Long-term ageing of concrete structures in Finnish rock caverns as application facilities for low- and intermediate-level nuclear waste

Olli-Pekka Kari

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Olli-Pekka Kari

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Abstract

In the Finnish disposal concept concrete-made engineered barriers ensuring the safety of low- and intermediate-level waste repositories in rock caverns are designed to remain serviceable for hundreds of years. With regard to the ageing of the concrete, the lifetime of the disposal facilities will be divided into the periods before and after the closing of the caverns, when the concrete will be exposed to two different sets of environmental conditions.

The research pointed out that the ageing of concrete in the disposal conditions is a complex physiochemical phenomenon that cannot be predicted by diffusion models based only on Fick's second law for periods considerably exceeding the period covered experimentally. A thermodynamic model, which considers ion-ion and ion-cement hydrate interactions as well as the properties of the gas phase in multi-ionic transport in concrete, was introduced in the study. A statistical methodology was presented for evaluating the effect of uncertainties on the results.

A range of experimental data extracted from sulphate-resistant Portland cement concretes exposed to natural carbonation or the penetration of aggressive substances under submersion for 13 years in a controlled environment was used for evaluating the thermodynamic model. The theory of the model was shown to give a plausible basis for estimating the long-term ageing phenomena of concretes, particularly in practical applications where the design periods of structures are hundreds of years. The thermodynamic simulation method also makes it possible to observe the latent factors involved in the deterioration of the concrete. The method considered is general and can be applied to different concrete mixes by defining their case-specific initial values.

Generally, the sulphate-resistant type of concrete with a water-to-cement ratio of 0.43 performed satisfactorily during the simulated period of 500 years, but the initiation of the corrosion of the steel reinforcement cannot be excluded. The leaching of calcium-bearing components from the concrete affects the strength of the concrete. However, the main detrimental reactions of the concrete take place at a depth of less than 50 millimetres from the exposed surface, which is typically a relatively small part of the whole structural thickness and, especially, of the total set of multiple technical barriers.

Statistical analyses of the factors and the consideration of uncertainties in the simulation results can be used for improving the reliability of the thermodynamic model. The role of the aggregates in the deterioration of the concrete should also be evaluated in the future and more sophisticated models for the alteration of calcium silicate hydrate are necessary if the timescale is significantly extended beyond 500 years.

Keywords simulation, concrete, deterioration, ion-cement hydrate interaction

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Kalliotilassa olevan betonirakenteen pitkäaikaissäilyvyys sovelluksena suomalaisen matala- ja keskiaktiivisen ydinjätteen loppusijoitus

Julkaisija Insinööritieteiden korkeakoulu**Yksikkö** Rakennustekniikan laitos**Sarja** Aalto University publication series DOCTORAL DISSERTATIONS 9/2015**Tutkimusala** Talonrakennustekniikka**Käsikirjoituksen pvm** 18.08.2014**Väitöspäivä** 27.02.2015**Julkaisuluvan myöntämispäivä** 20.10.2014**Kieli** Englanti☐ **Monografia**☒ **Yhdistelmäväitöskirja (yhteenvedo-osa + erillisartikkelit)****Tiivistelmä**

Suomalaisessa loppusijoituskonseptissa matala- ja keskiaktiiviset ydinjätteet sijoitetaan kalliotiloihin, joissa ovat betonirakenteiset vapautumisesteet suunnitellaan useiden satojen vuosien käyttöä varten. Betonirakenteen ikääntymistä voidaan ajallisesti tarkastella tilojen sulkemista edeltävänä ja sen jälkeisenä ajanjaksona. Ympäristöolosuhteet eroavat ajanjaksoilla toisistaan altistaen rakenteen erilaisille ikääntymisilmiöille.

Tutkimuksessa osoitettiin ikääntymisilmiöiden olevan fysikaalisesti ja kemiallisesti monimutkaisia hallittaviksi ainoastaan Fick:n toiseen lakiin perustuvilla diffuusiomalleilla, mikäli tarkasteltava ajanjakso on merkittävästi pidempi kuin kokeellisesti katettu ajanjakso. Tutkimuksessa sovellettu termodynaaminen malli ottaa huomioon sekä ionien että sementti-hydraattien välisen vuorovaikutuksen aineiden kulkeutuessa kaasu- ja nestefaasissa ympäristöstä betonirakenteeseen. Mallin epävarmuuksien arvioimiseksi esitettiin tilastollinen menetelmä.

Termodynaamisen mallin kelpoisuutta arvioitiin monipuolisilla laboratoriokokeilla. Kokeissa käytettiin sulfaatinkestävästä sementistä valmistettuja betonikoekappaleita, jotka olivat altistuneet 13 vuoden ajan kontrolloidusti joko ilmasäilytyksessä tapahtuvalle karbonatisoitumiselle tai liuossäilytyksessä aggressiivisten ionien tunkeutumiselle. Mallin osoitettiin olevan teoreettisesti uskottava arvioitaessa betonirakenteen ikääntymistä erityisesti sovelluksissa, joiden suunniteltu käyttöikä on useita satoja vuosia. Mallilla voidaan lisäksi tunnistaa jo suunnitteluvaiheessa betonin turmeltumiseen vaikuttavia piileviä tekijöitä. Kehitetty termodynaamiseen lähestymistapaan perustuva malli on yleinen ja sitä voidaan soveltaa eri betonilaaduille määrittämällä kokeellisesti niille ominaiset alkuarvot.

Tarkasteltu sulfaatinkestävästä sementistä valmistettu betoni, jonka vesi-sementtisuhte oli 0.43, suoriutui kohtuullisesti simuloidusta 500 vuoden ajanjaksosta ydinjätteiden loppusijoitustilojen rakenteena. Betoniterästen korroosiota ei kuitenkaan voida sulkea pois. Kalsiumia sisältävien komponenttien liukeneminen sementtipastasta vaikuttaa myös betonin lujuuteen tarkasteluajanjaksolla. Laskentatulosten perusteella turmeltumisilmiöt tapahtuvat kuitenkin alle 50 millimetrin syvyydellä altistuspinnasta, mitä voidaan pitää vähäisenä suhteessa betonirakenteiden vapautumisesteiden kokonaispaksuuteen.

Tilastollisia menetelmiä eri osatekijöistä ja epävarmuuksista voidaan käyttää mallin luotettavuuden kehittämisessä. Kiviaineksen merkitystä betonin vaurioitumiseen tulisi edelleen arvioida. Mikäli simuloitava ajanjakso on merkittävästi pidempi kuin 500 vuotta, on tarpeen kehittää kalsium-silikaatti-hydraattien liukenemiskäyttäytymisen mallinnusta.

Avainsanat simulaatio, betoni, turmeltuminen, ionien ja sementti-hydraattien vuorovaikutus**ISBN (painettu)** 978-952-60-6051-4**ISBN (pdf)** 978-952-60-6052-1**ISSN-L** 1799-4934**ISSN (painettu)** 1799-4934**ISSN (pdf)** 1799-4942**Julkaisupaikka** Helsinki**Painopaikka** Helsinki**Vuosi** 2015**Sivumäärä** 144**urn** <http://urn.fi/URN:ISBN:978-952-60-6052-1>

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December 17, 2014

Olli-Pekka Juhani Kari

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List of abbreviations and symbols

List of abbreviations

AFm	Aluminium monosulphate, $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-mono}$
Aft	Aluminium trisulphate, $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-tri}$
BJH	Barrett-Joynet-Halenda method
C/S	CaO-to-SiO ₂ ratio
C ₂ S	Dicalcium silicate, $2\text{CaO}\cdot\text{SiO}_2$
C ₃ S	Tricalcium silicate, $3\text{CaO}\cdot\text{SiO}_2$
C ₃ A	Tricalcium aluminate, $3\text{CaO}\cdot\text{Al}_2\text{O}_3$
C ₄ AF	Tetracalcium aluminoferrite, $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$
$\bar{\text{C}}$	Carbon dioxide, CO ₂
CH	Calcium hydroxide
C-S-H	Calcium silicate hydrate
DDL	Diffuse double layer
EDL	Electrical double layer
EDS	Energy dispersive X-ray analyser
HCP	Hydrated cement paste
IHP	Inner Helmholtz plane
ILW	Intermediate-level waste
ITZ	Interfacial transition zone
LLW	Low-level waste
MCD	Multi-component diffusion
MIP	Mercury intrusion porosimetry
M-S-H	Magnesium silicate hydrate
OHP	Outer Helmholtz plane

OPC	Ordinary Portland cement
RCM	Rapid chloride migration
RH	Relative humidity
$\overline{S}$	Sulphur trioxide, SO_3
SEM	Scanning electron microscope
SiOH	Silanol sites
SRPC	Sulphate-resistant Portland cement
T	Temperature
TG/DTA	Thermogravimetric and differential thermal analysis
w/c	Water-to-cement ratio
XRD	X-ray diffraction

List of symbols

A	specific surface area [m^2/g] or temperature-dependent coefficient for Debye-Hückel activity model [-]
a_i	activity of ion i [-] or ion-specific fitting parameter [-]
B	temperature-dependent coefficient for Debye-Hückel activity model [-]
b_i	ion-specific fitting parameter [-]
$c_{DDL,i}$	concentration of ion in the DDL [mol]
c_i	concentration of ion [mol]
C_i	initial content of ion [% by mass of concrete]
C_s	calculated content of ion at the exposed surface [% by mass of concrete]
C_x	content of ion at the average depth x [m] after the exposure time t [s] [% by mass of concrete]
$D_{e,i}$	effective diffusivity [m^2/s]
D_{go}	diffusivity of CO_2 in free atmosphere [m^2/s]
D_{nss}	diffusion coefficient of ion [m^2/s]
D_{nssm}	non-steady-state chloride migration coefficient [m^2/s]
$D_{p,i,j}$	pore water diffusivity [m^2/s]
$D_{w,cl}$	diffusion coefficient of chlorides in water [m^2/s]
$D_{w,i,j}$	diffusion coefficient in pore solution [m^2/s]

$erf(x)$	complementary error function [-]
F	Faraday constant [C/mol]
J_i	flux of a species i [mol/m ² /s]
k	empirical coefficient describing the speed of carbonation [mm/√year]
K	thermodynamic equilibrium constant at a given temperature T [K]
k_a	empirical coefficient describing the speed of accelerated carbonation [mm/√year]
K_g	constant of Henry's law for the gas component [atm]
k_n	empirical coefficient describing the speed of natural carbonation [mm/√year]
K_p	thermodynamic equilibrium constant for the phase p [-]
$\log K$	equilibrium constant [-]
n	total number of ionic species i in aqueous solution [-]
$n_{i,g}$	stoichiometric coefficient of species in the dissolution equation [-]
$n_{i,p}$	stoichiometric coefficient of ion i in the phase p [-]
P_g	partial pressure of gas component g calculated using activities in the aqueous phase [atm]
R	universal gas constant [J/(molK)]
S	solid concentration [g/m ³]
t	exposure time [years]
u_i	mobility of ion i in water [m ² /s/V]
x	depth of carbonation [mm]
Z	valence of an adsorbing ion [+/-]
z_i	charge number of ionic species i in solution [-]
β_r	aleatoric uncertainty [-]
β_u	epistemic uncertainty [-]
γ_i	activity coefficient of ion I [-]
$\Delta_f G_T^o$	standard Gibbs free energy of formation for a species at the temperature T [K] [J/mol]
$\Delta_r G_T^o$	standard Gibbs energy of reaction for a species at the temperature T [K] [J/mol]

$\Delta_r H^\circ$	standard heat of reaction [J/mol]
ε	water-filled porosity [-] or dielectric constant of water in Poisson-Boltzmann equation [-]
ε_o	permittivity of free space [C/Vm]
μ	electrochemical potential [J/mol]
σ	surface charge density [C/m ²]
τ	tortuosity factor [-]
ψ	electrical potential [V]
Γ	adsorption density [mol/m ²]

List of publications

The doctoral dissertation consists of a summary and of the following publications, which are referred to in the text by their numerals:

- 1.** Kari, O.P. and Puttonen, J., 2009. Modelling the Durability of Concrete for Nuclear Waste Disposal Facilities. In: Long Term Performance of Cementitious Barriers and Reinforced Concrete in Nuclear Power Plants and Waste Management, Cadarache, France, March 30-April 2, 2009. RILEM Proceedings PRO 64. ISBN 978-2-31158-072-1.
- 2.** Kari, O.P. and Puttonen, J., 2009. Modelling Concrete Degradation for the Life Span of over 500 Years. In: ConMat '09 – 4th International Conference on Construction Materials: Performance, Innovations and Structural Implications, Nagoya, Japan, August 24-26, 2009.
- 3.** Kari, O.P., Elakneswaran, Y., Nawa, T., and Puttonen, J., 2013. A model for a long-term diffusion of multispecies in concrete based on ion-cement-hydrate interaction. *Journal of Materials Science*, 48, 4243-4259. ISSN 0022-2461. <http://dx.doi.org/10.1007/s10853-013-7239-3>.
- 4.** Kari, O.P., Puttonen, J., and Skantz, E., 2014. Reactive transport modelling of long-term carbonation. *Cement and Concrete Composites*, 52, 42-53. ISSN 0958-9465. <http://dx.doi.org/10.1016/j.cemconcomp.2014.05.003>.
- 5.** Kari, O.P. and Puttonen J., 2014. Simulation of concrete deterioration in Finnish rock cavern conditions for final disposal of nuclear waste. *Annals of Nuclear Energy*, 72, 20-30. ISSN 0306-4549. <http://dx.doi.org/10.1016/j.anucene.2014.04.035>.

