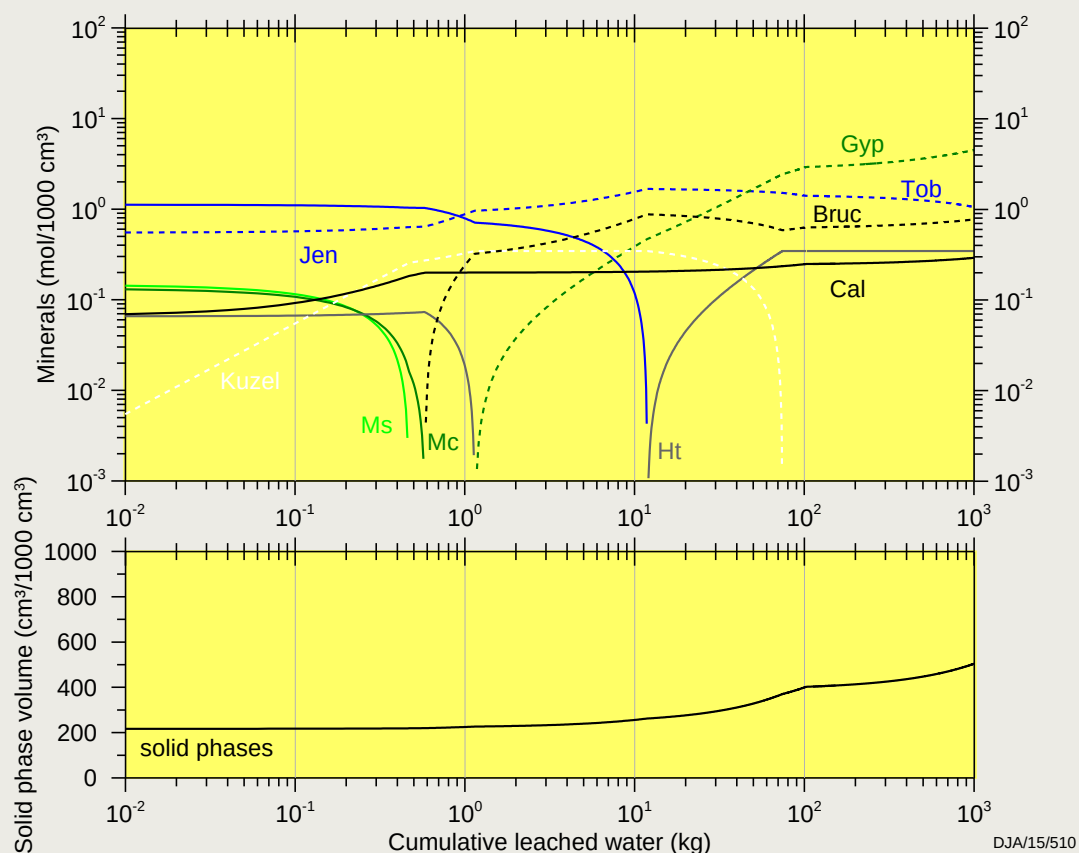


Figure 5-6 Geochemical evolution of concrete (proxy for CEM II/A-B (V)) in contact with Boom Clay water (case 1; sample 104 in [136] with a pH of 7.5). Minerals are: Ms: Monosulphoaluminat, Jen: jennite, Cal: calcite, Mc: monocarboaluminate, Kuzel: Kuzels Salt, Ht: hydrotalcite, Tob: tobermorite, Bruc: brucite, Gyp: gypsum.

5.2. Reactive transport model for chemical degradation of concrete

A general flowchart of the integrated model approach to link transport models for water and solutes with geochemical reactions, including models for updating transport properties (porosity, diffusivity and permeability) is presented in Figure 5-7 (Perko et al. [15]). Three processes are considered: (i) water flow, (i) *solute transport*, *i.e.* the transport of aqueous species, and (iii) *chemistry*, *i.e.* the exchange of solute components between the aqueous and the solid phases. These three processes are strongly coupled. In this particular case, the volume fraction of cement minerals and the volume fraction of C-S-H gel. For brevity, in this section, mainly the solute transport, chemical model and the porosity and diffusivity update will be discussed as these are more relevant in the context of deep disposal. Water flow and permeability updates are indeed important when flow gradients are appreciable.

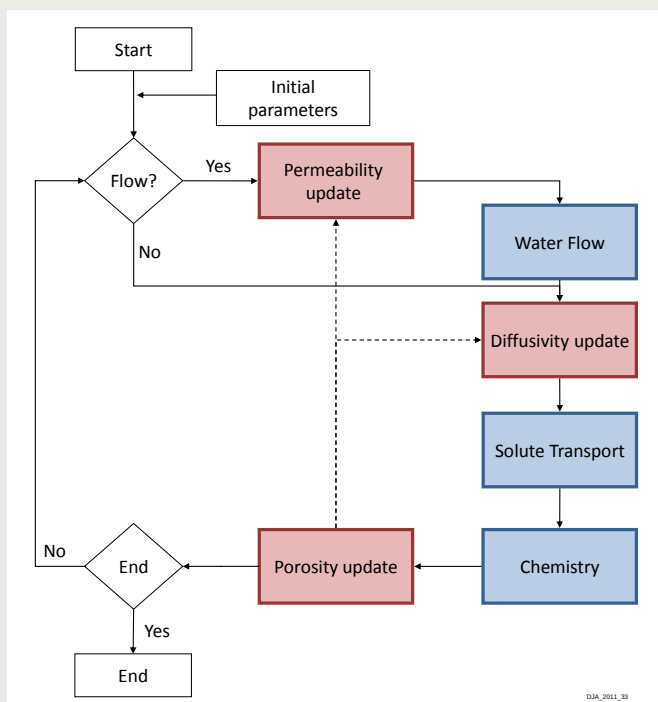


Figure 5-7 Flow chart of the calculation procedure for coupling transport processes, geochemical processes and affected transport properties.

5.2.1. Solute transport model

Transport of chemical components in the aqueous phase is described by the standard advection-dispersion-reaction equation:

$$\frac{\partial \theta c_j}{\partial t} = \frac{\partial}{\partial z} \left(\theta D_{hd} \frac{\partial c_j}{\partial z} \right) + R_j \quad \text{Equation 10}$$

where c_j is the total concentration [mol kg⁻¹ of water] of the j^{th} component ($j = 1, \dots, N_c$ where N_c is the total number of components) and R_j is the source-sink term due to geochemical reactions of the j^{th} component [mol kg⁻¹ water T⁻¹]. Although R_j accounts for all kinds of aqueous kinetic reactions and heterogeneous equilibrium or kinetic reactions, R_j contains here only changes due to equilibrium cement phase dissolution and precipitation:

$$R_j = - \sum_m \Delta M_m \nu_{mj} \quad \text{Equation 11}$$

where M_m is the amount of the m^{th} solid phase in the system ($m = 1, \dots, N_m$, where N_m is the number of solid phases/minerals present as pure phases or as solid solutions), and ν_{mj} is the stoichiometric coefficient of the j^{th} component in the m^{th} solid phase. The hydrodynamic dispersion coefficient [L^2/T] is defined as:

$$D_{\text{hd}} = \lambda \frac{q}{\theta} + D_p \quad \text{Equation 12}$$

where λ is the dispersivity (L), and D_p is the pore diffusion coefficient [L^2/T], which is linked to D_0 as ([5], Saetta *et al.* [139]):

$$D_p = \tau D_{0,\text{ref}} S(\theta) G(T) H(t) M(.) \quad \text{Equation 13}$$

$D_{0,\text{ref}}$ is the free aqueous diffusion coefficient [L^2/T] at the reference temperature (293.15 K). τ is a geometry factor accounting for microscopic geometry factors as tortuosity, connectivity and constrictivity. The remaining factors $S(\theta)$, $G(T)$, $H(t)$ and $M(.)$ are correction factors accounting for, respectively, water saturation, temperature, hydration degree of the concrete, and pore structural changes due to geochemical reactions (the dot indicates that we do not define at this stage which are the geochemical state variables controlling M). Under deep geological conditions, the cementitious components will be saturated and hence $S(\theta)=1$. Full hydration can also be assumed, thus $H(t)=1$. Also, isothermal conditions are considered which gives a constant value of $G(T)$, which is obtained by the van't Hoff equation (Li and Gregory [140]). For isothermal conditions, $G(T)D_{0,\text{ref}}$ can be lumped in a single term D_0 . The geometry factor τ and the correction factor for pore structural changes due to geochemical reactions, $M(.)$, are lumped in one overall geometry factor $\mathfrak{Z}(.)$. The evolution of the overall geometry factor depends on the capillary porosity, which evolves as chemical degradation proceeds. The pore diffusion coefficient is thus calculated via:

$$D_p = \mathfrak{Z}(.)D_0 \quad \text{Equation 14}$$

5.2.2. Chemistry

The chemistry model consists in calculating thermodynamic equilibrium between aqueous components and cement minerals. Three types of geochemical processes should be included: aqueous speciation reactions, equilibrium with pure solid phases and equilibrium with (ideal) solid solutions. The geochemical model was discussed in section 5.1.1 and details on general principles of thermodynamic equilibrium in geochemical systems and on the thermodynamic database for cement minerals can be found in Jacques [38] and Jacques *et al.* [39].