Author's contribution

The author of the thesis is the principal writer of all the publications in which Professor J. Puttonen provided major comments as co-author. The third publication was written in cooperation with Hokkaido University, Japan, and was also reviewed by Professor T. Nawa and Dr. Y. Elakneswaran as co-authors. In the fourth publication, co-author Ms. E. Skantz performed a major part of the experimental work and provided inputs to the literature review.

1. Introduction

1.1 Background

The concrete-made engineered barriers of the repositories for low- and intermediate-level wastes (Figure 1), which are located at a depth of 50-100 metres, are required to be serviceable for at least 500 years¹ (STUK 2003). As modern concrete has only been used as a construction material for less than 150 years, there is a lack of direct experience of concrete structures with a service life even close to that demanded. Simulations are needed to justify the proper long-term behaviour of concrete in these waste facilities, where concrete is subjected to two completely different sets of environmental conditions. The operational phase covers the period before the closure of the caverns, followed by the post-closure period, when the caverns will be filled with groundwater.

Figure 1. Low- and intermediate-level waste repository at the Olkiluoto disposal site (STUK 2013).

¹ Differs from the concept for high-level wastes, where the timescale demanded is enormously longer.

During the operational period of the repository, dank air with a relative humidity of 70%, temperature of 12 °C, and initial carbon dioxide content of 500-600 ppm will surround the facilities. The estimated length of this period can exceed 100 years. During that period the concrete structures will be exposed to aerial carbonation, intensified by the relative humidity, which is nearly optimal for the carbonation process. The main impact of carbonation on concrete made of Portland cement is that it reduces the alkalinity of the concrete and also changes its major compounds, pore solution, and pore structure. This may not only result in the corrosion of the steel reinforcement but may also make the products of cement hydration unstable. A high pH value is fundamentally maintained and buffered by calcium hydroxide and, therefore, during the service life of the concrete its dissolution is one of the main indicators of deterioration. The dissolution and decomposition of the major hydrated phases of the cement paste, such as calcium silicate hydrate (C-S-H), significantly alter its microstructural properties, permeability, adsorption potential etc. affecting the further deterioration of the concrete during the post-closure period of the caverns.

After the sealing of the repository, saline brackish groundwater, which mainly penetrates into the concrete by diffusion via a system of pores, cracks, and defects in the concrete, will gradually fill the disposal zone. The groundwater is slightly alkaline, with a pH between 7 and 9, and contains moderate levels of ions that are harmful to the concrete and its steel reinforcement (Leivo et al. 1997). These ions can even be more destructive when the interaction between the ions penetrating into the concrete and cement hydrates is taken into account. As a single factor, chlorides are important because of their impact on the corrosion of the steel reinforcement. The system is physiochemically complex and the competition between the carbon, sulphate, and chloride ions is expected to take place at least in the AFt ($\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-tri}$) and AFm ($\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-mono}$) phases (Lagerblad and Trägårdh 1994). The major components of the cement paste can also leach out, which, during the interaction and equilibration with the surrounding groundwater, changes the chemistry of the pore solution, resulting in the disintegration of the cement paste. As a whole, the deterioration process in the concrete progresses by transporting substances from the exposed surface to maintain the chemical equilibrium of the process. After the sealing of the caverns, the exposure conditions are assumed to remain constant.

1.2 Research problem

A lot of work has been carried out on predicting concrete carbonation (Papadakis et al. 1991, Ceukelaire et al. 1993, Castro et al. 2004, Meier et al. 2005, Khunthongkeaw et al. 2006, Sisomphon et al. 2007, McPolin et al. 2009) and the penetration of aggressive ions, particularly chlorides (Maage et al. 1996, Ferreira 2004, Johannesson et al. 2007, Samson and Marchand 2007, Thomas and Bentz 2008, Hosokawa et al. 2011) from the surrounding environment into concrete. The leaching of the cement matrix has also been

widely studied (Fagerlund 2000, Mainguy et al. 2000, Gérard et al. 2002, Ekström 2003). A typical approach to the mathematical examination of deterioration phenomena has been to analyse ageing phenomena separately by applying standards which define the guidelines for testing materials, such as CEN/TS 12390-11. If case-specific experimental results have been available, empirical models based on Fick's second law have been fitted to them directly. The more advanced approaches used in those models usually consider all the prevailing time-dependent deterioration phenomena by multiplying the diffusion or other similar coefficients by different factors (Poulsen and Mejlbro 2006). The deterioration caused by the interaction between different ageing phenomena can be more harmful than the deterioration induced by a single ageing phenomenon. The importance of interaction was recognised qualitatively in Publications 1 and 2 and Kari et al. (2008, 2009, 2010), where the finite element approach was applied to solve coupled equations of different ageing phenomena in 2D or 3D geometries. However, the main disadvantages of the methods based on Fick's second law are that the physical and chemical interactions between the ions in the solution and between species and solid surfaces are considered implicitly even if they have a direct effect on the speed of the deterioration process. Therefore, the application of those models to estimate the deterioration of the concrete for periods that considerably exceed the period covered experimentally may not be convincing.

Modelling based on thermodynamic equilibrium (Damidot et al. 2011) offers a versatile and theoretically robust approach for predicting ion-cement-hydrates interactions during the long-term ageing of concrete. Existing thermodynamic models for applications comparable with this study, such as Höglund (2001), have usually been limited in terms of surface complexation reactions and, consequently, of multi-ionic transport. Furthermore, these models were typically restricted to the post-closure period and the results were not validated by long-term experimental data received from concrete specimens. Thermodynamic databases, such as BRGM's Thermoddem (Thermoddem 2014), and computer codes for geochemical applications have improved remarkably in recent years, increasing the options for applying thermodynamic analyses to cementitious systems.

The two fundamental questions to be clarified are, first, the effect of the interaction between different complex phenomena on the ageing of reinforced concrete, and second, the definition of a method suitable for the simulation of the ageing of concrete in rock caverns for nuclear waste facilities.

1.3 Objectives and limitations

The primary object of this work is to introduce a model for estimating the long-term ageing of concrete in Finnish rock caverns for the disposal of low- and intermediate-level nuclear waste. In the modelling the objective is to take the time-dependent physical chemistry of the concrete during long-term exposure in two different sets of environmental conditions into account, and also to introduce a statistical methodology for evaluating the uncertainties of

the model. The implementation of the model is carried out with commonly available software.

The research is limited in terms of concrete type. Neither the propagation period of the possible corrosion of the steel reinforcement nor the load-bearing capacity of structures as a result of the deterioration of materials is within the scope of the study. The model is developed for a mechanically unbroken concrete matrix and the effects of cracking are excluded.

1.4 Outline of the thesis

The outcomes of the research are presented in seven chapters. A flowchart of the structure of the thesis is shown in Figure 2.

Following this Introduction, which defines the research problem, Chapter 2 describes the ageing processes of concrete in Finnish rock caverns and focuses on the theoretical background to the mathematical modelling or simulations. The basic cement chemistry defining the properties of the concrete microstructure formed in the case and directly affecting the deterioration of the concrete is presented at the beginning of the chapter. The main ageing phenomena and the transport processes into the concrete are also discussed, with particular consideration being given to the ion-cement-hydrate interaction.

Chapter 3 presents the mathematical formulation of the problem, introducing the methods that are typically used and a thermodynamic model for estimating the ageing of concrete. The thermodynamic model consists of phase equilibrium, surface complexation, and multicomponent diffusion models that also include gas phase calculations. This chapter describes the governing equations needed for idealising the physical problem. The mathematical formulation is described in Publications 3-5.

The experimental work performed for the calculation and evaluation of the models is discussed in Chapter 4. The concrete specimens used by Teollisuuden Voima Oyj (TVO) and Fortum Power and Heat Oyj in a joint research programme launched in 1997 (Ipatti 2004) were exploited in the laboratory work. The concrete specimens used in the programme were stored in a controlled environment for over 13 years. The specimens were submerged in chemical water solutions or they were surrounded by air only. The laboratory tests carried out on the specimens included analyses of cement hydrates, porosity properties, pH value, pore solution, element distribution, and the penetration of aggressive species. The experimental work is discussed in Publications 1-5.

In Chapter 5, the results of the calculations performed by the two different methods are compared with the values achieved experimentally. The

applicability of the models for estimating the deterioration phenomena is evaluated. The fundamental ageing phenomena in the operational phase and in the post-closure period, which are discussed in Publications 3 and 4, are also described in Chapter 5.

Chapter 6 presents a simulation of the ageing of concrete in facilities for low- and intermediate-level nuclear waste by using the thermodynamic model that will be introduced. An operational phase of 100 years and a post-closure period of 400 years are assumed in case-specific simulations, which are presented and highlighted in Publication 5.

Finally, conclusions, major findings, and recommendations for further research are discussed in Chapter 7.

Figure 2. Flowchart of the thesis.

2. Ageing of concrete structures in Finnish rock caverns

2.1 General

As usual, in this study too a concrete structure means a combination of two materials, concrete and steel reinforcement. In the conditions at the disposal facility the deterioration of the concrete is important and will be considered, but the prerequisite for the initiation of the corrosion of the reinforcement will probably be met before the deterioration of the concrete becomes critical for its structural behaviour (Publications 1 and 2 and Kari et al. 2008, 2009, 2010). The mechanism of the corrosion of the reinforcement can be considered as a two-stage process (Martin-Perez 1999):

- the initiation period, during which the steel remains passive. The onset of corrosion corresponds to the depassivation of the reinforcement resulting from the reduced alkalinity of the concrete or the accumulation of harmful substances in the layer of reinforcing steel;
- the propagation period, during which the structure deteriorates as a result of the corrosion of the reinforcement. The phase lasts until an unacceptable degree of corrosion damage has occurred.

In this study, the period until the initiation of corrosion of the steel reinforcement is examined. Therefore, after the propagation period neither the consequential effects of the corrosion of the reinforcement resulting in the deterioration of the concrete (loss of reinforcing cross-sectional area and accumulation of corrosion products) nor the controlling factors of corrosion (e.g. the oxygen supply) are included in the study. The facilities will, however, fulfil their function as a barrier as long as any solid concrete surrounds them and a bond between the reinforcement bars and the concrete exists.

2.2 Individual factors affecting the ageing of concrete

2.2.1 Concrete microstructure

Concrete can be considered as a composite material with phases of hydrated cement paste (HCP), aggregates, and, basically, an interfacial transition zone

(ITZ). The structure and composition of the HCP is the main factor affecting the properties and long-term performance of the concrete. The composition of the cement has the main impact on the hydration products formed. The water-to-cement ratio, manufacturing, curing, possible chemical admixtures, and other factors have their own influence on the properties of the HCP. Only Portland cement CEM I is considered in this study and, particularly, its sulphate-resistant type, where the contents of C_3A and SO_3 are limited. The main components of this type of cement are given in Table 1.

Table 1. Main components of sulphate-resistant CEM I cement (Finnsementti 2014).

Chemical properties of clinker	[%]
CaO	64...66
SiO ₂	20...22
Al ₂ O ₃	3.1...3.6
Fe ₂ O ₃	3.4...4.5
MgO	2.5...3.5
SO ₃	2.5...2.9
C ₃ A	≤ 3.0

The degree of hydration is assumed to approach the maximum attainable. The temperature is limited to the values in the disposal environment and experimental work (10-24 °C). The main hydration products formed under the conditions determined and their principal properties are the following.

- Calcium-silicate-hydrate, C-S-H

C-S-H is the most important hydration product. It occupies a major part of the volume of the cement paste and is responsible for the strength and other important properties of the paste. More than 30 crystalline calcium silicate hydrate phases are known. The structures are highly complex, and range from semicrystalline to nearly amorphous (Taylor 1997). The exact structure is not known, but it has a broad similarity to the crystalline minerals tobermorite ($C_5S_6H_9$, approximately) and jennite ($C_9S_6H_{11}$) (Chen 2004).

The Ca/Si ratio of the C-S-H is near 1.8 for fresh hydrated Portland cement. The deterioration processes of concrete lower the ratio as a result of the incongruent dissolution behaviour of the C-S-H, which controls the long-term pH buffer (Sugiyama and Fujita 2006, Soler 2007, Grandia et al. 2010).

A network of very fine pores gives a high specific surface area for the C-S-H phase. As a matter of fact, the total surface area of the cement paste is essentially determined by the C-S-H gel content. The surface area is closely related to many crucial properties of the paste (Thomas et al. 1999). Reactive sites available for the release or adsorption of substances have an important impact on ageing.

- Calcium hydroxide, CH

$Ca(OH)_2$ is the primary crystalline compound in cement paste and is closely linked with C-S-H. Its volume is approximately 25% of the

cement paste. The solubility of CH in the unaltered concrete is controlled by the temperature and alkali contents (Na^+ , K^+) (Lagerblad 2001). Calcium hydroxide is an important component for maintaining pore solution alkalinity. It is easily soluble, and, therefore, a weak link considering, for instance, the leaching phenomenon.

- Aluminium-Iron-mono, AFm

AFm phases have the general formula $[\text{Ca}_2(\text{Al}, \text{Fe})(\text{OH})_6] \cdot \text{X} \cdot x\text{H}_2\text{O}$, where X denotes one formula unit of a single-charged anion, or half a formula unit of a double-charged anion (Taylor 1997). Many different anions or anion complexes can serve as X, of which the most important are OH^- , SO_4^{2-} , Cl^- , and CO_3^{2-} . The most common AFm phases which it is relevant to consider are (A can be replaced by F): $\text{C}_4\text{A}\bar{\text{S}}\text{H}_{12}$ (monosulphate), C_4AH_x , $\text{C}_4\text{A}\bar{\text{C}}_{0.5}\text{H}_x$, $\text{C}_4\text{A}\bar{\text{C}}\text{H}_x$, and C_2AH_8 . The monocarbonate-type phases can be formed instead of monosulphates in the presence of limestone (Schmidt 2007). Other types of AFm phases, such as Friedel's salt, $\text{C}_3\text{A} \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$, can also form when concrete is exposed to chlorides.

- Aluminium-Iron-tri, AFt

AFt phases have the general constitutional formula $[\text{Ca}_3(\text{Al}, \text{Fe})(\text{OH})_6 \cdot 12\text{H}_2\text{O}]_2 \cdot \text{X}_3 \cdot x\text{H}_2\text{O}$, where x is, normally at least, ≤ 2 and X represents one formula unit of a double-charged ion, or with reservations, two formula units of a single-charged anion. In the normal case X is SO_4^{2-} , but it may also be CO_3^{2-} or Cl^- (Taylor 1997, Lagerblad 2001). The most important AFt phase is ettringite ($\text{C}_3\text{A} \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$). The other AFt type that can exist in the specific conditions is thaumasite $(\text{CaSiO}_3)_2(\text{CaSO}_4)_2(\text{CaCO}_3)_2 \cdot 30\text{H}_2\text{O}$, which is structurally very similar to ettringite.

- Other important phases

Brucite ($\text{Mg}(\text{OH})_2$) is isostructural with CH, and can be formed during the hydration of MgO, and also when external Mg is involved. The forming of hydrotalcite-type phases (M_4AH_{10}), which are structurally related to brucite, is also possible (Taylor 1997).

The volume of the hydrated cement paste is less than the initial total volume of water and cement, leading to the formation of capillary pores. The random layered structure of the C-S-H gel creates interstitial pores (gel pores). Very small-scale interlayer pores are also formed between the C-S layers. The concrete contains entrapped air voids caused by typical manufacturing processes and entrained air voids, if these are added in order to improve certain properties (Bertolini 2004). The pore system formed mainly depends on the water-to-binder ratio, cement type, and quality of the concrete. When the concrete is properly manufactured, the cement paste is well hydrated, and

a low water-to-cement ratio is assumed, the pore sizes of different pore types can be categorised characteristically as follows (Taylor 1997, Bertolini 2004): interlayer pores < 2 nm; gel pores 2-10 nm; capillary pores 10 nm-5 µm; air voids 5 µm-5 mm. The pore sizes in the ITZ area are between 20 and 50 µm, making the porosity much higher locally than that of the bulk cement paste. Microcracks are also more likely to form in the ITZ area. It is important to determine the distribution of the pore types as each pore type has a particular impact on the durability properties of the concrete. The hydrated cement phase changes with time, mainly as a result of the natural hydration process and the interaction between the HCP and environmental substances. Therefore, the ratios between the different pore types can change with time as well.

The connectivity of the pores and the tortuosity and constrictivity of the pore system are major factors affecting the transport properties of concrete. If the capillary pore system is not continuous, the transport processes are controlled by the small gel pores (Bertolini 2004). The percolation through the ITZ area is important, but the entire pore system should be considered in mass transport (Wong et al. 2009). The mixing water that is not used for the hydration remains in the pore system of capillary and gel pores that provides the transport medium for the substances. Water can take many forms in the pore system (Bertolini 2004). The absolute amount of free water in the pores under equilibrium conditions depends on the humidity of the surrounding environment, excluding the amounts of water combined chemically and both adsorbed and interlayer water under certain conditions. The principal dissolved ions in the pore solution are cations of K^+ , Na^+ , and Ca^{2+} and anions of SO_4^{2-} and OH^- . There is a charge balance between the cations and anions. The composition of the pore solution mainly depends on the cement type. Environmental factors, such as the ingress of ions from the exposed surface into the concrete, can change the pore solution as well. The pore solution of Portland cement concretes is naturally alkaline. The hydration produces a solution which consists of mainly NaOH and KOH, leading to a pH between 13 and 14 (Bertolini 2004).

2.2.2 Carbonation

During the operational period, the concrete is exposed to aerial carbonation caused by carbon dioxide in the atmosphere (Publications 1, 2, and 5 and Kari et al. 2008, 2009, 2010). After the rock cavern has been sealed and filled with groundwater, carbonation can also occur in the submerged conditions as a result of the presence of bicarbonate anions in the groundwater.

The aerial carbonation process can be summarised by the following reaction mechanism (Meier et al. 2005)

where the atmospheric carbon dioxide diffuses into the unsaturated concrete and dissolves into the pore solution, mainly as HCO_3^- and CO_3^{2-} . They react

with calcium hydroxide that has also been dissolved into the pore water to form calcium carbonate, as well as other CO_2 -based cement hydrates. Free water and calcium carbonate, which quickly forms a solid matrix, are the main products of the reaction. The amount of solid $\text{Ca}(\text{OH})_2$ helps to maintain a high pH as long as $\text{Ca}(\text{OH})_2$ is available for reaction (Sideris 2006). The stabilities of the calcium silicate hydrate (C-S-H), Afm, and AFt phases are also dependent on the high pH and Ca ions in the pore solution. After the consumption of $\text{Ca}(\text{OH})_2$, the C-S-H first decalcifies and then decomposes, further reducing the pH value and the concentration of Ca ions. This leads to the decomposition of the other main phases into new compounds and the alteration of the concrete (Lagerblad 2005). The residues from complete carbonation in addition to calcite are amorphous silica, hydrocarboaluminates, and different Al and Fe hydroxides. The pH value drops to around 8 at that point (Lagerblad and Trägårdh 1994). The carbonation rate and carbon dioxide diffusion are generally dependent on the relative humidity, temperature, external CO_2 concentration, and material characteristics of the concrete, such as the type of cement.

The main harmful effect of carbonation is the reduced alkalinity of the concrete, which enables the reinforcement to corrode. The formation of CaCO_3 , which has a different density and molar volume from $\text{Ca}(\text{OH})_2$, causes the precipitated carbonates to cling to the pore walls, which may reduce the porosity of the concrete (Meier et al. 2005). On the other hand, the precipitation and dissolution of the cement hydrates may cause variations in the porosity inside the concrete.

The amounts of carbonating cement hydrates, mainly the amount of calcium hydroxide, are the key factors affecting the resistance of the concrete against carbonation. The rate of carbonation also depends on the porosity properties of the concrete. The capillary porosity and tortuosity of the pore structure directly affect the diffusion of the carbon dioxide.

However, the most important factor affecting the carbonation rate and CO_2 diffusivity is the relative humidity. The carbonation process can occur in the presence of water and carbon dioxide in the pore solution. Water is required for CO_2 transport and thus in a completely dry concrete the process does not exist. On the other hand, in a fully saturated concrete, the carbonation rate is typically slow as the carbon dioxide diffusion is remarkably slower in pure water than in air (Bertolini et al. 2004). In general, the maximum rate of carbonation occurs at a relative humidity of 60-70%.

It should be noted that after the cavern has been closed, the concentration of carbon dioxide may grow as a result of the biodegradation of organic wastes until the space is submerged (Leivo et al. 1997), which can accelerate the carbonation process. In the same reference it is assumed, however, that all the carbon dioxide produced is consumed by the corrosion of the waste drums. This phase can be expected to happen relatively fast as well. The transformation of the bicarbonate anions present in groundwater, such as HCO_3^- , to carbonate ions, is possible in the submerged stage and leads to the stabilisation of the AFt and AFm phases (Lagerblad and Trägårdh 1994).

2.2.3 Penetration of aggressive ions

The main aggressive ions and their combinations in the groundwater in the disposal environment during the post-closure period are expected to be the chloride, sulphate, and magnesium ions (Publications 1, 2, and 5 and Kari et al. 2008, 2009, 2010). The amounts of the other types of ions and acids, excluding the carbonates, are negligible from the point of view of the ageing.

Chlorides

The presence of chlorides in the groundwater is evaluated as being the main concern for the corrosion of the steel reinforcement under these conditions. Chloride ions penetrate into the concrete and start destroying the protective environment of the steel reinforcement, leading to the onset of the corrosion process. In general, chloride ions do not readily form detrimental solid phases which can cause cracking and expansion. On the contrary, the binding of the ions might slow down the penetration (Glasser et al. 2008). Inside the concrete, chloride ions can be present in three different forms (Neville 1995, Elakneswaran 2009):

- chemically bound to the hydration products of the cement;
- physically adsorbed on the surfaces of the cement gel as a result of electrical forces and van der Waals interactions between the surfaces and the chloride;
- dissolved in the pore solution.

The main form of the chemical binding of chlorides is the reaction with C_3A in Portland cement, leading to the formation of Friedel's salt. The Al can be replaced by Fe(III) in the process. Ion-exchange reactions leading to the formation of other types of compounds are also possible. The concentrations of the ions, mainly Cl^- , SO_4^{2-} , and OH^- , greatly affect the binding of the chlorides as they are competing for the same positions in the AFm mineral structure (Lagerblad and Trägårdh 1994). The binding capacity of OPC concrete has been shown to be heavily dependent on the C-S-H gel content in the concrete, regardless of the water-to-binder ratio and the addition of aggregates (Tang and Nilsson 1993).

Aluminate phases can dissolve and become part of a chloride or sulphate complex (Lagerblad and Trägårdh 1994). The possible decomposition of ettringite can release sulphates, whereas the dissolution of CH as a result of leaching or carbonation releases chlorides. The system is physiochemically complex and the competition between the carbon, sulphate, and chloride ions is expected to take place at least in the AFt and AFm phases (Lagerblad and Trägårdh 1994).

Sulphates

The cement paste originally contains sulphates bound to the aluminium- and ferrite-rich phases. The changing of the sulphate concentration in the cement paste as a result of the ingress of sulphates from the surrounding environment

causes volumetric changes in the cement hydrates, which can lead to the expansion or even disintegration of the concrete. The major generally detrimental reactions are the reactions of the sulphates with CH to form gypsum and with C₃A to form ettringite (Bertolini 2004):

Precipitation and dissolution of the other types of cement hydrates are also likely to happen. At lower concentrations of sulphate (<1000 ppm SO₄²⁻), the primary product deposited is ettringite rather than gypsum, which is the main product at higher concentrations (Bucea and Sirivivatnanon 2003). The stability of the AFt and AFm phases is clearly controlled by the concentration of sulphates in the pore solution, but also by the alkali content at the temperatures relevant in the study. Therefore, if CH is leached or carbonation has occurred, the phases break down (Lagerblad and Trägårdh 1994).

When cements or concretes contain a source of carbonates, the formation of thaumasite is possible (Schmidt 2007), which might also result in severe weakening of the concrete (Skalny et al. 2002, Aguilera et al. 2003, Collett 2004). Experimental evidence supports two points of view about the mechanism of thaumasite formation (Aguilera et al. 2003):

- the formation of thaumasite occurs as a consequence of the evolution of ettringite when it incorporates Si⁴⁺ into its structure, replacing the Al³⁺ ions;
- thaumasite formation is the result of the interaction between sulphates and carbonates (present in the aqueous phase of the cement) and the C-S-H gel.

Therefore, the carbonation of the concrete may have an influence on the formation of thaumasite. However, there is a lack of knowledge about the essential factors affecting the formation of thaumasite. Neither the relation between the amount of thaumasite formed and the reduction in the strength of the concrete nor the exact threshold concentration for a complete breakdown of a mortar or a concrete is known. Additionally, neither the influence of the degree of carbonation on the formation of thaumasite nor the relationship between the C₃A content of the cement and the formation of thaumasite is known (Aguilera et al. 2003).

Each cation associated with sulphate ions affects the deterioration of the concrete in different ways. The reactions of the ions in solutions can be essentially separate, and the consequences are concentration-dependent. For instance, with Na₂SO₄, the reaction involves the SO₄²⁻ ions, but with MgSO₄ the Mg²⁺ also participates (Taylor 1997). In general, the overall corrosive action of magnesium sulphate is greater than that of other types of sulphates at equal concentrations (Skalny et al. 2002).