5.2.3. Porosity update

The calculation steps are outlined below:

1. Calculation of the volume fraction of the hardened cement paste, ϕ_{hp} , by summing of the products of the amount of a cement mineral, M_m [moles/dm³ concrete], multiplied by its molar volume, V_m [cm³ / mole].

2. The porosity, η , is obtained at each time step by subtracting the volume fraction of the cement hydrates, ϕ_{hp} , and the volume fraction of the aggregates, ϕ_a , (which is assumed to be constant because the aggregates do not react) from 1.
3. The gel porosity, ϕ_{gp} , is linked to the volume fraction of the C-S-H phases, ϕ_{ch} , with a proportionality factor a^* . The proportionality factor expresses the volume of the gel pores per volume unit of C-S-H phases. It is calculated from the initial gel porosity and the initial C-S-H volume. It is assumed that it remains constant when the composition of the C-S-H phase changes with chemical degradation.
4. The capillary porosity, ϕ_{cp} , is then obtained by the difference between porosity and gel porosity.

5.2.4. Diffusivity update

The changes in the pore diffusion coefficient are accounted for by defining an updated overall geometry factor, $\mathfrak{I}(\cdot)$ ($= \tau M(\cdot)$), which depends indirectly on the geochemical state variables via the total porosity (or ϕ_{cp} and ϕ_{gp}). Several conceptual models and constitutive relations are reported in the literature for $\mathfrak{I}(\cdot)$ (see e.g. [5] and Stora *et al.* [141]). One approach to determine the overall geometry factor using the capillary porosity is detailed below:

1. The capillary porosity, ϕ_{cp} , which is expressed as dm^3/dm^3 concrete, is rescaled to the capillary porosity for the hardened cement paste, $\phi_{cp,c}$, which is expressed as dm^3/dm^3 hardened cement paste. The rescaling is done using the volume fraction of the aggregates, ϕ_a .
2. The overall geometry factor for the hardened cement paste, $\mathfrak{I}_c$, is calculated with function f_1 (for definition, see below) based on the capillary porosity per volume of hardened cement paste, $\phi_{cp,c}$.
3. The overall geometry factor for the concrete, $\mathfrak{I}$, is calculated using $\mathfrak{I}_c$ and a function f_2 (for definition, see below) accounting for the effect of aggregates and the ITZ.

The function f_1 that relate the capillary porosity to $\mathfrak{I}_c$ is based on the general effective medium homogenization scheme (Oh and Jang [142]) and can be expressed as follows:

$$f_1 = \mathfrak{I}_c = \frac{1}{\phi_{cp,c}} \left(m_\phi + \sqrt{m_\phi^2 + \frac{\phi_{cp,c}}{1-\phi_{cp,c}} \left(\frac{D_s}{D_0} \right)^{1/n}} \right)^n \quad \text{Equation 15}$$

with

$$m_\phi = \frac{1}{2} \left[\left(\frac{D_s}{D_0} \right)^{1/n} + \frac{\phi_{cp}}{1-\phi_{cp,c}} \left(1 - \left(\frac{D_s}{D_0} \right)^{1/n} \right) - \frac{\phi_{cp,c}}{1-\phi_{cp,c}} \right] \quad \text{Equation 16}$$

where n is the percolation coefficient [-] and D_s is the diffusivity of the solid phase [$\text{L}^2 \text{T}^{-1}$] (the C-S-H gel) representing the diffusivity when the capillary porosity is zero (also called self-diffusion coefficient). For Portland cement pastes, Oh and Yang [142] calibrated D_s/D_0 and n resulting in values of respectively 2×10^{-4} and a n value of 2.7. However, these values change significantly with cement type (e.g. addition of pozzolans decreases D_s/D_0). Therefore, the sensitivity of these parameters has to be assessed.

The function f_2 is then used to derive the overall geometry factor of concrete $\mathfrak{J}$. The function f_2 is based on the composite sphere assemblage (CSA) model with the assumption that the aggregates are impermeable. Accounting for the ITZ and impermeable aggregate particle inclusions, f_2 has following form [142]:

$$f_2 = 1 + \frac{\varphi_a}{\frac{1}{2(D_i / D_{hp})\varepsilon - 1} + \frac{1 - \varphi_a}{3}} \quad \text{Equation 17}$$

where D_i is the diffusion coefficient in the ITZ [L^2T^{-1}], D_{hp} is the diffusion coefficient of the hardened cement paste [L^2T^{-1}] ($D_{hp} = \mathfrak{J}_c D_0$), and ε is the ratio of the interface thickness over the radius of the aggregate particle inclusion.

5.3. Mechanical model for decalcification

From the studies concerning the influence of calcium leaching on the residual mechanical behaviour of materials (section 3.1), it is established that leaching will lead to a loss in global strength due to chemical decohesion along with an important loss of frictional performance. Essentially, the material becomes more brittle, including a loss of fracture energy. Noting that the maximum overburden pressure is about 10 MPa, a direct approach would be to carry out leaching experiments under triaxial stress states for the candidate material and determine the critical leaching degree at which the compressive strength of the material drops below 10 MPa (similar to Huang and Qian [87]). The time taken to reach this critical leaching degree under in situ conditions can be numerically simulated based on a simplified geochemical model described in section 5.1.

Alternatively, a simplified leaching-damage model can also be used to get a rough quantitative approximation of damage evolution and hence reduction in the Young's modulus of the cementitious EBS components. There are several leaching-damage models mostly based on coupling a transport equation with an isotropic damage model. The two way coupling between the two processes is typically achieved by two independent variables: (i) a mechanical damage variable (d), which captures the effect due to load, and (ii) a chemical damage (ageing) variable (V) that captures the effect due to the leaching. The diffusion coefficient (D) in the transport equation is defined as a function of the chemical concentration, which can either be the solid Ca (C_s) or pore water Ca (C) concentration. One such model is that proposed by Gerrard et al. [143] and further explored for its validity by Bellego et al. [144]. For brevity, only the two main governing equations are presented here.

$$\frac{\partial C_s}{\partial C} \frac{\partial C}{\partial t} = \nabla \cdot (D(C) \nabla C) \quad \text{Equation 18}$$

$$\nabla \cdot [(1-d)(1-V)\Lambda_{ijkl}\varepsilon_{kl}] = 0 \quad \text{Equation 19}$$

where Λ_{ijkl} is a 4th order macroscopic stiffness tensor, ε_{kl} is a 2nd order strain tensor and other terms as explained above. Note that d is based on Mazar's damage model [145] and V is related to the pore water concentration C according to [143]. Refer to [144] for the input parameters.

5.4. Mechanical model for sulphate attack

In terms of mechanical behaviour, the main response of concrete due to the sulphate attack is cracking induced by precipitation of ettringite and gypsum. There are a number of models, which consider the reactive transport of relevant chemical species (Ca^{2+} and SO_4^{2-}) and their effect on the mechanical behaviour. Almost all models consider some form of coupling between the chemical transport and mechanical damage and are solved via a numerical approach. There are 1D and more general 3D models. Here a general 3D model proposed by Bary [146, 147] is presented. Unlike other models, this author uses combined transport of both calcium and sulphate to capture both leaching and sulphate attack. Bary's chemo-mechanical model essentially uses three governing equations: (i) sulphate transport (Equation 13) (ii) calcium transport (also Equation (13)) and (iii) stress-strain equilibrium with damage mechanics (Equation 14). These are presented below:

$$\phi \frac{\partial C_i}{\partial t} = \nabla \cdot (D(C_i) \nabla C_i) - \frac{\partial S_i}{\partial t} - \phi \left(v_i^{\text{ettr}} \bar{N}_{\text{ettr}}^g + v_i^{\text{gyp}} \bar{N}_{\text{gyp}}^g \right) - \frac{\partial \phi_{\text{ini}}}{\partial t} C_i + C_i \phi \left(v_i^{\text{ettr}} \bar{N}_{\text{ettr}}^g \bar{V}_{\text{ettr}} + v_i^{\text{gyp}} \bar{N}_{\text{gyp}}^g \bar{V}_{\text{gyp}} \right) \quad \text{Equation 20}$$

$$\nabla \cdot \left[(1-d) (\mathbf{K}_{\text{mor}} : (\boldsymbol{\varepsilon} - \boldsymbol{\varepsilon}^*) - \alpha_{\text{mor}}^{\text{AFm}} p_c \mathbf{1}) \right] = 0 \quad \text{Equation 21}$$

where C_i is the pore water concentration of the primary species (i.e. C_{Ca} and C_{SO_4}), ϕ is the total porosity, ϕ_{ini} is the initial total porosity, S_i is the solid phase concentration of the primary species, $\bar{N}_j^g$ is the rate of formation (positive) or dissolution (negative) of the secondary phase j containing the species i , v_i^j is the stoichiometric coefficient of species i involved in the formation of j , and $\bar{V}_{\text{ettr}}$ and $\bar{V}_{\text{gyp}}$ are the molar volumes of ettringite and gypsum, respectively.

The governing equation for damage is almost the same as for decalcification except that there is an additional pressure term analogous to thermoelasticity in the effective stress definition. $\mathbf{K}_{\text{mor}}$ and $\boldsymbol{\varepsilon}$ are the same as Λ_{ijkl} and ε_{kl} in Equation (12), respectively, but for mortar. $\boldsymbol{\varepsilon}^*$ is a macroscopic bulk strain introduced to capture the expansions due to ettringite formation. The coefficient $\alpha_{\text{mor}}^{\text{AFm}}$ is a scalar and quantifies at the macroscale the effects of the crystallization pressures acting at the microscale in the growing AFm crystals, and essentially a function of bulk and shear modulus of different mortar phases, including porosity. p_c is the crystallization pressure defined as:

$$p_c = \frac{RT}{\bar{V}_{\text{ett}}} \ln \left(\frac{C_{\text{Ca}}^2 C_{\text{SO}_4}^2}{C_{\text{Ca}}^{02} C_{\text{SO}_4}^{02}} \right) \quad \text{Equation 22}$$

where R is the universal gas constant, T the temperature and C_{Ca}^0 and $C_{\text{SO}_4}^0$ are the pore water concentrations of calcium and sulphate at equilibrium, respectively. Refer to Bary [146] for a more detailed description of the terms and material parameters.

It is important to note that as with any model, this approach also has some limitations as pointed out by Bary [146]. It was found that for constrained displacement problems, i.e. no free expansions, the model predicts unusually high degree of cracking and compressive stresses, which has to be remedied by linking the growth of ettringite with the macroscopic stresses (inhibition of growth) and/or via consideration of creep/relaxation effect.

6. Conclusions

This report presented the current understanding of chemical and mechanical cement degradation processes based on a selected number of literatures. Specific attention was paid to studies carried out in the context of deep disposal applications, where possible. An attempt was also made to describe the preliminary implications of such degradation processes on safety functions of the repository components based on rather limited information, in a tabulated form (Table 1 to Table 12). A geochemical conceptual model based on thermodynamics, and state of the art reactive transport model were proposed to help in the understanding of spatio-temporal behaviour of concrete geochemistry. Though not within the scope of this work package, an additional step was taken in carrying out preliminary geochemical calculations, including pertinent uncertainty analyses to gain a first level understanding of the chemical degradation processes of concrete. Also included were some simplified mathematical models, which are capable of exploring the chemo-mechanical behaviour, associated with decalcification and sulphate attack. These are just one of the many models available in the literatures.

The chemical degradation covered major long term processes such as (i) decalcification and leaching, (ii) carbonation mainly under saturated condition, (iii) sulphate attack, (iv) chloride ingress, and (v) degradation because of interaction of cement with the waste form. The mechanical degradation covered major processes such as mechanical consequences associated with (i) decalcification and leaching, (ii) carbonation, (iii) sulphate attack, (iv) corrosion induced cracking, (v) freeze-thaw, (vi) long term temperature variation, and (vii) long term creep. Apart from the characteristics of the cement, aggregates and additives used in the makeup of the candidate concrete or mortar, the main drivers for these degradation processes are the native pore water composition, chemical nature of the waste form, presence of steel, saturated conditions, thermal field, availability of oxygen and diffusion.

The literatures suggest that all the processes discussed have an impact on the performance of the cementitious components; however, such processes are going to be predominantly active in the long term. Short term impact can be attributed to temperature variation, atmospheric carbonation and sulphate attack; the latter is especially relevant during the operational phase from the point of view of retrievability.

Based on Table 1 to Table 12, the following salient impacts can be extracted, without particular reference to the repository components:

- **Decalcification and leaching:**
 - a very slow process requiring tens of thousands of years to leach out. Thus a high pH environment is likely to be preserved at the overpack surface by the buffer (**CEM I**). However, high alkalinity is also detrimental to the dissolution rate of the waste forms, in case of contact. The specific implication of **foam (CEM I)** on leaching, although expected to be low, is not known. Because portlandite is consumed by fly ash reactivity and transformed into C-S-H phases, state II of **CEM II** concrete degradation will be non-existent (provided all fly ash has reacted) or shorter compared to **CEM I**.
 - All cementitious components directly impact the sorption, hydraulic conductivity of the Boom Clay, but the radial extent seems to be limited over the long term.
 - Self-sealing capacity of the Boom Clay may be affected due to mineralogical transformation. However, the radial extent of the perturbed zone will be limited and in fact governed by the extent of calcium ingress into the Boom Clay.

- Leaching will lead to mechanical degradation of cementitious components, which can promote transport of deleterious substances from the Boom Clay towards the overpack. However, the time scale is governed by the leaching rate.
- **Carbonation (under saturated conditions):**
 - May prove to be beneficial in terms of minimizing the dissolution rate of the waste form due to its lower pH environment.
 - Pore clogging is likely to minimize the rate of alkaline plume thus having limited impact on the sorption property of the Boom Clay and also limiting transport of deleterious substances towards the overpack.
 - In mechanical terms, there may be potential embrittlement, but depends on the carbonation depth under saturated conditions, which is likely to be limited due to pore clogging. This is a very long term process.
- **Sulphate attack:**
 - Potentially can cause cracking of the cementitious components, especially the concrete liners during the operational phase. Preliminary calculations for **CEM II** suggest that ettringite formation is limited; however, gypsum precipitation can be appreciable, which can impose expansive strains.
 - Given the uncertainty of the water composition, quantitative assessment is difficult at this stage.
 - The cracking in general can lead to preferential flow of high pH pore water from the cementitious barriers into the clay. The resultant high pH can affect radionuclide sorption of the clay, positively or negatively depends on the radionuclide.
- **Chloride** does not give rise to any cement degradation product that affects the safety functions. It only affects the corrosion rate of the waste package, which in turn allows high pH pore fluid to come in contact with the waste form thus making it unstable.
- High pH will negatively affect the rate of **dissolution of waste**. Note that high pH state itself is not a cement degradation process as it is a design requirement.
- **Corrosion products and H₂ gas** released during the corrosion process can cause potential cracking of the concrete buffer in the longer term. Cracked buffer allows faster travel of deleterious substances that may promote increase in corrosion rate, which in turn may expose the vitrified waste to the high pH environment.
- **Freeze-thaw** process does not appear to be of major concern under deep geological conditions, where severe temperature cycles are less likely.
- During the **thermal phase**, tensile stresses may develop due to thermal expansion of water within the saturated buffer and backfill. This may potentially enhance corrosion of the overpack due to transport of deleterious substances towards the overpack, which in turn may expose vitrified waste to the high pH environment.
- The effect of **long term creep** due to decalcification is also a process to be explored. However, there is no information to evaluate its importance.

The following salient observations could be made from the preliminary geochemical calculations:

- The uncertainties related to the pore water composition do not influence significantly the dissolution of portlandite.
- The pH is of particular interest because it determines the amount of calcite formed.
- The uncertainties do have an effect on the amount of water needed to leach the C-S-H phases, which is linked to a pH decrease. Note that there is also uncertainty with respect to the geochemical model for the C-S-H.
- Cl is only buffered during precipitation of Friedel's salt or Kunzel salt, the latter being less soluble and resulting in smaller Cl concentrations for small amounts of leached water.
- Calculations show no tendency for ettringite formation as the thermodynamics dictates that sulphate reacts to form Friedel's salt.
- a different leaching pathway was calculated for the CEM II-based concrete, the portlandite content is much lower (all Ca is in C-S-H when all fly ash has reacted) but leaching of the C-S-H phases goes slower.