Magnesium

Magnesium ions can also replace the calcium in the portlandite and form brucite. The formation does not lead to a significant increase in the volume. As a matter of fact, brucite that has formed near the exposed surface of the concrete might protect the interior from dissolution (Lagerblad and Trägårdh 1994). On the other hand, the brucite is insoluble and poorly alkaline, which reduces the pH of the pore solution, affecting the stability of the C-S-H. The decomposition of the C-S-H and the formation of M-S-H from the C-S-H, in addition to the possible formation of gypsum and ettringite, can result in the disintegration of the concrete (Dehwah et al. 2002, Glasser et al. 2008).

2.2.4 Leaching of the cement paste

The leaching of concrete by percolating or flowing water may cause severe damage. Pure water can remove alkali hydroxides, dissolve CH, and decompose hydrated silicate and aluminate phases (Taylor 1997). The leaching can be regarded as an intrusion of acid into the cement paste. This is due to the fact that the cement paste is formed and is in equilibrium with a pore solution with a pH of 13-14, and in the leaching process the pore solution equilibrates with the surrounding water with a pH of 6-7. Leaching changes the chemistry of the pore solution of the concrete, which in turn results in chemical changes and the dissolution of the cement paste (Lagerblad 2001). The leaching process affects the porosity of the cement paste, which is linked directly to the type and proportions of the existing solid phases during the process (Mainguy et al. 2000). As a result of the leaching process, all the CaO is lost, leading to serious disintegration of the cement paste (Taylor 1997).

The calcium concentration in the pore solution can be used as a good indicator of chemical deterioration, regardless of the fact that the thermodynamic equilibrium between solid and liquid phases is determined by all the ions dissolved in the solution (Gérard et al. 2002, Carde and Francois 1997). Therefore, the leaching process is mainly attributed to decalcification, which leaves behind a shell of silica and metal hydroxides (Lagerblad 2001). Calcium hydroxide is the first phase to dissolve when the pH in the pore solution decreases. In practice, sequential decompositions of hydrated calcium silicates and aluminate phases take place simultaneously with the dissolution of CH as a result of the greater specific area of the phases (Lagerblad and Trägårdh 1994). The dissolution behaviour of the C-S-H is incongruent and dependent on the Ca/Si ratio of the phase (Soler 2007), which gradually decreases between the sound and leached zones (Glasser et al. 2008). The dissolution of calcium hydroxide and hydrated calcium silicate phases is most rapid in groundwaters which contain dissolved CO₂ and low concentrations of calcium carbonate or bicarbonate ions. On the other hand, the carbonation of the CH near the exposed surface delays the calcium removal (Lagerblad and Trägårdh 1994).

In the water-filled caverns, the velocity of the groundwater flow is not high enough to cause the erosion of structures, but sufficient to transport away the leached material (Publications 1, 2, and 5 and Kari et al. 2008, 2009, 2010). In

the absence of a pressure difference the diffusion through the surface of the concrete controls the leaching process.

2.3 Transport processes into concrete and ion-cement-hydrate interaction

The penetration of substances into the concrete from the surrounding environment may occur via the system of pores, cracks, and defects of the concrete. The transport mechanisms usually take place in several ways. However, in this case the environmental conditions are stable and hydrostatic pressure does not create a pressure difference over the concrete structures. Thus, the structure presumably only has a low level of tensile stress. Therefore, it is reasonable to assume that the penetration of substances occurs mainly through unbroken concrete, which is also the topic of this study. As the environmental conditions are constant for a long period of time, excluding the short period after the operational phase, during which convective flow may briefly occur, diffusion through the pores is expected to be the predominant phenomenon during both exposure periods in the absence of an electrical field and cracks (Publications 1-5 and Kari et al. 2008, 2009, 2010). In addition to the pore structure of the cement paste, the diffusion of substances into the concrete is affected by aggregates (Delagrave et al. 1997, Garboczi and Bentz 1997, Care 2003). This is mainly due to two factors: the presence of ITZ and the increase in the tortuosity of the diffusion path caused by the aggregates. The ions penetrate into the concrete, accompanied by other ions and other ionic species, which can interact with cement hydrates either physically or chemically. The binding processes reduce the concentration of the ions in the pore solution, which affects the rate of the transport of the substances.

The multi-ionic transport is significantly influenced by the surface properties of the cement hydrates. The electrical charge is formed on the surface of the cement hydrates when they are in contact with the electrolyte solution resulting from the dissociation, ionic dissolution, and adsorption mechanisms. In the polar medium, oppositely charged counter-ions are attracted towards the surface while similarly charged co-ions are repelled away from the surface. This leads to the formation of an electrical double layer (EDL) at the interface between the solid and liquid phases, which restores the electroneutrality of the solution (Elakneswaran 2009).

According to the generally accepted Stern model (Figure 3), the EDL can be described as the Stern layer and the diffuse layer. In the Stern layer, ions are strongly adsorbed to the surface. The layer consists of specifically adsorbed ions in the inner Helmholtz plane (IHP) and non-specifically adsorbed counterions in the outer Helmholtz plane (OHP). The diffuse layer begins at the OHP (Zhanga and Zhao 2009). In the IHP the ions are bound to the surface by an electrostatic potential and a specific chemical interaction potential. The diffuse layer can be viewed as a cloud of hydrated ions that transit from the significant excess of counter-ions in the fixed charge layer to a balance of cations and anions in the free solution. The magnitude of the

surface potential is related to the surface charge and thickness of the EDL (Elakneswaran 2009). The latter is mainly dependent on the ionic strength or electrolyte concentration.

Figure 3. Schematic figure of the EDL at the solid/solution interface inside the pore.

As a result, two ionic diffusion processes occur in the cement paste: one through the EDL and the other through the free solution. It has been reported that anions diffuse through the free solution and cations through the EDL, where the concentrations of cations are high (Chatterji and Kawamura 1992). The adsorption of ions affects the electrochemical behaviour of the hydrated cement. As the main hydration product the C-S-H has a high specific surface area and mass percentage in the cement matrix; the EDL on the surface of the C-S-H plays an important role in cementitious materials.

C-S-H can physically bind substantial amounts of chlorides and other ions. The silanol surface groups (SiOH) of the C-S-H contain all the reactive sites available for the release or adsorption of protons and also for the adsorption of cations and anions (Elakneswaran 2009 and 2010). The high pH in the solution in equilibrium with the C-S-H leads to a negative charged surface ($\equiv\text{SiO}^-$) according to the reaction

It has been suggested that calcium ions behave as potential determining ions on the surface of the C-S-H and, finally, neutralise its surface charges by forming ionic bonds with silanol sites:

Chloride ions can be physically adsorbed either by making an ionic bond with unionised SiOH as

or by neutralising the positive surface charge through the reaction

The other ions also affect the surface chemistry of the C-S-H. Their adsorption obeys the same principle. The reactions of the other ions can be written as

The adsorption reactions reduce the amount of ionic species in the pore solution. The size of the pores and the surface site density of the C-S-H also significantly influence the rate of penetration of ionic species through cementitious materials.

2.4 Initiation of steel reinforcement corrosion

The initiation of corrosion of the steel reinforcement may be considered to occur when the pH of the concrete is no longer high enough to suppress corrosion or when the content of the major substances, that is, chlorides, has exceeded the threshold limit determined for corrosion. The protective passive film of steel is considered to be undergoing destruction when the $\text{pH} < 11.5$ (Balonis 2010). An even more complicated approach than using the pH of the concrete is to estimate the threshold limit of chlorides. In the literature, the threshold values defined for the amount of chlorides are in conflict. The main reason is that the threshold value is dependent on numerous factors (Diamond 1986, Taylor et al. 2000, Ferreira 2004, Angst et al. 2009). The reduced alkalinity of the concrete resulting from the leaching or carbonation also reduces the threshold chloride concentration. Thus, the critical amount of chlorides may plausibly be evaluated as a relation between the Cl^{-} and OH^{-} ions in the pore solution (Hausman 1967).

3. Mathematical models for estimating concrete ageing

3.1 Modelling assumptions and limitations

In Finnish nuclear waste repositories the main ageing processes of the concrete are identified to be carbonation, the ingress of aggressive species, and leaching during their operational phase and post-closure period (Publications 1-5 and Kari et al. 2008, 2009, 2010). After the construction phase, the atmospheric carbon dioxide diffuses in the gaseous phase into the concrete, where it dissolves in the pore water. The reactions and interaction with the cement hydrates and other ions take place in the pores. The hydrated phases dissolve or precipitate to achieve equilibrium. The ions that are present can be physically adsorbed on the charged pore surface, mainly on the C-S-H, where an electrical double layer has been formed and which also affects the ionic transport. Consequently, the diffusion happens through a charge-free solution and the EDL. The precipitation and dissolution of the substances and the altered composition of the pore solution change the pore volume of the concrete and affect the diffusion of the carbon dioxide and the components related to it. During the post-closure period the ions in the groundwater penetrate into the saturated concrete. Leaching of the cement paste may also occur. The reactions and interaction with the cement hydrates and other ions take place in the pores, generally following the same principles as during the operational phase.

In this chapter, the use of a phenomenon-specific linear diffusion equation and thermodynamic model are presented as methods for simulating the ageing of the concrete. In the simulations, some assumptions about more case-specific factors affecting destructive phenomena have also been made to study general rather than case-specific tendencies of the ageing of the concrete:

- the aggregates of the concrete are not reactive;
- the effects of the nuclear wastes on the deterioration are not considered (e.g. a possible increase in temperature, harmful substances resulting from the decomposition of the wastes, production of carbon dioxide);
- the cracking of the concrete is not included in the simulation;

- concrete admixtures and the possible presence of microbes in the groundwater are not considered.

3.2 Diffusion models based only on Fick's second law

3.2.1 Concrete carbonation in the operational phase

A classical approach for estimating carbonation as a function of time is to fit the results of the carbonation depths measured by phenolphthalein to the empirical model which obeys a basic square root assumption of carbonation as

$$x = k \cdot \sqrt{t} \quad (3.1)$$

where x is the depth of the carbonation [mm], t is the exposure time [years], and k is the empirical coefficient which describes the speed of the carbonation [mm/ $\sqrt{\text{year}}$]. k is assumed to be constant for the whole service life of the concrete. A common feature of the classical models presented in the literature (Papadakis et al. 1991, Ceukelaire and Nieuwenburg 1993, Khunthongkeaw 2006) is that they can be reduced to Equation 3.1, where the coefficient k sums up the influence of various factors (Castro 2004). Therefore, the k value is usually determined through the relationship between the CO_2 concentration [%] in the accelerated a and natural n environments as

$$\frac{k_a}{k_n} = \sqrt{\frac{[\text{CO}_2]_a}{[\text{CO}_2]_n}} \quad (3.2)$$

3.2.2 Penetration of aggressive ions during the post-closure period

The penetration of aggressive species into concrete is often estimated by applying the method which is presented in the standard CEN/TS 12390-11 for determining the chloride resistance of the concrete. The boundary value of the diffusion equation of the method is solved by fitting. The calculated content of the ion at the exposed surface of the concrete and its diffusion coefficient are determined by fitting an error function to the relevant points of the experimental data of the concentration of ions using a non-linear regression analysis based on least squares. The error function is defined as

$$C_x = C_i + (C_s - C_i) \left(1 - \text{erf} \left(x \sqrt{\frac{D_{nss}}{t}} \right) \right) \quad (3.3)$$

where C_x is the content of ion at the average depth x [m] after the exposure time t [s] [% by mass of concrete], C_s is the calculated content of ion at the exposed surface [% by mass of concrete], C_i is the initial content of ion [% by

mass of concrete], D_{nss} is the diffusion coefficient of ion [m^2/s], and $\text{erf}(x)$ is the complementary error function [-].

3.3 Thermodynamic model

The thermodynamic model (Publications 3-5) considers ion-ion and ion-solid interactions, as well as the properties of the gas phase in multi-ionic transport in concrete. The model consists of phase equilibrium, surface complexation, and multicomponent diffusion modules. Gas phase calculations have been integrated into the model in order to consider the presence and transport of gas components. The model was implemented in the PHREEQC geochemical software. A flowchart of the model is presented in Figure 4. In this chapter, the basic structure and the governing equations are described and discussed.

Figure 4. Flowchart of the thermodynamic model.

3.3.1 Phase equilibrium

The phase equilibrium calculations are used to define the behaviour of the cement hydrate phases being inspected that can react reversibly with an aqueous solution to achieve equilibrium. The common mineral phases which may be found in the cement matrix of the case have been selected for the inspection. Thermodynamic equilibrium reactions take place between the solid phases and the pore solution, as well as between the solid phases and the exposure solution. The gas phase is equilibrated with the aqueous phase. The phases will dissolve or precipitate to achieve equilibrium or will dissolve completely. The equilibrium reactions are expressed by the mass-action equations in PHREEQC (Appelo and Postma, 2009). In general, the pure phase equilibrium can be written as

$$K_p = \prod_i (y_i c_i)^{n_{i,p}} \quad (3.4)$$

where K_p is the thermodynamic equilibrium constant for the phase p [-], γ_i is the activity coefficient of ion i [-], c_i is the concentration of ion i [mol], and $n_{i,p}$ is the stoichiometric coefficient of ion i in the phase p [-]. The equilibrium reactions are expressed by the mass-action equations using the extended Debye-Hückel activity model (Appelo and Postma, 2009) as

$$\log \gamma_i = -\frac{Az_i^2\sqrt{I}}{1 + Ba_i\sqrt{I}} + b_i I \quad (3.5)$$

where A [-] and B [-] are the temperature-dependent coefficients, whereas a_i [-] and b_i [-] are the ion-specific fitting parameters. The ionic strength I of the solution can be written as

$$I = 0.5 \sum_{i=1}^n z_i^2 c_i \quad (3.6)$$

where z_i is the charge number of ionic species i in solution [-] and n is the total number of ionic species i in aqueous solution [-]. The ionic strengths of the solutions in the research are low enough to justify the use of the aqueous model incorporated in the PHREEQC software.