Finally, some important caveats that deserve to be mentioned:

- The main focus of this study is on the long term degradation processes and not on degradation during the construction phase of the repository components, for example, thermal cracking, plastic or drying shrinkage cracking, etc. Indeed very early age degradation can have impact on the long term performance of cementitious components.
- It is reiterated that it is not a trivial task to identify potential implications of the degradation processes because interactions between the processes over the long term are extremely complex and at this point in time there is a clear lack of phenomenological understanding and relevant data of such processes for the given material. These require most often thorough experimental, field and numerical studies. Therefore, the term potential implications should be viewed cautiously as these are preliminary in nature and which should be confirmed by further research.
- The degradation processes discussed in Chapters 2 and 3 are mostly without considering the combined effect of other related (coupled) processes. This gap is mainly because of non-availability of information.

7. Recommendations

While there are innumerable scientific issues that need to be tackled to gain a greater understanding of the processes and their potential implications, the following initial recommendations are worthy of consideration:

- Uncertainties in the Boom Clay pore water composition should be reduced.
- A full geochemical assessment similar to Jacques et al. [13] and Wang et al. [19] should be performed to gain an overall understanding of coupled geochemical processes under deep geological conditions. Note that there are many concrete types: CEM I concrete, CEM I/Foam concrete, CEM II concrete and CEM III concrete. The interaction of Boom Clay pore water with these has to be examined.
- Related to the above point, spatio-temporal evolution of chemical degradation of concrete should be explored.
- Particular attention should be paid for the mechanical behaviour of concrete under buried conditions, for which data is extremely scarce.
- The information available in the current literatures are mostly generic (i.e. not site specific) and cannot always be extrapolated for long term. Therefore, site specific and process specific studies should be pursued.
- Data on the long term behaviour of foam concrete is scarce and deserves attention.
- Study of reactivity of fly ash with cement needs further work.
- The effect of gypsum precipitation on the mechanical behaviour of liners is needs to be investigated.

8. Acknowledgements

We gratefully acknowledge contributions from Bruno Kursten and Karel Lemmens to this report and to Yu Li and Eef Weetjens for a critical review of this report.

Appendix 1 - CEMDATA08 in PHREEQC format

```
#CEMENT PHASE DATABASE
#
#Valid range : 0 - 50°C
#
#Temperature dependence described by three-term analytical model
#
#
#Based on CEMDATA07 version 07.02 (14.08.2008)
#
#http://www.empa.ch/plugin/template/empa/*/62204
#
#
#Information: D. Jacques (2009): Benchmarking of the cement model and detrimental chemical
reactions including temperature dependent parameters
#
#Project near surface disposal of category A waste at Dessel
#
#NIRAS-MP5-03 DATA-LT(NF) Version 1
#
#NIROND-TR 2008-30 E
#
#Thaumasite added on 28-05-2010
#
#Adaptations for Friedelsalt and Kunzelsalt on 26/01/2015
#
#Addition of CSHQ model of Kulik (only for 25°C!)
#
#Addition of CSH3T model of Kulik (only for 25°C!)
```

SOLUTION_MASTER_SPECIES

```
#
#ATOMIC WEIGHTS
#Naturally occurring elements: IUPAC 1993 Table 1 rounded to 0.001
#Radioelements: Mass number of longest-lived isotope
#
#
#
#
```

#	elemen	species	alk	gfw_formula	element_gfw	atomic number
#						
H		H+	-1.0	H	1.008	# 1
H(0)		H2	0.0	H		#
H(1)		H+	-1.0	H		#
E		e-	0.0	0.0	0.0	#
O		H2O	0.0	O	15.999	# 8
O(0)		O2	0.0	O		#
O(-2)		H2O	0.0	O		#
C		HCO3-	1.0	C	12.011	# 6
C(+4)		HCO3-	1.0	HCO3-		#
C(-4)		CH4	0.0	CH4		#
Alkalinity		HCO3-	1.0	HCO3-	61.016	#
Ca		Ca+2	0.0	Ca	40.078	# 20
Si		Si(OH)4	0.0	Si	28.086	# 14
K		K+	0.0	K	39.098	# 19
Mg		Mg+2	0.0	Mg	24.305	# 12
Al		Al+3	0.0	Al	26.982	# 13
S		SO4-2	0.0	S	32.067	# 16
S(-2)		HS-	1.0	HS		#
S(2)		S2O3-2	0.0	S2O3		#
S(4)		SO3-2	0.0	SO3		#
S(6)		SO4-2	0.0	SO4		#
Fe		Fe+2	0.0	Fe	55.845	# 26
Fe(2)		Fe+2	0.0	Fe		#
Fe(3)		Fe+3	0.0	Fe		#
Br		Br-	0.0	Br	79.904	# 35
Cl		Cl-	0.0	Cl	35.453	# 17
N		NO3-	0.0	N	14.007	# 7
N(0)		N2	0.0	N2		#
N(-3)		NH4+	0.0	NH4		#
N(5)		NO3-	0.0	NO3		#
Na		Na+	0.0	Na	22.99	# 11

SOLUTION_SPECIES

PMATCH MASTER SPECIES

```

H+          = H+
  log_k      0.0
  -gamma     9.00    0.064

e-          = e-
  log_k      0.0

H2O         = H2O
  log_k      0.0
  -gamma     0.00    0.0#64

HCO3-       = HCO3-
  log_k      0.0
  -gamma     5.40    0.064

Ca+2        = Ca+2
  log_k      0.0
  -gamma     4.86    0.064 # 0.01564

Si(OH)4     = Si(OH)4
  log_k      0.0
  -gamma     0.00    0.0#64

```

#b parameter not changed from here on for primary master species

```

Al+3        = Al+3
  log_k      0.0
  -gamma     6.65    0.064 # 0.19

Fe+2        = Fe+2
  log_k      0.0
  -gamma     5.08    0.064 # 0.16

K+          = K+
  log_k      0.0
  -gamma     3.71    0.064 # 0.01

Mg+2        = Mg+2
  log_k      0.0
  -gamma     5.46    0.064 # 0.22

SO4-2       = SO4-2
  log_k      0.0
  -gamma     5.31    0.064 # -0.07

Br-         = Br-
  log_k      0.0
  -gamma     3.00    0.064 # 0.00

Cl-         = Cl-
  log_k      0.0
  -gamma     3.71    0.01

NO3-        = NO3-
  log_k      0.0
  -gamma     3.00    0.064 # 0.00

Na+         = Na+
  log_k      0.0
  -gamma     4.32    0.064 # 0.06

```

PMATCH SECONDARY MASTER SPECIES

```

+1.000Al+3      +1.000SO4-2      = AlSO4+ ; -gamma      4.00
0.064 ; log_K    3.900111      ; -analytical_expression -59.74759294081      0
2048.61497066133      22.9451885920 0
+1.000Al+3      +2.000SO4-2      = Al(SO4)2- ; -gamma      4.00
0.0640 ; log_K    5.900097      ; -analytical_expression -129.37633673647      0
5505.68803129935      47.2073519666 0
+1.000Al+3      +2.000H2O      -2.000H+      = Al(OH)2+ ;
-gamma      4.00    0.0640      ; log_K      -10.5937      ; -analytical_expression
32.53631959378 0      -6492.54044012403      -8.6321382739 0