Cement hydrate phases are defined by chemical reactions, an equilibrium constant, and enthalpy (Elakneswaran 2010). The thermodynamic equilibrium constant, K [-], at a given temperature T [K] can be expressed as

$$K = \exp\left(-\frac{\Delta_r G_T^0}{RT}\right) \quad (3.7)$$

where R is the universal gas constant [J/(molK)] and $\Delta_r G_T^0$ [J/mol] is the standard Gibbs energy of reaction for a species at the temperature T [K] given as

$$\Delta_r G_T^0 = \sum \Delta_f G_{T,products}^0 - \sum \Delta_f G_{T,reactants}^0 \quad (3.8)$$

where $\Delta_f G_T^0$ [J/mol] is the standard Gibbs free energy of formation for a species at the temperature T .

The thermodynamic properties of the cement hydrates which were selected for the analyses of the work were prepared in the correct format for the calculations with the values found in the literature. In Table 2, the data needed for the solid phases being investigated, that is, the equilibrium constants ($\log K$) and the standard heats of reactions ($\Delta_r H^\circ$) for the dissolution reactions of cement hydrates, are given. C-S-H alteration, including incongruent dissolution, is considered through discrete mineral compositions.

Table 2. Thermodynamic properties for the phases investigated.

Phase	Reaction equation	log K	$\Delta_r H^\circ$ [kJ/mol]	Ref.*
Portlandite	$\text{Ca(OH)}_2 + 2\text{H}^+ = 1\text{Ca}^{2+} + 2\text{H}_2\text{O}$	22.81	-130.11	(a)
Calcite	$\text{CaCO}_3 + 1\text{H}^+ = 1\text{HCO}_3^- + 1\text{Ca}^{2+}$	1.85	-25.33	(b)
C-S-H (C/S 1.6)	$\text{Ca}_{1.60}\text{SiO}_{3.6}:2.58\text{H}_2\text{O} + 3.2\text{H}^+ = 1.6\text{Ca}^{2+} + 2.18\text{H}_2\text{O} + 1\text{H}_4\text{SiO}_4$	28.00	-133.31	(a)
C-S-H (C/S 1.2)	$\text{Ca}_{1.20}\text{SiO}_{3.2}:2.06\text{H}_2\text{O} + 2.4\text{H}^+ = 1.2\text{Ca}^{2+} + 1.26\text{H}_2\text{O} + 1\text{H}_4\text{SiO}_4$	19.30	-88.60	(a)
C-S-H (C/S 0.8)	$\text{Ca}_{0.80}\text{SiO}_{2.8}:1.54\text{H}_2\text{O} + 1.6\text{H}^+ = 0.8\text{Ca}^{2+} + 0.34\text{H}_2\text{O} + 1\text{H}_4\text{SiO}_4$	11.05	-47.65	(a)
$\text{SiO}_{2,\text{am}}$	$\text{SiO}_2 + 2\text{H}_2\text{O} = 1\text{H}_4\text{SiO}_4$	-2.70	13.62	(b)
Tobermorite 11A	$\text{Ca}_5\text{Si}_6\text{H}_{11}\text{O}_{22.5} + 10\text{H}^+ + 1.5\text{H}_2\text{O} = 5\text{Ca}^{2+} + 6\text{H}_4\text{SiO}_4$	65.58	-372.50	(a)
Tobermorite 14A	$\text{Ca}_5\text{Si}_6\text{H}_{21}\text{O}_{27.5} + 10\text{H}^+ = 5\text{Ca}^{2+} + 3.5\text{H}_2\text{O} + 6\text{H}_4\text{SiO}_4$	62.94	-307.42	(a)
Jennite	$\text{Ca}_5\text{Si}_6\text{H}_{22}\text{O}_{32} + 18\text{H}^+ = 9\text{Ca}^{2+} + 6\text{H}_4\text{SiO}_4 + 8\text{H}_2\text{O}$	147.34	-751.77	(a)
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} = 1\text{Ca}^{2+} + 2\text{H}_2\text{O} + 1\text{SO}_4^{2-}$	-4.61	-1.05	(b)
Ettringite	$\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}:26\text{H}_2\text{O} + 12\text{H}^+ = 2\text{Al}^{3+} + 6\text{Ca}^{2+} + 38\text{H}_2\text{O} + 3\text{SO}_4^{2-}$	57.01	-379.83	(c)
Fe-ettringite	$\text{Ca}_6\text{Fe}_2(\text{SO}_4)_3(\text{OH})_{12}:26\text{H}_2\text{O} + 12\text{H}^+ = 2\text{Fe}^{3+} + 6\text{Ca}^{2+} + 38\text{H}_2\text{O} + 3\text{SO}_4^{2-}$	54.59	-146.58	(c)
Monosulphoaluminate	$\text{Ca}_4\text{Al}_2\text{SO}_{10}:12\text{H}_2\text{O} + 12\text{H}^+ = 2\text{Al}^{3+} + 4\text{Ca}^{2+} + 18\text{H}_2\text{O} + 1\text{SO}_4^{2-}$	73.08	-539.40	(c)
Fe-Monosulphate	$\text{Ca}_4\text{Fe}_2\text{SO}_{10}:12\text{H}_2\text{O} + 12\text{H}^+ = 2\text{Fe}^{3+} + 4\text{Ca}^{2+} + 18\text{H}_2\text{O} + 1\text{SO}_4^{2-}$	66.07	-279.84	(c)
Monocarboaluminate	$\text{Ca}_4\text{Al}_2\text{O}_6(\text{CO}_3):11\text{H}_2\text{O} + 13\text{H}^+ = 2\text{Al}^{3+} + 1\text{HCO}_3^- + 4\text{Ca}^{2+} + 17\text{H}_2\text{O}$	80.57	-530.63	(c)
Fe-monocarbonate	$\text{Ca}_4\text{Fe}_2\text{O}_6(\text{CO}_3):11\text{H}_2\text{O} + 13\text{H}^+ = 2\text{Fe}^{3+} + 1\text{HCO}_3^- + 4\text{Ca}^{2+} + 17\text{H}_2\text{O}$	15.05	15.72	(d)
Hemicarboaluminate	$\text{Ca}_5\text{Al}_4\text{CO}_{16}:22\text{H}_2\text{O} + 27\text{H}^+ = 4\text{Al}^{3+} + 1\text{HCO}_3^- + 8\text{Ca}^{2+} + 35\text{H}_2\text{O}$	183.70	-1204.54	(c)
Fe-hemicarbonate	$\text{Ca}_5\text{Fe}_4\text{CO}_{16}:22\text{H}_2\text{O} + 27\text{H}^+ = 4\text{Fe}^{3+} + 1\text{HCO}_3^- + 8\text{Ca}^{2+} + 35\text{H}_2\text{O}$	67.83	-342.06	(d)
C_4AH_{13}	$\text{Ca}_4\text{Al}_2\text{O}_7:13\text{H}_2\text{O} + 14\text{H}^+ = 2\text{Al}^{3+} + 4\text{Ca}^{2+} + 20\text{H}_2\text{O}$	103.67	-647.40	(c)
C_4FH_{13}	$\text{Ca}_4\text{Fe}_2\text{O}_7:13\text{H}_2\text{O} + 14\text{H}^+ = 2\text{Fe}^{3+} + 4\text{Ca}^{2+} + 20\text{H}_2\text{O}$	95.14	-371.44	(c)
Hydrotalcite	$\text{Mg}_4\text{Al}_2\text{O}_7:10\text{H}_2\text{O} + 14\text{H}^+ = 2\text{Al}^{3+} + 4\text{Mg}^{2+} + 17\text{H}_2\text{O}$	73.76	-584.22	(c)
Brucite	$\text{Mg(OH)}_2 + 2\text{H}^+ = 1\text{Mg}^{2+} + 2\text{H}_2\text{O}$	17.11	-114.52	(e)
Dolomite	$\text{CaMg(CO}_3)_2 + 2\text{H}^+ = 2\text{HCO}_3^- + 1\text{Ca}^{2+} + 1\text{Mg}^{2+}$	3.53	-65.36	(b)
Periclase	$\text{MgO} + 2\text{H}^+ = 1\text{Mg}^{2+} + 1\text{H}_2\text{O}$	21.59	-151.23	(b)
Hydromagnesite	$\text{Mg}_5(\text{OH})_2(\text{CO}_3)_4:4\text{H}_2\text{O} + 6\text{H}^+ = 4\text{HCO}_3^- + 5\text{Mg}^{2+} + 6\text{H}_2\text{O}$	31.00	-293.70	(b)
Thaumasite	$\text{CaSiO}_3\text{CaSO}_4\text{CaCO}_3:15\text{H}_2\text{O} + 3\text{H}^+ = 1\text{HCO}_3^- + 3\text{Ca}^{2+} + 1\text{SO}_4^{2-} + 1\text{H}_4\text{SiO}_4 + 14\text{H}_2\text{O}$	10.31	-9.04	(c)
Friedel's salt	$\text{Ca}_4\text{Al}_2\text{Cl}_2\text{O}_6:10\text{H}_2\text{O} + 12\text{H}^+ = 2\text{Al}^{3+} + 4\text{Ca}^{2+} + 2\text{Cl}^- + 16\text{H}_2\text{O}$	74.95	-486.20	(a)
Fe-Friedel's salt	$\text{Ca}_4\text{Fe}_2\text{Cl}_2\text{O}_6:10\text{H}_2\text{O} + 12\text{H}^+ = 2\text{Fe}^{3+} + 4\text{Ca}^{2+} + 2\text{Cl}^- + 16\text{H}_2\text{O}$	53.16	-454.67	(f)
C_2S	$\text{Ca}_2\text{SiO}_4 + 4\text{H}^+ = 2\text{Ca}^{2+} + \text{H}_4\text{SiO}_4$	38.57	-243.17	(g)
C_3S	$\text{Ca}_3\text{SiO}_5 + 6\text{H}^+ = 3\text{Ca}^{2+} + \text{H}_4\text{SiO}_4 + \text{H}_2\text{O}$	73.34	-443.46	(g)
C_3A	$\text{Ca}_3\text{Al}_2\text{O}_6 + 12\text{H}^+ = 2\text{Al}^{3+} + 3\text{Ca}^{2+} + 6\text{H}_2\text{O}$	155.57	-857.81	(g)
C_4AF	$\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10} + 20\text{H}^+ = 2\text{Al}^{3+} + 2\text{Fe}^{3+} + 4\text{Ca}^{2+} + 10\text{H}_2\text{O}$	140.30	-1121.48	(g)

*) a = Blanc et al. 2010a, b = Blanc et al. 2006, c = Blanc et al. 2010b, d = Lothenbach et al. 2008, e = Blanc et al. 2008, f = Dilnesa 2012, g = Babushkin 1985.

3.3.2 Surface complexation reactions

The adsorption of ions on the charged surface of the pores is modelled through surface complexation reactions. The generalised two-layer surface complexation model (Dzombak and Morel 1990) (Figure 5) explicitly calculates the composition of the diffuse layer (Borkovec and Westall 1983). All specifically adsorbed ions are assigned to the Stern layer and all non-specifically adsorbed ions to the diffuse layer. A Gouy-Chapman distribution of ions is assumed in the diffuse layer.

Figure 5. The generalised two-layer surface complexation model (Elakneswaran 2009)

The surface charge density σ [C/m²] is the amount of charge per area of the surface, as follows (Dzombak and Morel 1990):

$$\begin{aligned} \sigma &= \frac{F}{AS} [(=XOH_2^+) + (=XOM^+) - (=XO^-) - (=XA^-)] \\ &= F[\Gamma_H - \Gamma_{OH} + \sum(Z_M \Gamma_M) + \sum(Z_A \Gamma_A)] \end{aligned} \quad (3.9)$$

In the equation F is the Faraday constant [C/mol], A is the specific surface area [m²/g], S is the solid concentration [g/m³], and Z is the valence of an adsorbing ion [+/-]. The adsorption densities [mol/m²] are represented by the symbol Γ . Γ_H and Γ_{OH} represent the adsorption densities of the protons and hydroxyl ions, respectively, whereas Γ_M and Γ_A are used for the cations and anions adsorbed in the process. The Boltzmann distribution, the net charge density σ at a distance x [m] from a charged surface, can be written as (Pashley 2004)

$$\sigma(x) = \sum_{i=1}^n Z_i F c_i \exp\left(-\frac{Z_i F \psi(x)}{RT}\right) \quad (3.10)$$

where ψ is the electrical potential [V] at a distance x from the adsorbed layer. In the common case, where the electrical field is generated by a charged flat surface (such as an electrode), Equation 3.10 can be rewritten as the Poisson-Boltzmann equation

$$\frac{d^2\psi(x)}{dx^2} = -\frac{\sigma(x)}{\varepsilon_0\varepsilon} = -\frac{F}{\varepsilon_0\varepsilon} \sum_{i=1}^n Z_i c_i \exp\left(-\frac{Z_i F \psi(x)}{RT}\right) \quad (3.11)$$

where ε is the dielectric constant of water [-] and ε_0 is the permittivity of free space equal to 8.854×10^{-12} [C/Vm]. The Gouy-Chapman theory is used for its derivation, which is assumed for the ionic distribution in the diffuse layer. As presented in Figure 5, the surface charge σ is always balanced by the excess charge σ_d in the diffuse layer:

$$\sigma + \sigma_d = 0 \quad (3.12)$$

Assuming that the surface of the C-S-H consists only of silanol sites ($\equiv\text{SiOH}$), its density can be calculated by using the structural model of silicate (Viallis-Terrisse et al. 2001), leading to a surface site density of 4.878 sites/nm². The equilibrium constants for the surface reactions, which are considered to be the most relevant in the study, are given in Table 3.