```

```

+1.000Al+3      +4.000H2O      -4.000H+      = Al(OH)4- ;
-gamma      4.00      0.0640      ; log_K      -22.8786      ; -analytical_expression
      32.96015215706 0      -10341.60374731900      -8.5473467468 0
+1.000Al+3      +3.000H2O      -3.000H+      = Al(OH)3 ;
-gamma      0.00      0.00      ; log_K      -16.4319      ; -analytical_expression
      91.66401813525 0      -11712.97320105170      -27.8112600743 0
+1.000Al+3      +1.000H2O      -1.000H+      = AlOH+2 ;
-gamma      4.00      0.0640      ; log_K      -4.95693      ; -analytical_expression
      34.57025049802 0      -869.70655319713      13.1464151225 0
+1.000Al(OH)4-      +1.000Si(OH)4      -1.000H2O      =
Al(OH)6SiO- ;      -gamma      4.00      0.0640      ; log_K      3.600009      ; -
analytical_expression 0.00000000000 0      1073.39477649456      0.00000000000 0
+1.000Al+3      +1.000SiO(OH)3-      = AlSiO(OH)3+2 ;      -gamma      4.00
0.0640      ; log_K      7.400086      ; -analytical_expression      0.00000000000 0
      2206.33554059029      0.00000000000 0
+1.000Ca+2      -1.000H+      +1.000HCO3-      = CaCO3 ;
-gamma      0.00      0.0      ; log_K      -7.10471      ; -analytical_expression
      18.67700851789 0      -2532.27825260820      -6.9868218332 0
+1.000Ca+2      +1.000HCO3-      = CaHCO3+ ;      -gamma      4.00
0.064      ; log_K      1.105633      ; -analytical_expression      -103.46104593645 0
      4604.38192941364      36.0178771810 0
+1.000Ca+2      +1.000SO4-2      = CaSO4 ;      -gamma      0.00      0.0640
      ; log_K      2.300088      ; -analytical_expression      -64.25337074408 0
      2770.03421100362      23.1418327719 0
+1.000Ca+2      +1.000H2O      -1.000H+      = CaOH+ ;
-gamma      4.00      0.064      ; log_K      -12.7798      ; -analytical_expression
      14.19214642856 0      -4635.48173840128      -4.6171091261 0
+1.000Ca+2      +1.000SiO(OH)3-      = CaSiO(OH)3+ ;      -gamma      4.00
0.064      ; log_K      1.200061      ; -analytical_expression      -88.10659232191 0
      3919.11589441343      30.7796851528 0
+1.000Ca+2      +1.000SiO2(OH)2-2      = CaSiO2(OH)2 ;      -gamma
0.00      0.0      ; log_K      4.600017      ; -analytical_expression      0.00003498360 0
      1371.64549038842      -0.0000120272 0
+1.000Fe+2      +1.000HCO3-      -1.000H+      = FeCO3 ;
-gamma      0.00      0.00      ; log_K      -5.94898      ; -analytical_expression
      16.83325757655 0      -1846.89625963213      -6.7038225945 0
+1.000Fe+2      +1.000HCO3-      = FeHCO3+ ;      -gamma      4.00      0.0640
      ; log_K      1.999985      ; -analytical_expression      -104.57077896404 0
      5270.65115685443      35.9245463653 0
+1.000Fe+2      +1.000H+      +1.000SO4-2      = FeHSO4+ ;
-gamma      4.00      0.0640      ; log_K      3.067952      ; -analytical_expression
      217.68294720087 0      9316.87298664815      76.5843086363 0
+1.000Fe+2      +1.000SO4-2      = FeSO4 ;      -gamma      0.00      0.00
      ; log_K      2.249983      ; -analytical_expression      -65.22644646497 0
      2644.89637498019      23.6844985453 0
+1.000Fe+2      +1.000Cl-      = FeCl+ ;      -gamma      4.00
0.0640      ; log_K      0.139978      ; -analytical_expression      -84.08990370509 0
      3692.01184090337      29.0358662146 0
+1.000Fe+2      +1.000H2O      -1.000H+      = FeOH+ ;
-gamma      4.00      0.0640      ; log_K      -9.49965      ; -analytical_expression
      7.35359137368 0      -2427.06600313247      2.4220308834 0
+1.000H+      +1.000SO4-2      +1.000Fe+3      = FeHSO4+2 ;
-gamma      4.00      0.0640      ; log_K      4.468082      ; -analytical_expression
      268.70278991437 0      13166.04041835980      92.5513349554 0
+1.000SO4-2      +1.000Fe+3      = FeSO4+ ;      -gamma      4.00
0.0640      ; log_K      4.040089      ; -analytical_expression      -61.88124256446 0
      2185.38358231463      23.6787255052 0
+2.000SO4-2      +1.000Fe+3      = Fe(SO4)2- ;      -gamma      4.00
0.0640      ; log_K      5.380128      ; -analytical_expression      -131.48050051289 0
      5443.75324149227      47.9311468746 0
+1.000Fe+2      -1.000e-      = Fe+3 ;      -gamma      9.00      0.0640
      ; log_K      -13.0201      ; -analytical_expression      6.52902464956 0
      2917.27751554918      -5.3251484453 0
+3.000H2O      -3.000H+      +1.000Fe+3      =
Fe(OH)3 ;      ; log_K      -12.5594      ; -analytical_expression      147.12395569469
      0      -13347.13553589500      -46.4423038760 0
+2.000H2O      -2.000H+      +2.000Fe+3      =
Fe2(OH)2+4 ;      -gamma      4.00      0.0640      ; log_K      -2.94948      ; -
analytical_expression 6.94584777011 0      -2950.65882826826      0.0000120272 0
+4.000H2O      -4.000H+      +3.000Fe+3      =
Fe3(OH)4+5 ;      -gamma      9.00      0.0640      ; log_K      -6.29892      ; -
analytical_expression 4.18235662859 0      -3125.11656793865      0.0000240543 0
+1.000Cl-      +1.000Fe+3      = FeCl+2 ;      -gamma      4.00
0.0640      ; log_K      1.480017      ; -analytical_expression      -72.69030177926 0
      3122.83931417149      25.7418657263 0

```

```

+2.000Cl-          +1.000Fe+3          = FeCl2+ ;      -gamma      4.00
0.0640 ; log_K      2.129977          ; -analytical_expression -215.95223084886      0
9794.48642498307      74.8585304486      0
+3.000Cl-          +1.000Fe+3          = FeCl3 ;      -gamma      0.00
0.0640 ; log_K      1.129985          ; -analytical_expression -285.45375024869      0
13355.40022646740      97.7088246932      0
+1.000H2O          -1.000H+          +1.000Fe+3          = FeOH+2 ;
-gamma      4.00      0.0640      ; log_K      -2.18961      ; -analytical_expression
16.59946235915      0      -2732.42292291182      -3.8894655247      0
+2.000H2O          -2.000H+          +1.000Fe+3          =
Fe(OH)2+ ;      -gamma      4.00      0.0640 ; log_K      -5.66961      ; -
analytical_expression 78.23475365977      0      -7306.78682417424      -24.0049022733      0
+4.000H2O          -4.000H+          +1.000Fe+3          = Fe(OH)4-
;      -gamma      4.00      0.0640 ; log_K      -21.5993      ; -analytical_expression
117.57797560593      0      -14082.57228041010      -37.1561282625      0
+1.000Fe+3          +1.000SiO(OH)3-      = FeSiO(OH)3+2 ;      -gamma      4.00
0.0640 ; log_K      9.699999      ; -analytical_expression      0.00006996720      0
2892.15594977973      -0.0000240543      0
+1.000K+          +1.000SO4-2          = KSO4- ;      -gamma      4.00      0.0640
; log_K      0.850029      ; -analytical_expression      -72.97654888147      0
3150.05834400053      25.5660285453      0
+1.000K+          +1.000H2O          -1.000H+          = KOH ;      -
gamma      0.00      0.00      ; log_K      -14.4597      ; -analytical_expression
55.77230945322      0      -5964.47470504443      -20.2983699581      0
+1.000Mg+2          -1.000H+          +1.000HCO3-      = MgCO3 ;
-gamma      0.00      0.00      ; log_K      -7.34928      ; -analytical_expression
17.81062888483      0      -2178.42833934954      -7.2149771905      0
+1.000Mg+2          +1.000HCO3-      = MgHCO3+ ;      -gamma      4.00
0.064 ; log_K      1.068142      ; -analytical_expression      -107.35949477825      0
4739.07110899493      37.3957094285      0
+1.000Mg+2          +1.000H2O          -1.000H+          = MgOH+ ;
-gamma      4.00      0.0640      ; log_K      -11.4397      ; -analytical_expression
27.03763638067      0      -2051.24072933459      9.0841192085      0
+1.000Mg+2          +1.000SO4-2          = MgSO4 ;      -gamma      0.00      0.00
; log_K      2.36999      ; -analytical_expression      -65.50267875609      0
2716.83921823504      23.7471600852      0
+1.000Mg+2          +1.000SiO(OH)3-      = MgSiO(OH)3+ ;      -gamma      4.00
0.0640 ; log_K      1.499989      ; -analytical_expression      -92.66274049892      0
4338.36419953797      32.1739946190      0
+1.000Mg+2          +1.000SiO2(OH)2-2      = MgSiO2(OH)2 ;      -gamma      0.00
0.00 ; log_K      5.700009      ; -analytical_expression      0.00003498360      0
1699.67075541936      -0.0000120272      0
+1.000Na+          -1.000H+          +1.000HCO3-      = NaCO3- ; -
gamma      4.00      0.0640      ; log_K      -9.05897      ; -analytical_expression
8.57582729935      0      -417.55748897161      -6.5608195793      0
+1.000Na+          +1.000HCO3-      = NaHCO3 ;      -gamma      0.00      0.00
; log_K      -0.25      ; -analytical_expression      -69.04984593286      0
3027.60721771434      23.7006149490      0
+1.000Na+          +1.000SO4-2          = NaSO4- ;      -gamma      4.00
0.0640 ; log_K      0.700065      ; -analytical_expression      -67.94698554238      0
2908.64969369569      23.8000796198      0
+1.000Na+          +1.000H2O          -1.000H+          = NaOH ;
-gamma      0.00      0.00      ; log_K      -14.1797      ; -analytical_expression
40.02241563584      0      -4902.58161996995      -15.2600694449      0
+1.000Si(OH)4          -1.000H+          = SiO(OH)3- ;      -gamma      4.00
0.064 ; log_K      -9.80974      ; -analytical_expression      67.70633238796      0
4741.99183185177      -24.8993626804      0
+1.000Si(OH)4          -2.000H+          = SiO2(OH)2-2 ;      -gamma      4.00
0.064 ; log_K      -23.1397      ; -analytical_expression      -10.00067913457      0
-3917.49762695022      0.0000120272      0
+1.000H+          -1.000H2O          +1.000HCO3-      = CO2 ;
-gamma      0.00      0.0      ; log_K      6.351807      ; -analytical_expression
118.94289041477      0      6009.06305396012      42.4908984414      0
-1.000H+          +1.000HCO3-      = CO3-2 ;      -gamma      5.40
0.064 ; log_K      -10.3289      ; -analytical_expression      81.27367428255      0
4731.00208183675      -30.6072155785      0
+1.000HCO3-      +9.000H+          +8.000e-      -3.000H2O
= CH4 ;      -gamma      0.00      0.0 ; log_K      27.8481      ; -analytical_expression
177.87782773202      0      21721.88220712880      64.7294909742      0
+1.000NH4+          -1.000H+          = NH3 ;      -gamma      0.00      0.00
; log_K      -9.23697      ; -analytical_expression      -3.59831980108      0
2549.62881993208      1.1769785592      0
+1.000NO3-      +10.000H+          +8.000e-      -3.000H2O
= NH4+ ;      -gamma      2.50      0.0640 ; log_K      119.1361      ; -
analytical_expression -116.84941401789      0      46557.19607874130      43.2967186280      0

```

```

+2.000NO3-          +12.000H+          +10.000e-          -6.000H2O
= N2 ;      -gamma      0.00      0.00 ; log_K      207.2662      ; -analytical_expression
      -275.27055430258      0      81299.07928897020      98.6135081923 0
+2.000SO4-2          +10.000H+          +8.000e-          -5.000H2O
= S2O3-2 ;      -gamma      4.00      0.0640 ; log_K      38.01267      ; -
analytical_expression -214.77995703953      0      24017.66212043470      80.6443193886 0

+1.000H+          +1.000SO3-2          = HSO3- ;      -gamma      4.00
0.0640 ; log_K      7.219989      ; -analytical_expression      -87.59223471343      0
      3812.55224613743      33.1491573165 0
+1.000SO4-2          +2.000H+          +2.000e-          -1.000H2O
= SO3-2 ;      -gamma      4.50      0.0640 ; log_K      -3.39725      ; -
analytical_expression -20.01098159798      0      1624.20845779751      7.2712643319 0

+1.000H+          +1.000SO4-2          = HSO4- ;      -gamma      4.00
0.0640 ; log_K      1.987722      ; -analytical_expression      -95.44960727141      0
      3428.44243310458      34.7309703157 0
+1.000HS-          +1.000H+          = H2S ;      -gamma      0.00      0.00
; log_K      6.989962      ; -analytical_expression      -92.54543936710      0
      5444.49694476074      32.8459524374 0
+1.000SO4-2          +9.000H+          +8.000e-          -4.000H2O
= HS- ;      -gamma      3.50      0.0640 ; log_K      33.68888      ; -
analytical_expression -148.49636393000      0      20433.96976138830      56.9613843750 0

+1.000HS-          -1.000H+          = S-2 ;      -gamma      5.00      0.0640
; log_K      -19      ; -analytical_expression      0.00001044666 0      -
5667.31548660147      0.0000000000 0
+1.000H2O          -1.000H+          = OH- ;      -gamma      10.65      0.064
; log_K      -13.9998      ; -analytical_expression      69.84779493355 0      -
6215.12596863142      -25.4612719210 0
+2.000H+          +2.000e-          = H2 ;      -gamma      0.00      0.0
; log_K      -3.10597      ; -analytical_expression      -55.35493262717      0
      2808.32060172984      20.0675686240 0
+2.000H2O          -4.000H+          -4.000e-          = O2 ;
-gamma      0.00      0.0      ; log_K      -85.9855      ; -analytical_expression      -
30.79426700990 0      -27925.53838584180      10.0321005086 0

```

PHASES

```

CH4(g) ;      CH4          = +1.000CH4          ; log_K
      -2.8565 ; -analytical_expression      -89.63393582234      0      4440.29675525994
      29.0478933816 0
CO2(g) ;      CO2          = +1.000H+          -1.000H2O
+1.000HCO3-          ; log_K      -7.81956      ; -analytical_expression
      41.87683954485 0      -1740.14204852581      -17.7229926959 0
H2(g) ;      H2          = +1.000H2          ; log_K      -3.10597
; -analytical_expression      -52.09936672097      0      2359.52736654890
      16.6015796481 0
O2(g) ;      O2          = +1.000O2          ; log_K      -2.8812 ; -
analytical_expression -76.67437063690      0      3828.93234444672      24.6329609322 0

H2S(g) ;      H2S          = +1.000HS-          +1.000H+ ; log_K      -
8.00993 ; -analytical_expression      37.63799849734 0      -2225.98872774971      -
15.4105293036 0
N2(g) ;      N2          = +1.000N2          ; log_K      -3.18743      ; -
analytical_expression -76.72711536033      0      3734.51086475577      24.6580977111 0

SiO2am ; SiO2 + 1OH- + 1H2O = SiO(OH)3- ; log_K      1.475988      ; -
analytical_expression -2.14181238156 0      664.05554528339      0.5620295123 0 ; -Vm 29

CSHtob1 ; (CaO)2(SiO2)2.4(H2O)3.2 + 1.2 H2O = 2 Ca++ + 2.4 SiO(OH)3- + 1.6OH- ; log_K
      -19.1991      ; -analytical_expression      240.84653128714      0      -
13954.21726608490      -86.1775378224 0 ; -Vm 141
CSHjen ; (CaO)1.666667(SiO2)(H2O)2.1 + 0.566667 H2O = 1.666667Ca++ + SiO(OH)3- + 2.333334OH-
; log_K      -13.1659      ; -analytical_expression      211.28870953694      0
      -10574.51261009040      -76.3734723995 0 ; -Vm 78
CSHtob2 ; (CaO)0.83333(SiO2)(H2O)1.3333 + 0.50003H2O = 0.83333Ca++ + SiO(OH)3- + 0.66666OH-
; log_K      -8.0014 ; -analytical_expression      100.35344189250      0      -
5814.81586527851      -35.9075880599 0 ; -Vm 59
C2AH8 ; Ca2Al2(OH)10:3H2O = 2Ca++ + 2Al(OH)4- + 2OH- + 3H2O; log_K      -13.5622      ; -
analytical_expression 154.48530223981      0      -8994.12914254083      -55.7212631893 0