Table 3. The equilibrium constants log K for the surface reactions considered (Elakneswaran 2010).

Reaction equation	log K
$\equiv\text{SiOH} + \text{OH}^- \rightleftharpoons \equiv\text{SiO}^- + \text{H}_2\text{O}$	-12.70
$\equiv\text{SiOH} + \text{Ca}^{2+} \rightleftharpoons \equiv\text{SiOCa}^+ + \text{H}^+$	-9.40
$\equiv\text{SiOH} + \text{Ca}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \equiv\text{SiOCaSO}_4^- + \text{H}^+$	-6.00
$\equiv\text{SiOH} + \text{Ca}^{2+} + \text{Cl}^- \rightleftharpoons \equiv\text{SiOCaCl} + \text{H}^+$	-8.90
$\equiv\text{SiOH} + \text{Na}^+ \rightleftharpoons \equiv\text{SiONa} + \text{H}^+$	-13.64
$\equiv\text{SiOH} + \text{K}^+ \rightleftharpoons \equiv\text{SiOK} + \text{H}^+$	-13.64
$\equiv\text{SiOH} + \text{Cl}^- \rightleftharpoons \equiv\text{SiOHCl}$	-0.35

3.3.3 Multicomponent diffusion (MCD)

The multicomponent diffusion process in which each solute diffuses by its own diffusion coefficients but the ion fluxes are modified to maintain a charge balance during transport through a charge-free pore solution and the diffuse double layer (DDL) is simulated by the MCD module available in PHREEQC.

The electrochemical potential μ [J/mol] of a species i is given by

$$\mu_i = \mu_i^0 + RT \ln(a_i) + z_i F \psi \quad (3.13)$$

where μ^0 is the standard electrochemical potential [J/mol], a_i is the activity of an ion i [-], and ψ is the electrical potential [V]. The diffusive flux of an ion i in a solution induced by chemical and electrical potential gradients can be expressed as

$$J_i = -\frac{u_i c_i}{|z_i| F} \frac{\delta \mu_i}{\delta x} - \frac{u_i z_i c_i}{|z_i|} \frac{\delta \psi}{\delta x} \quad (3.14)$$

where J_i is the flux of a species i [mol/m²/s] and u_i is the mobility of an ion i in water [m²/s/V]. The gradient of electrical potential $\delta \psi / \delta x$ originates from the different transport velocities of the ions, which creates a charge and an associated potential. That potential may differ from the one in Equation 3.13, which comes from a charged surface and is fixed without inducing an electrical current. If there is no electrical current, $\sum z_i J_i$ is zero. The zero charge flux condition permits the expression of the electrical potential gradient in Equation 3.14 as (Anthony et al. 2007)

$$\frac{\delta \psi}{\delta x} = -\frac{\sum_{j=1}^n \frac{u_j z_j c_j}{|z_j| F} \frac{\delta \mu_j}{\delta x}}{\sum_{j=1}^n \frac{u_j z_j^2 c_j}{|z_j|}} \quad (3.15)$$

where the subscript j is introduced to show that these species stem from the potential term. Equation 3.15 can be substituted into 3.14, resulting in

$$J_i = -\frac{u_i c_i}{|z_i| F} \frac{\delta \mu_i}{\delta x} + \frac{u_i z_i c_i}{|z_i|} \frac{\sum_{j=1}^n \frac{u_j z_j c_j}{|z_j| F} \frac{\delta \mu_j}{\delta x}}{\sum_{j=1}^n \frac{u_j z_j^2 c_j}{|z_j|}} \quad (3.16)$$

The mobility is related to the diffusion coefficient in the pore solution $D_{w,i}$ [m²/s] by

$$D_{w,i} = \frac{u_i RT}{|z_i| F} \quad (3.17)$$

By combining Equation 3.17 and the gradient of the chemical potential

$$\frac{\delta \mu_i}{\delta c_i} = \frac{RT}{c_i} \left(\frac{\delta \ln(\gamma_i)}{\delta \ln(c_i)} + 1 \right) \quad (3.18)$$

Equation 3.16 can be rewritten as

$$J_i = -D_{w,i} \left(\frac{\delta \ln(\gamma_i)}{\delta \ln(c_i)} + 1 \right) \frac{\delta c_i}{\delta x} + D_{w,i} z_i c_i \frac{\sum_{j=1}^n D_{w,j} z_j \left(\frac{\delta \ln(\gamma_j)}{\delta \ln(c_j)} + 1 \right) \frac{\delta c_j}{\delta x}}{\sum_{j=1}^n D_{w,j} z_j^2 c_j} \quad (3.19)$$

Equations for diffusive flux can be used for both a charge-free solution and the DDL as defined in Anthony et al. (2007). Only the concentrations c_i and c_j are different in a charge-free solution and the DDL. The concentrations of ions in the DDL $c_{DDL,i}$ are calculated with the Donnan approximation, which assumes a single potential for the DDL as an entity:

$$c_{DDL,i} = c_i \exp \left(\frac{-z_i F \psi_{DDL}}{RT} \right) \quad (3.20)$$

The electroneutrality condition is achieved in the DDL through

$$\sum z_i c_{DDL,i} + \sigma_{DDL} = 0 \quad (3.21)$$

The diffusion coefficients $D_{w,i,j}$ in the pore solution used in the study are given in Table 4. These values have been derived for different temperatures in free water from the data given in Mills and Lobo (1989). The local variations in the porosity caused by the precipitation and dissolution of the solid phases are taken into account through the pore water diffusivity $D_{p,i,j}$ [m²/s] of an ion i as

$$D_{p,i,j} = D_{w,i,j} \cdot \tau \cdot \varepsilon \quad (3.22)$$

where ε is the water-filled porosity [-] and τ the tortuosity factor [-]. The tortuosity has been defined for the pore system of concrete by considering both the ITZ effect and the tortuosity effect of the aggregate through the actual ion transport pathway.

Table 4. Diffusion coefficients in pore solution at different temperatures used in the study (Mills and Lobo 1989).

Diffusion coefficients $D_{w,i,j}$	10 ⁻⁹ [m ² /s] at 12°C	10 ⁻⁹ [m ² /s] at 22°C
Na ⁺	0.95	1.26
K ⁺	1.42	1.85
Mg ²⁺	0.51	0.66
Ca ²⁺	0.56	0.74
SO ₄ ²⁻	0.75	0.99
HCO ₃ ⁻	1.19	1.19
Cl ⁻	1.46	-

3.3.4 Gas phase calculations during aerial carbonation

From the partial pressure and the volume of the gas phase, the mole of the component will be calculated by the ideal gas law (Parkhurst and Appelo 1999). The pressure is fixed and the carbon dioxide concentration in the gas phase is determined through its partial pressure. The diffusion of gaseous carbon dioxide through the unsaturated pores is calculated simultaneously as a separate process, and the recalculated concentrations are used as an initial value for the cells after each time step. The diffusivity is defined as

$$D_{gCO_2} = D_{g0} \cdot \tau \cdot (1 - \varepsilon) \quad (3.23)$$

where D_{g0} is the diffusivity of CO_2 in a free atmosphere [$1.34 \cdot 10^{-5} \text{ m}^2/\text{s}$] (Maekawa et al. 2009). The diffusivity is assumed to be the same in a free atmosphere and in the air-filled pores. The volume of the gas phase during the exposure is dependent, therefore, on the saturation stage and the composition of the hydrated phases, specifically on the changes caused by the dissolution or precipitation of the cement hydrates to the pore volume. In the study, the length of the inspection time is considered to be relatively long and the conditions have been stabilised before the exposure is started. The experimental arrangements and the environmental conditions in the real application allow the use of virgin desorption paths for the concretes. Therefore, the degree of pore volume saturated by the pore solution can be defined as a constant depending directly on the prevailing relative humidity. In general, the partial pressure of a gas component may be written in terms of aqueous phase activities as follows (Parkhurst and Appelo 1999):

$$P_g = K_g^{-1} \prod_i (\gamma_i c_i)^{n_{i,g}} \quad (3.24)$$

where P_g is the partial pressure of the gas component g calculated using activities in the aqueous phase [atm], K_g is the constant of Henry's law for the gas component [atm], and $n_{i,g}$ is the stoichiometric coefficient of the species in the dissolution equation [-].

3.4 Evaluation of uncertainties in the thermodynamic model

In the research, aleatoric and epistemic uncertainties are considered by applying the methodology developed to describe component capacities against seismic actions (Zenter et al. 2008). When the problem is being considered, epistemic uncertainty represents the uncertainty resulting from the methods used in the experiments, analyses, and calculations, whereas aleatoric uncertainty represents the natural variation of the concrete. A significant source of uncertainties in the modelling originates from the heterogeneity of the concrete, which increases the variation of the experimental results used for defining the initial values. The variation can be qualified with an adequate

number of measurements, but the reduction of uncertainties may also require the development of measurement technology. The capacity of the concrete structure is defined here as its ability to resist the deterioration that is defined. Failure is assumed when the specific deterioration phenomenon reaches the determined depth. In this study, the depth of the deterioration is defined as the depth where the deterioration phenomenon has significantly altered the original composition of the concrete, which can be identified, for example, by the total dissolution of major components.

Applying the methodology presented for the component capacity (Zenter et al. 2008), the deterioration X is modelled as a random variable with log-normal distribution, that is, $X = X_m \cdot \varepsilon$, where X_m is the median capacity and ε is a log-normally distributed random variable with a unity median and the logarithmic standard deviation β . Concurrently, the occurrence curve represents the probability of the occurrence of a given deterioration x .

Failure caused by the deterioration phenomenon, based on the criterion used, is possible when the deterioration is more than or equal to the concrete cover. Then, the probability of failure conditioned on the deterioration x is given by the cumulative distribution function of occurrence X , yielding:

$$P_{f|x}(x) = \int_0^a -\frac{1}{\sqrt{2\pi}\beta x} e^{-\frac{1}{2}\left(\frac{\ln x - \lambda}{\beta}\right)^2} dx = \Phi\left(\frac{\ln(a/A_m)}{\beta}\right) \quad (3.25)$$

where $\Phi(x)$ is the standard Gaussian cumulative distribution function. Thus, the deterioration is defined by two parameters, which are the median occurrence X_m and the logarithmic standard deviation β (Zenter et al. 2008).

The conditional probability of failure, or in this case, its occurrence, is described by the equation:

$$P(x \leq a_{c\%}) = \Phi\left(\frac{\ln \frac{a}{A_M} + \beta_u \cdot \Phi^{-1}(C_{c\%})}{\beta_r}\right) \quad (3.26)$$

where $P(X \leq a_{c\%})$ is the probability that X is smaller than or as large as a on a certain confidence level $c\%$, β_u is the epistemic uncertainty, and β_r is the aleatoric uncertainty. The aleatoric uncertainty may be assumed to obey the logarithmic standard deviation as the deterioration is always a positive value. The epistemic uncertainty is also considered to be log-normally distributed for mathematical convenience. The range of measurement results can be calculated from the occurrence curves. In this calculation, a 95% confidence level was chosen and the values were taken from the probability points 0.05 and 0.95.

$$x(P = 0.05, 95\% \text{ confidence level}) = a_m e^{-\Phi^{-1}(0.95)(\beta_r + \beta_u)} \quad (3.27)$$

$$x(P = 0.95, 95\% \text{ confidence level}) = a_m e^{\Phi^{-1}(0.95)(\beta_r - \beta_u)} \quad (3.28)$$

4. Experimental work

An experimental programme was conducted to provide data to validate the modelling approach. The studies of the programme (Publications 1-5 and Kari et al. 2008, 2009, 2010) were carried out using specimens that were fabricated in 1997 (Ipatti 2004). These studies included analyses of cement hydrates, porosity properties, pH value, pore solution, element distribution, and the penetration of aggressive species. The results of the studies were also used for the parameters of the models based on the diffusion equation. The initial values of the specimens before the exposure tests are also presented in this chapter.