```

C2FH8 ; Ca2Fe2(OH)10:3H2O = 2Ca++ + 2Fe(OH)4- + 2OH- + 3H2O; log_K -17.602 ; -
 analytical_expression 299.40318587869 0 -18138.64886929690 -103.5235991057
 0
 hydrogarnetOH ; Ca3Al2(OH)12 = 3Ca++ + 2Al(OH)4- + 4OH- ; log_K -20.8411 ; -
 analytical_expression 291.27318390754 0 -13720.16812376770 -107.5364633634
 0
 hydrogarnetFe ; Ca3Fe2(OH)12 = 3Ca++ + 2Fe(OH)4- + 4OH- ; log_K -25.158 ; -
 analytical_expression 437.20835028023 0 -23213.52271974500 -155.3909971844
 0
 C4AH13 ; Ca4Al2(OH)14:6H2O = 4Ca++ + 2Al(OH)4- + 6OH- + 6H2O ; log_K -25.4033
 ; -analytical_expression 407.04628084006 0 -21037.51384617330 -
 146.2503502912 0
 C4FH13 ; Ca4Fe2(OH)14:6H2O = 4Ca++ + 2Fe(OH)4- + 6OH- + 6H2O ; log_K -29.4028
 ; -analytical_expression 552.15552475835 0 -30178.01620624420 -
 194.1184748109 0
 Ettringite ; Ca6Al2(SO4)3(OH)12:26H2O = 6Ca++ + 2Al(OH)4- + 3SO4-- + 4OH- + 26H2O; log_K
 -44.9085 ; -analytical_expression 529.27779378424 0 -
 34439.99676380200 -185.3386429266 0 ; -Vm 707
 tricarboaluminate ; Ca6Al2(CO3)3(OH)12:26H2O = 6Ca++ + 2Al(OH)4- + 3CO3-- + 4OH- + 26H2O ;
 log_K -46.5085 ; -analytical_expression 526.28378030499 0 -
 32615.50770370250 -187.2629896410 0 ; -Vm 650
 Fe-ettringite ; Ca6Fe2(SO4)3(OH)12:26H2O = 6Ca++ + 2Fe(OH)4- + 3SO4-- + 4OH- + 26H2O ;
 log_K -44.0084 ; -analytical_expression 674.03730619220 0 -
 42106.04906255390 -233.0864957767 0
 monosulfoaluminate ; Ca4Al2(SO4)(OH)12:6H2O = 4Ca++ + 2Al(OH)4- + SO4-- + 4OH- + 6H2O ;
 log_K -29.2628 ; -analytical_expression 404.92625454716 0 -
 21017.60772698490 -146.9719803091 0
 Fe-monosulfate ; Ca4Fe2(SO4)(OH)12:6H2O = 4Ca++ + 2Fe(OH)4- + SO4-- + 4OH- + 6H2O; log_K
 -33.2028 ; -analytical_expression 549.68566248846 0 -
 30126.34439200350 -194.7198331591 0
 stratlingite ; Ca2Al2SiO2(OH)10:3H2O = 2Ca++ + 2Al(OH)4- + 1SiO(OH)3- + OH- + 2H2O; log_K
 -19.7042 ; -analytical_expression 148.95692659946 0 -
 9589.95690828914 -55.1593539487 0
 Fe-stratlingite ; Ca2Fe2SiO2(OH)10:3H2O = 2Ca++ + 2Fe(OH)4- + 1SiO(OH)3- + OH- + 2H2O ;
 log_K -23.702 ; -analytical_expression 293.87516007432 0 -
 18722.47854424510 -102.9618101367 0
 hemicarboaluminate ; Ca4Al2(CO3)0.5(OH)13:5.5H2O = 4Ca++ + 2Al(OH)4- + 0.5CO3-- + 5OH- +
 5.5H2O ; log_K -29.1327 ; -analytical_expression 411.51063104013 0
 -21526.38118104660 -148.8963270235 0
 Fe-hemicarboaluminate ; Ca4Fe2(CO3)0.5(OH)13:5.5H2O = 4Ca++ + 2Fe(OH)4- + 0.5CO3-- + 5OH- + 5.5H2O
 ; log_K -33.1027 ; -analytical_expression 556.27003898143 0
 -30644.51984410740 -196.6441798735 0
 monocarboaluminate ; Ca4Al2(CO3)(OH)12:5H2O = 4Ca++ + 2Al(OH)4- + CO3-- + 4OH- + 5H2O ;
 log_K -31.4726 ; -analytical_expression 419.54622572991 0 -
 22668.16504663430 -151.5423037557 0 ; -Vm 262
 Fe-monocarbonate ; Ca4Fe2(CO3)(OH)12:5H2O = 4Ca++ + 2Fe(OH)4- + CO3-- + 4OH- + 5H2O ;
 log_K -35.5 ; -analytical_expression 554.47107047792 0 -
 31715.13432703260 -195.43556986521 0
 hydrotalliceOH ; Mg4Al2(OH)14:3H2O = 4Mg++ + 2Al(OH)4- + 6OH- + 3H2O ; log_K -
 56.0214 ; -analytical_expression 354.74992257809 0 -22738.24127204280 -
 135.1853566837 0
 hydrotalciteFe ; Mg4Fe2(OH)14:3H2O = 4Mg++ + 2Fe(OH)4- + 6OH- + 3H2O ; log_K -
 60.002 ; -analytical_expression 499.50943498605 0 -31856.37993510370 -
 182.9332095337 0
 CAH10 ; CaAl2(OH)8:6H2O = Ca++ + 2Al(OH)4- + 6H2O ; log_K -7.50282 ; -
 analytical_expression 19.33995799190 0 -4170.78109558596 -5.1912860770 0
 hydrogarnetSi ; Ca3Al2(SiO4)0.8(OH)8.8 + 2.4H2O = 3Ca++ + 2Al(OH)4- + 0.8 SiO(OH)3- + 3.2OH-
 ; log_K -29.8707 ; -analytical_expression 305.23780762563 0
 -16550.88410201760 -112.9922268420 0
 hydrotalciteC ; Mg4Al2(OH)12CO3:3H2O = 4Mg++ + 2Al(OH)4- + CO3-- + 4OH- + 3H2O ; log_K
 -51.142 ; -analytical_expression 358.37159560480 0 -21030.32915266930
 -136.9894317284 0
 syngenite ; K2Ca(SO4)2H2O = 2K+ + 1Ca++ + 2SO4-- + 1H2O ; log_K -7.2003 ; -
 analytical_expression 256.44664476696 0 -12598.84393306150 -89.4698545074 0

 Al(OH)3am ; Al(OH)3 = Al(OH)4- - 1OH- ; log_K 0.239427 ; -
 analytical_expression -48.08001615409 0 1546.32359095493 17.4322960704 0

 Fe(OH)3mic ; Fe(OH)3 = Fe(OH)4- - 1OH- ; log_K -4.60039 ; -
 analytical_expression 2.49263607431 0 -2892.86085047996 1.0555041728 0
 Calcite ; CaCO3 = +1.000Ca+2 -1.000H+
 +1.000HCO3- ; log_K 1.84897 ; -analytical_expression 49.00173153277 0 -
 958.45338123134 -17.7571498501 0 ; -Vm 37
 Portlandite ; Ca(OH)2 = +1.000Ca+2 +2.000H2O
 -2.000H+ ; log_K 22.79937 ; -analytical_expression -11.29923807115
 0 7303.68926279255 3.8839330279 0 ; -Vm 33

```

Anhydrite ; CaSO4 = +1.000Ca+2 +1.000SO4-2 ; log_K
-4.35754 ; -analytical_expression 131.22651283827 0 -
5228.78943438100 -47.7070807540 0 ; -Vm 46
Gypsum ; CaSO4:2H2O = +1.000Ca+2 +1.000SO4-2
+2.000H2O ; log_K -4.58147 ; -analytical_expression 111.52942046684
0 -5116.92285811085 -39.9882855394 0 ; -Vm 75
Hematite ; Fe2O3 = +3.000H2O -6.000H+
+2.000Fe+3 ; log_K 1.118973 ; -analytical_expression -11.36089784168
0 6572.14422725869 -3.8633665724 0
Brucite ; Mg(OH)2 = +1.000Mg+2 +2.000H2O -
2.000H+ ; log_K 16.83953 ; -analytical_expression -21.32005009039 0
6781.89650685512 6.2277873260 0 ; -Vm 25
Thaumasite ; (CaSiO3)2(CaSO4)2(CaCO3)2(H2O)30= 6.000 Ca+2 + 2 SiO(OH)3- + 2 CO3-2 + 2 SO4-2
+ 2 OH- + 26 H2O ; log_K -49.4078983 ; -analytical_expression
596.55829677308 0 -37214.18686948530 -210.5956935526 0
Friedelsalt ; Ca4Al2(OH)12.05Cl11.95:4H2O = 4 Ca++ + 2 Al(OH)4- + 1.95 Cl- + 4.05 OH- + 4H2O
; log_K -27.692843 ; -analytical_expression 413.03838067185 0
-22279.48905923220 -149.0165986931 0
Kuzelsalt ; Ca4Al2(SO4)0.5Cl(OH)12:6H2O = 4 Ca++ + 2 Al(OH)4- + Cl- + 0.5 SO4-- + 4 OH- +
6H2O ; log_K -28.5156699 ; -analytical_expression 399.05535884030 0
-27160.47627456530 -144.0854602376 0

```

#CSHQ model of Kulik - only 25°C

#from Table 6

CSHQ_TobH

(CaO)0.66666667(SiO2)1(H2O)1.5 = 0.66666667Ca++ + 1 SiO(OH)3- + 0.33333334OH- -0.16666667 H2O

log_K -6.190832

CSHQ_TobD

(CaO)0.8333333333(SiO2)0.6666666667(H2O)1.8333333333 = 0.8333333333 Ca++ + 0.6666666667 SiO(OH)3- + 0.9999999990 OH- + 0.3333333333 H2O

log_K -6.8995533

CSHQ_JenH

(CaO)1.3333333333(SiO2)1(H2O)2.1666666667 = 1.3333333333 Ca++ + 1 SiO(OH)3- + 1.6666666667 OH- -0.1666666667 H2O

log_K -10.96765

CSHQ_JenD

(CaO)1.5(SiO2)0.6666666667(H2O)2.5 = 1.5 Ca++ + 0.6666666667 SiO(OH)3- + 2.3333333333 OH- + 0.3333333333 H2O

log_K -10.47635

#CSH3T model of Kulik - only 25°C

#from Table 5

CSH3T_TobH

(CaO)(SiO2)1.5(H2O)2.5 = Ca++ + 1.5 SiO(OH)3- + 0.5OH- log_K -9.186248

CSH3T_T5C

(CaO)1.25(SiO2)1.25(H2O)2.5 = 1.25 Ca++ + 1.25 SiO(OH)3- + 1.25 OH- log_K -11.6253

CSH3T_T2C

(CaO)1.5(SiO2)(H2O)2.5 = 1.5 Ca++ + SiO(OH)3- + 2 OH- log_K -12.54436

Appendix 2 - Example input file phreeqc

```
#Case 1 - sample 104 - pH 7.5, Kuzelsalt

SOLUTION_MASTER_SPECIES
Nit-          Nit-          0.0          Nit-          14  #  1
Amm+          Amm+          0.0          Amm+          14  #  1
SOLUTION_SPECIES
Nit- = Nit-
  log_k        0.0
  -gamma       3.00      0.064

Amm+ = Amm+
  log_k        0.0
  -gamma       2.50      0.0640
PHASES
Na2O
Na2O + 2H+ = 2 Na+ + H2O
Log_k 24.94

K2O
K2O + 2H+ = 2 K+ + H2O
log_k 25.71

end
solution 1001
SELECTED_OUTPUT 1000
  -file CalculateVolume.prn; -reset false; -high_precision true
include$ punchforvolumes.txt
end

Selected_output 1000
-active false

include$ CalculateVolume.prn

USER_PRINT
-start
5 vol = 0
10 a=sys("phases",count,namepp$,type$,moles)
20 gosub 1000
30 a=sys("s_s",count,namepp$,type$,moles)
35 print "solid solution" count
36 if count>0 then print namepp$[1] type$[1]
40 gosub 2000
990 end

1000 for i=1 to count
1050 n$ = namepp$[i]
1060 nvolf$ = "Volume" + n$
1070 if(equi(n$) > 0.0) then vol=vol+CALC_VALUE(nvolf$)
1100 if(equi(n$) > 0.0) then PRINT n$ nvolf$ equi(n$) CALC_VALUE(nvolf$) vol
1900 next i
1990 return

2000 for i=1 to count
2050 n$ = namepp$[i]
2060 nvolf$ = "Volume" + n$
2070 if(s_s(n$) > 0.0) then vol=vol+CALC_VALUE(nvolf$)
2100 if(s_s(n$) > 0.0) then PRINT n$ nvolf$ s_s(n$) CALC_VALUE(nvolf$) vol
2900 next i
2990 return

-end

PRINT
  -species          false
  -warnings         -1

solution 10
-units g/l
O(0) 0.02
```

```

-density 1
-water 0.175
-temp 25

equilibrium_phases 10
#Na2O 0 0
#K2O 0 0
#fm-phases
  CAH10 0 0
#hydrotalictite
  hydrotalciteC 0 0
#other minerals
  calcite 0 0
  portlandite 0 0
  gypsum 0 0
  anhydrite 0 0
  brucite 0 0
  Al(OH)3am 0 0
  SiO2am 0 0
monocarboaluminate 0 0
hemicarboaluminate 0 0
stratlingite 0 0
C2AH8 0 0
hydrotalictiteOH 0 0
hydrogarnetOH 0 0
#Friedelsalt 0 0
Kuzelsalt 0 0

solid_solutions 10

# C-S-H

Tob_jen_ss
-comp CSHjen 0
-comp CSHTob2 0

#non ideal SS
AFm_ns
-comp2 C4AH13 0
-comp1 monosulfoaluminate 0
-Gugg_nondim 0.188 2.49

AFt_ns
-comp1 Ettringite 0
-comp2 tricarboaluminate 0
-Gugg_nondim -0.823 2.82

#composition of CEM II De Weerd et al, 2011 : 80% Clinker, 20% FA - fully reacted
Reaction 10
CaO 3.423652892
SiO2 1.670319867
Al2O3 0.344504271
MgO 0.262413037
CO2 0.199433333
SO3 0.061709707
Gypsum 0.083923768
1
save solution 1
save solid_solutions 1
save equilibrium_phases 1

end

use solid_solutions 1

use equilibrium_phases 1
#Calculate composition based on sample 104 - pH 6.7 - Al, C and C in equilibrium with some
minerals
#Calculated with phreeqc.dat
#
# Al 4.229e-08 4.229e-08 Equilibrium with Kaolinite
# C 4.969e-04 4.969e-04 Equilibrium with Calcite
# Ca 4.700e-02 4.700e-02
# Cl 5.460e-01 5.460e-01
# Fe 2.970e-04 2.970e-04

```



```

#      K      1.595e-02  1.595e-02
#      Mg     5.170e-02  5.170e-02
#      Na     4.430e-01  4.430e-01
#      S      6.500e-02  6.500e-02
#      Si     9.072e-05  9.072e-05  Equilibrium with Quartz
Solution 0 sample 104
pH 7.5
-unit mol/kgw
-temp 25
Al      4.229e-08
C       4.969e-04
Ca      4.700e-02
Cl      5.460e-01
Fe      2.970e-04
K       1.595e-02
Mg      5.170e-02
Na      4.430e-01
S       6.500e-02
Si      9.072e-05
-water 0.01

Solution 1 sample 104
pH 7.5
-unit mol/kgw
-temp 25
Al      4.229e-08
C       4.969e-04
Ca      4.700e-02
Cl      5.460e-01
Fe      2.970e-04
K       1.595e-02
Mg      5.170e-02
Na      4.430e-01
S       6.500e-02
Si      9.072e-05
end

ADVECTION
-cells 1
-shifts 250
-time_step 0.01 # seconds
-warnings true
-print_frequency 100

selected_output
-reset false
-ionic_strength true
-file OperaCasel.pse
-high_precision true

user_punch
-headings cum_water pH Ca Si C Mg Al S Na K Na2O K2O cal port C2A C4A hydrogar strat
moncarbo hemicarbo gyp hydrotal hydrotalC Al anhy bruc Si tob2 jen C4AH13 monosulfo ett
tricarbo por Cl Friedel Kuzelsolid
-start
10 PUNCH total_time
20 PUNCH -log10(act("H+"))
30 PUNCH tot("Ca") tot("Si") tot("C") tot("Mg") tot("Al") tot("S") tot("Na") tot("K")
40 PUNCH equi("Na2O") equi("K2O") equi("calcite") equi("Portlandite")
50 PUNCH equi("C2AH8") equi("CAH10") equi("hydrogarnetOH")
60 PUNCH equi("stratlingite") equi("monocarboaluminate") equi("hemicarboaluminate")
70 PUNCH equi("gypsum") equi("hydrotalceOH") equi("hydrotalciteC") equi("Al(OH)3am")
75 punch equi("anhydrite") equi("brucite") equi("SiO2am")
80 PUNCH S_S("CSHtob2") S_S("CSHjen") S_S("C4AH13") S_S("monosulfoaluminate")
S_S("ettringite") S_S("tricarboaluminate")

#cal por
500 vol = 0
510 a=sys("phases",count,namepp$,type$,moles)
520 gosub 1000
530 a=sys("s_s",count,namepp$,type$,moles)
540 gosub 2000
550 punch vol

920 update = (1000-vol)/1000
930 punch tot("Cl") equi("Friedelsalt") equi("Kuzelsalt")

```

```

990 end

1000 for i=1 to count
1050  n$ = namepp$(i)
1060  nvol$ = "Volume" + n$
1070  if(equi(n$) > 0.0) then vol=vol+CALC_VALUE(nvol$)
# 1100  if(equi(n$) > 0.0) then PRINT n$ nvol$ equi(n$) CALC_VALUE(nvol$) vol
1900 next i
1990 return

2000 for i=1 to count
2050  n$ = namepp$(i)
2060  nvol$ = "Volume" + n$
2070  if(s_s(n$) > 0.0) then vol=vol+CALC_VALUE(nvol$)
#2100  if(s_s(n$) > 0.0) then PRINT n$ nvol$ s_s(n$) CALC_VALUE(nvol$) vol
2900 next i
2990 return

-end

end
Solution 0 sample 104
pH 7.5
-unit mol/kgw
-temp 25
Al          4.229e-08
C           4.969e-04
Ca          4.700e-02
Cl          5.460e-01
Fe          2.970e-04
K           1.595e-02
Mg          5.170e-02
Na          4.430e-01
S           6.500e-02
Si          9.072e-05
-water 0.1
ADVECTION
  -cells 1
  -shifts 1000
  -time_step 0.1 # seconds
  -warnings true
  -print_frequency 10
end
Solution 0 sample 104
pH 7.5
-unit mol/kgw
-temp 25
Al          4.229e-08
C           4.969e-04
Ca          4.700e-02
Cl          5.460e-01
Fe          2.970e-04
K           1.595e-02
Mg          5.170e-02
Na          4.430e-01
S           6.500e-02
Si          9.072e-05
-water 1
ADVECTION
  -cells 1
  -shifts 900
  -time_step 1 # seconds
  -warnings true
  -print_frequency 10
end

```

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