4.1 Specimens and environmental conditions

Beam-shaped SRPC concrete specimens were cast for the tests and stored in constant environmental conditions in air or submerged in groundwater-type exposure solutions for 13 years at the time of the investigations. The dimensions of the specimens stored in air or in solution were $90 \times 90 \times 500$ mm³ and $100 \times 100 \times 500$ mm³, respectively. In addition, cement paste specimens were prepared for other laboratory tests using a cement type similar to that used in the concrete samples. The paste samples were cast in PE bottles.

The compositions of the two concrete mixes used, marked as SR04 (w/c 0.43) and SR05 (w/c 0.50), together with the composition of the cement used for their casting, are presented in Table 5. According to the petrographic analyses that were performed (Ipatti 2004) on the aggregates, potentially alkali-reactive aggregates, excessive amounts of micas, sulphates, or clay minerals were not observed. Feldspar (57%) and quartz (29%) were the main mineral constituents of the fine aggregates, whereas the main rock constituents in the aggregates were granite and diorite/amphibolite, with their relative proportions of the coarse aggregates being 65% and 15%, respectively.

Table 5. The compositions of the cement and concrete mixes used in the experiments (Ipatti 2004).

Cement composition	[%]	Concrete mix SR04	[kg/m ³]	Concrete mix SR05	[kg/m ³]
SiO ₂	20.21	CEM I 42,5SR	373	CEM I 42,5SR	317
Al ₂ O ₃	3.52	water	159	water	159
Fe ₂ O ₃	3.68	fine aggregate	1045	fine aggregate	1067
CaO	62.72	coarse aggregate	822	coarse aggregate	839
MgO	3.43	w/c	0.426	w/c	0.5
K ₂ O	0.40	air	2%	air	2%
Na ₂ O	0.35	28d comp. strength	58.5 Mpa	28d comp. strength	48 Mpa
P ₂ O ₅	0.11				
SO ₃	2.88				

4.1.1 Concrete carbonation

After the removal of the formwork at the age of one day, the air-stored specimens for the carbonation were kept in water for 28 days. In the next phase, the specimens were exposed to accelerated carbonation tests or natural carbonation. The specimens for the accelerated tests were stored in a carbonation chamber with environmental conditions of RH $70 \pm 5\%$, temperature 20 ± 2 °C, and CO₂ content $4 \pm 0.5\%$. The carbonation depth from each surface of the concrete pieces was measured with phenolphthalein solution. Pieces with a width of 20 millimetres were cut out from the end of the specimens at prescribed points in time. The specimens which were used for determining the natural carbonation were stored in average conditions of RH $70 \pm 5\%$ and temperature 12 ± 2 °C for the first 75 months and then for 81 months in conditions of RH $35 \pm 5\%$ and temperature 22 ± 2 °C. The average CO₂ content was 0.038%. The change of the environmental conditions in the middle phase also simulates the two similar phases of the industrial applications in mind.

4.1.2 Ingress of aggressive species and stability of concrete

The solution-stored specimens of the SR04 mixes were kept in a high-moisture room after the demoulding on the first day. Before the exposure tests were started at the age of 28 days, the specimens were coated with epoxy, excluding one of the longitudinal sides of each beam that was cast against the form fabric. In this way a one-dimensional penetration by aggressive species was achieved. The specimens were placed in an upright position in a tank equipped with protection against carbon dioxide penetration. The tank was filled with a specific exposure solution, the composition of which was kept constant. The composition of the solution was continuously controlled to monitor especially the amounts of aggressive species, that is, Cl⁻, SO₄²⁻, and Mg²⁺. The temperature was kept constant ($+12$ °C). The exposure solution is presented in Table 6.

Table 6. Exposure solution in the laboratory tests.

Exposure solution	[mMol/L]
Na ⁺	263.00
K ⁺	0.03
Mg ²⁺	11.50
Ca ²⁺	0.52
SO ₄ ²⁻	9.58
Cl ⁻	268.00
pH	8.60
T [°C]	12

4.2 Laboratory tests

4.2.1 Solid phase compounds

The quality and amount of solid phase compounds in the concrete specimens were studied by using X-ray diffraction (XRD). The XRD analyses were performed with a Philips PW 1710 diffractometer by CuK α radiation. Between 5° and 65° (2theta), the spectra were produced with a voltage of 40 kV and a current strength of 30 mA. The determination of the initial amounts of hydrates required the solid phase compounds also to be analysed before the start of the exposure tests using the cement paste samples at the hydration age of 28 days. After the exposure tests, three samples of concrete powder were taken from depths of 0-5, 8-12, and 18-22 millimetres and prepared (Vesikari and Koskinen 2012, 2013) for the XRD analyses.

The hydration products, the amount of bound water, and the other evaporable components were determined from the same concrete powder samples using TG/DTA thermogravimetric and differential thermal analysis. The TG/DTA analyses were performed with a Mettler TGA 851e thermobalance. The analytical parameters were the following: air 50 ml/min; crucible: Al₂O₃, 150 μ l; heating rate: 5 °C/min; maximum temperature: 1000 °C; sample size: 70-80 mg. The initial composition of the main hydrated cement phases presented in Table 7 was estimated by applying the Rietveld method.

Table 7. Estimated initial solid phase compositions according to the XRD and TG/DTA measurements for both concrete mixes.

Solid phase	SR04 [% wt of concrete]	SR05 [% wt of concrete]
Portlandite	2.1	1.8
Ettringite	0.3	0.2
Calcite	1.2	1.1
Periclase	0.2	0.2
Alite	0.5	0.4
Belite	0.3	0.2
Celite	<< 0.1	<< 0.1
Ferrite	0.1	< 0.1
Amorphous	10.9	9.4

4.2.2 Element distributions

Cross-sectional samples with ground and polished surfaces were prepared (Vesikari and Koskinen 2012, 2013) from the concrete specimens. The samples were cut perpendicular to the original concrete surface, the cuts reaching approximately to a depth of 15 millimetres from the external surface of the sample. The average element distributions in these concrete samples were determined by an energy-dispersive X-ray analyser (EDS) that was connected to a Hitachi S-3400N scanning electron microscope (SEM). The elements that were analysed were calcium, magnesium, chlorine, sulphur, sodium, aluminium, and iron. The EDS can detect carbon and elements heavier than that. As lighter elements and trace elements ($< 0.5\%$) are necessarily not detected in the analysis, the results received by the EDS can be considered semi-quantitative.

4.2.3 Pore solution composition

The initial pore solution of the SR04 specimens was extracted using the steel-die method at a hydration age of 28 days. The chemical composition was analysed with ion chromatography. The initial pH values were also determined directly from the pore solution by a standard pH electrode. Because of the nature of the measurements of the composition of the pore solution, the results have a large dispersion and the interpretation of the results may anyway include some subjectivity. The chemical composition depends mainly on the type of cement and exposure conditions (Bertolini 2004). As the amounts of alkali ions, which are the most dominant components in the reaction, can be reliably estimated (Brouwers and vanEijk 2003), the pore solution composition of the SR05 was calculated on the basis of the values measured for the SR04. The pore solution compositions and initial pH values determined are presented in Table 8.

Table 8. Initial pore solution compositions and pH values for both concrete mixes.

Pore solution	SR04 [mMol/L]	SR05 [mMol/L]
Na	45	30
K	235	180
Ca	2	2
S	26	26
pH	13.5	13.3

4.2.4 pH values of concrete

The pH values of the concrete specimens under the exposure tests were determined from concrete powder suspensions according to the method of Räsänen and Penttala (2004). The solution for the measurement was prepared by mixing 15 grams of concrete powder with 22.5 grams of distilled water. The mixing time was 15 minutes on an IKAMAG RH magnetic mixer. The pH values were measured from the suspension with Fennolab WTW InoLab pH 720 equipment using a WTW SenTix 41 electrode.

4.2.5 Porosity distribution

The total porosity and the distribution of the air, capillary, and gel pores of the concrete samples were ascertained by the capillary water uptake test (Vesikari and Koskinen 2012, 2013) according to the VTT 358-86 method. Three flat samples with a thickness of 15 millimetres were cut out from the specimens at the depths of 0-15, 18-33, and 36-51 millimetres. First, the initial weights were measured by drying the specimens at a temperature of +50 °C, when only the gel pores are filled with water. In the second phase, the specimens were placed on a grating to absorb water through their lower surfaces. Finally, the total porosity of the specimens and their weights in water and air were measured after applying a water pressure of 15 MPa to the specimens and drying them in an oven at a temperature of 105 °C.

The increase in the weights and the time dependency during the second phase were monitored. In the water uptake curve two parts were observed. In the first part, in addition to the gel pores, which were already filled, the capillary pores were filling with water and the air-filled pores were encapsulated in water but remained air-filled. In the second phase, all the capillary pores were filled and the increase in weight took place only through the slow filling of the air pores. The water content at the bending point of the water uptake curve is assumed to present the combined volume of the gel and capillary pores in the concrete. The rest of the porosity consists of the air pores, which were filled in the test by applying a high water pressure to the specimens. The different pore types can be determined from the weight differences at different phases and the total volume of the specimens. As a result, the initial total porosity was 0.124 for the SR04 and 0.131 for the SR05. The initial ratios of the air, capillary, and gel pores were 0.20, 0.65, and 0.15 for the SR04 specimens stored in air, and 0.20, 0.51, and 0.29 for those stored in solution. The initial ratios were 0.21, 0.60, and 0.19 respectively for the SR05 specimens stored in air.

To determine the specific surface area of the C-S-H according to Equation 3.9 and the more detailed properties of the pore system of both concrete mixes, the results of mercury intrusion porosimetry (MIP) and nitrogen gas adsorption (for smaller pores) techniques were combined. Cylindrical samples with a diameter and length of 15 millimetres were drilled from the core of the air-stored specimens and their surfaces were exposed to the air. The isothermal nitrogen adsorption was carried out by using Quantachrome Autosorb Automated Gas Sorption and the mercury intrusion porosimetry by Quantachrome Poremaster. The Barrett-Joyner-Halenda method (BJH method) (Aligizaki 2006) was used for the smaller pores. Prior to the porosity measurements the samples were subjected to vacuum drying. As a result, values of 30 m²/g (SR04) and 35 m²/g (SR05) for the specific surface areas of the C-S-H were calculated. The calculation was carried out by adjusting the pore sizes in the model to correspond with the experimental values.

4.2.6 Tortuosity properties

The tortuosity factor τ of the pore structure of the concrete was indirectly determined through the measurement of the chloride migration coefficient by using rapid chloride migration (RCM) testing. The tortuosity factor τ [-] can be achieved through applying a non-steady-state chloride migration coefficient D_{nssm} [m²/s] as

$$\tau = \frac{D_{nssm}}{D_{w,cl} \cdot \varepsilon} \quad (4.1)$$

where $D_{w,cl}$ is the diffusion coefficient of chlorides in water [m²/s].

The RCM test was performed with the PROOVE'it rapid chloride penetration test equipment according to the Nordtest method NT BUILD 492. For determining the initial tortuosity values, three concrete specimens with diameters of 100 millimetres and a length of 50 millimetres were cast using similar concrete mixes to SR04 and SR05. The initial values obtained for the tortuosity factor τ were 0.052 [-] for the SR04 specimens stored in air and 0.038 [-] for those stored in solution. The initial tortuosity factor was 0.130 [-] for the SR05 specimens stored in air.

4.2.7 Chloride profiles by titrations

The amounts of chlorides in the concretes were measured using powder samples, which were prepared from the specimens. The chloride contents were determined according to the ASTM standards for acid-soluble chloride (ASTM C 1152/C 1152M) and for water-soluble chloride (ASTM C 1218/C 1218M). The titrations were performed a day after grinding.

5. Comparison between experimental results and models

The results obtained by the numerical methods described in Chapter 3 and the experimental studies in Chapter 4 are presented and discussed in this chapter. The applicability of the models for estimating the deterioration phenomena is also evaluated. The phenomena in the air-stored (Chapter 4.1.1 and Publication 4) and solution-stored specimens (Chapter 4.1.2 and Publication 3) are inspected. A comparison between the experimental and calculated results with the models based on the diffusion equation is made for carbonation and chloride ingress.

5.1 Comparison between experimental values and results received by diffusion models based only on Fick's second law

5.1.1 Concrete carbonation

The depth of the carbonation was regularly determined for both concretes by phenolphthalein during the 70 months of the accelerated carbonation tests. The duration of the accelerated test can be considered remarkably long. Figure 6 represents the results of the accelerated tests and the best fits of Equation 3.1 to the data points leading to values of 1.84 and 2.18 mm/ $\sqrt{\text{month}}$ for the parameter k in Equation 3.1 or k_a in Equation 3.2 (the exposure time t defined in months) for the SR04 and SR05 concretes, respectively. In the accelerated tests, the speed of the carbonation k_a is approximately ten times faster than the coefficient of natural carbonation k_n according to Equation 3.2. As a result, the natural carbonation should be 2.3 and 2.7 millimetres after 13 years according to the reduced k values in Equation 3.1. The carbonation depths measured by phenolphthalein for the SR04 and SR05 concrete mixes held for 13 years under natural CO₂ concentration were 3.0 millimetres and 7.5 millimetres, respectively. The results reveal that the carbonation depths based on the values obtained with the accelerated tests clearly deviate from the depths of the measured natural carbonation, especially in the case of the SR05. Generally, the carbonation proceeded faster than the accelerated tests suggested.

Figure 6. Carbonation depths achieved in accelerated carbonation test measured by phenolphthalein (Ipatti 2004), and the best-fitting of the results to Equation 3.1 (Publication 4).

In the accelerated tests, the progress of the carbonation of the concrete did not obey Equation 3.1, especially in the early stages of testing. Neither can the observed intersection of the measured values of the carbonation depths of the concrete mixes be predicted by Equation 3.1. The length of the accelerated test was long compared to commonly used test periods, which should increase the validity of the method. The natural conditions were not as stressful from the carbonation viewpoint as the accelerated tests, where the surrounding temperature was 20 ± 2 °C, whereas the temperature in the natural conditions was 12 ± 2 °C for 75 months. During the last 81 months the temperature was 22 ± 2 °C in the natural conditions but the relative humidity was only 35% compared to 70% in the accelerated test.

5.1.2 Chloride ingress

The fitting of all the available case-specific long-term experimental results of the total chloride ingress (Publication 3, Vesikari and Koskinen 2012) to Equation 3.3 gave large variations for the values of the diffusion coefficients D_{nss} and surface chloride content C_s , which were $0.30\text{--}3.29 \times 10^{-12}$ m²/s and 0.042–0.094% by mass of concrete, respectively. The median values were $D_{nss} = 0.85 \times 10^{-12}$ m²/s and $C_s = 0.062$ % by mass of concrete. Significant variations in the constants D_{nss} and C_s resulted not only from the different experimental data, but also from the expected precision of the method according to CEN/TS 12390-11. Chlorides can also concentrate near the exposed surface and the chloride content may, therefore, reach a much higher value than assumed by the fixed value of C_s in the method. As the D_{nss} and C_s determine the changes in the time-dependent chloride content in the analysis, the variations in these values directly affect the reliability and plausibility of the results.

5.2 Comparison between experimental values and results received by the thermodynamic model

The calculations for evaluating the model were performed by using the SR04 and SR05 concrete mixes with the input values presented in Table 9.

Table 9. Input values used in the calculations for evaluating the model.

Parameter	Values		
Composition of SR04 and SR05 concrete mixes	Table 5		
Properties of the solid phases investigated	Table 2		
Surface reactions considered	Table 3		
Diffusion coefficients in the pore solution	Table 4		
Initial solid phase compounds	Table 7		
Initial pore solution composition and pH	Table 8		
Initial porosity and tortuosity	SR04	0.124	0.052 air-stored
			0.038 solution-stored
	SR05	0.131	0.130
Ratios of air, capillary, and gel pores	SR04	0.20;0.65;0.15	air-stored
		0.20;0.51;0.29	solution-stored
	SR05	0.21;0.60;0.19	
Specific surface area of C-S-H	SR04	30 m ² /g	
	SR05	35 m ² /g	
Surface site density	4.878 sites/nm ²		
Environmental conditions	air-stored	Chapter 4.1.1	
	solution-stored	Table 6	

The total time was adjusted to match the duration of the exposure time of 13 years in the experiments, also taking into account the change in the environmental conditions of the natural carbonation tests after 75 months. The time and space discretisation fulfilled the Neumann criterion, given as (Marty 2009)

$$N_{eu} = \frac{2D_{ei}\Delta t}{\Delta x^2} \leq 1 \quad (5.1)$$

where Δx and Δt refer to a cell length and a time step, respectively. According to the criterion, 3 millimetres and 7 hours were used for Δx and Δt in all the cases. The total length analysed was 30 millimetres. The precipitation/dissolution of substances during the exposure was evaluated and its effects on the porosity of the concrete and, further, on diffusivities were considered by recalculating their values after each time step in the program.

5.2.1 Air-stored SR04 and SR05 specimens

Distribution of solid phases and pH value

The measured solid phases of the binder matrix of all the specimens consisted mainly of portlandite and calcite. In addition, traces of ettringite were observed. The phenomena that clearly originate from the carbonation process were the precipitation of calcite and dissolution of portlandite near the exposed surface. The phenomena were noticed in all the samples but were more pronounced in the case of the SR05. The measured phenolphthalein front did not clearly correspond with any specific experimental substance. The depth of the phenolphthalein front seems to indicate the depth where the pH has lowered by about 0.5 units from its initial value, but the physical and chemical changes have taken place beyond that front. Professor Page stated (McPolin et al. 2009) that phenolphthalein does not give a precise measurement of the pH of the concrete. The pH values measured by phenolphthalein have been noticed to have a large dispersion and, therefore, the pH might be higher than that identified by the phenolphthalein test (McPolin et al. 2009). The aggregates and cement type used also affect the phenomena. The comparison between the experimental data and the calculated distributions of portlandite and calcite and the simulated pH value profiles are presented in Figure 7, where the values of the cement hydrates are given in relation to their initial quantities.

The calculated distributions of portlandite and calcite, as well as the simulated pH value profiles, were supported by the experimental results. Generally, the calculated results also indicated that the carbonation reduces the pH value. Further, in the case of the SR05, where the carbonation is certainly more pronounced than in the case of the SR04, the pH values were lower near the exposed surface. However, the high cement content of the SR04 and, thus, the presence of a large amount of portlandite and other compounds, such as potassium and sodium oxides, maintains a higher pH value. At a depth of 15 millimetres in both of the concretes, the pH values remained constant. The model predicted slightly higher pH values than those obtained experimentally.

The model also predicted that ettringite and the C-S-H gel would both dissolve near the exposed surface (Figure 8). Concluding from earlier studies (Maekawa et al. 2009, Thiery et al. 2007), they were probably precipitated mainly as calcite. The traces of ettringite were noticed by XRD deeper in the case of the SR05 than the SR04 mix. The simulated results also suggested that the C-S-H gel was dissolved near the exposed surface more with the SR05 than the SR04, which is in accordance with the experimental results. The simulations suggested that the other cement hydrates would remain basically stable throughout the exposure period, except the hydrotalcite that was both dissolved and precipitated, mainly depending on the behaviour of the ettringite. The behaviour of the hydrotalcite cannot, however, be confirmed experimentally because of its low amount.

SR04

SR05

Figure 7. Distributions of Ca(OH)_2 and CaCO_3 and pH value of suspension in the SR04 and SR05 concretes after 13 years of exposure according to the experiments and the model. The calculated data points are connected directly by the curves (Publication 4).

SR04

SR05

Figure 8. Distribution of solid phases in the SR04 and SR05 concretes after 13 years of exposure according to the model (Publication 4).

Distribution of elements

The simulated distributions and experimentally determined values of the total amount of calcium are presented in Figure 9. The model predicted the precipitation of calcium near the exposed surface of the SR05 concrete. This tendency is in line with the experimental results. The model did not result in a similar precipitation of calcium with the SR04 concrete, which was also consistent with the experiments. The calcium originates mainly from the precipitation of calcite.

Figure 9. Distribution of total calcium in the SR04 and SR05 concretes after 13 years of exposure according to the model and the experiments (Vesikari and Koskinen 2012, 2013 and Publication 4).

Porosity distribution

The porosity properties of both concrete mixes varied near the exposed surface. The densities of both mixes increased, which was related to the increased weight of the cement gel. The formation of cement hydrates with higher specific weights that occurred reduced the porosity of the gel. This particular phenomenon happened in both concrete mixes but was, however, stronger with the SR05. The capillary porosity of the SR05 also increased by approximately 5% within a depth range of 0-15 millimetres, whereas it remained almost unchanged in the SR04. The average values calculated for the layer that was investigated (0-15 mm) corresponded with those obtained experimentally. Figure 10 represents the distribution of the measured sizes of the pores with their volumes and the total density of the concrete mixes exposed to natural carbonation for 13 years. The values were obtained by the capillary water uptake test. The total volume and density distributions obtained by the calculations are given in the same figure.

The model gave clear local variations in the total porosity distributions. Near the exposed surface two high and two low peaks were obtained for the SR05. The behaviour of the SR04 was more even. The comparison between the calculated and experimental values of the total porosities is difficult. The experimental values are zone-specific averages and may not detect a possible non-linearity near the boundary zone. However, in the total porosities the calculations showed a partly decreasing trend similar to that of the results achieved experimentally. In the SR05 concretes the layers with a high porosity were likely to be a consequence of the dissolution of portlandite. Similar dissolution layers with significantly elevated porosities have also been observed (Rimmelé et al. 2008) when Portland cement was exposed to CO₂-rich fluids. At the depth of 18-33 millimetres, the calculated total porosity

values matched with the experiments as the cement hydrates remained stable there.

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MODEL

Figure 10. Distribution of pore types and their absolute volumes, and density ρ in the SR04 and SR05 concretes after 13 years of exposure at the depths of 0-15 mm and 18-33 mm according to the experiments (Vesikari and Koskinen 2012, 2013 and Publication 4). The calculated total porosity and density distributions are given as a comparison.

5.2.2 Solution-stored SR04 specimens

Solid phase compounds

After the exposure tests, the calculated distribution of the solid phases in the concrete (Figure 11) corresponds with the observations in the XRD and TG/DTA analyses, which are reported in more detail in Publication 3. The major part of the hydrated phases remained stable throughout the exposure period, as supported by the results received from both the calculations and the experiments. The portlandite phase did not show major dissolution (or noticeable precipitation), except near the exposed surface of the concrete.

The amount of calcite was slightly higher on the outermost area measured (0-5 millimetres) by XRD and TG/DTA than deeper in the concrete but neither the stability of the portlandite nor the result of the calculations, or the other test results (phenolphthalein treatment), suggested that significant carbonation or precipitation of calcite had taken place. Thus, the amount of calcite phase is probably of the same order near the surface as deeper in the concrete.

The results of the calculations indicate minor precipitation of ettringite near the exposed surface and the possible formation of the Fe type of ettringite in that area as well. The experimental results showed traces of ettringite but as there was a relatively small amount of hydrated cement paste in the total sample the other phenomena predicted by the calculations cannot be confirmed with certainty.

Furthermore, the model predicted, and the test results indicated, that a relatively low amount of brucite should have been formed in all the samples during the exposure period, but the amount expected was so low that it would not have been possible to detect it experimentally. The formation of a small amount of the other Mg- and Fe-related phases such as hydrotalcite and Fe-monocarbonate is possible according to the calculations but remains inconclusive according to the test results. It should be noted, however, that the possible formation of ettringite can destabilise the hydrotalcite in the areas near the exposed surface. The formation of ettringite and the lack of AFm phase may also be the reason why Friedel's salt was neither predicted nor observed. The amorphous phase, which most probably consists of C-S-H gel, showed stable behaviour in the calculations as well. The other phases investigated in the calculations (Table 2) did not significantly dissolve or precipitate.

Figure 11. Distribution of the solid phases after 13 years of exposure according to the model (Publication 3).

Distribution of elements

The distribution of elements after the exposure tests was measured by the EDS method and calculated by means of the thermodynamic model. The results of the studies are presented in Figure 12. The model predicted the dissolution of calcium near the exposed surface of the concrete. Similarly, in the EDS results a decrease in the amount of calcium near the exposed surface was observed. The dissolution of calcium-containing cement hydrates near the surface of the specimen may be an explanation for the calcium leaching. This presumably leads to a decrease in the pH value of the concrete, which was also observed experimentally. The EDS test results agreed with the results of the calculations for the behaviour of aggressive elements (here Mg, S, and Cl). The amounts of Mg and Cl elements were higher near the exposed surface than deeper in the concrete, whereas the amount of S was almost in equilibrium with the exposure solution. The increased level of Mg near the surface of the concrete was mainly controlled by the formation of small amounts of brucite. The predicted minor precipitation of ettringite might have had an effect on the amount of sulphur, equilibrating it with the exposure solution. The amounts of the other elements investigated are assumed to be controlled mainly by the aggregates, particularly near the exposed surface.

EXPERIMENTS

MODEL

Figure 12. Total composition of elements after 13 years of exposure according to the model and EDS experiments (Vesikari and Koskinen 2012 and Publication 3).

Total porosity distribution and pH value

The total porosity and pH values measured from the exposed concrete specimens showed the same trend as the results of the calculations (Figure 13). The porosity of the specimens reached its minimum value at a depth of five millimetres from the exposed surface. Near the surface of the specimen the porosity increased according to the model. This result is most likely, but could not be confirmed experimentally. The preparation of the concrete specimens for reliable porosity analysis in the area very near the exposed surface is

difficult and it was not reasonable to use the limited number of concrete specimens available for the analysis. The most probable reasons for the change in the total porosity distribution inside the specimen are the precipitation/dissolution reactions of the cement hydrates and the possible leaching of calcium from the cement hydrates on the surface.

The same factors presumably affect the behaviour of the pH value in the concrete, which dropped from its initial value in the zone being investigated and showed a decreasing trend from the inside of the specimen, reaching its minimum value near the surface of the concrete. According to the results and as suggested in McPolin et al. (2009), the concrete powder method can be considered here as being more indicative than an exact pH value indicator. That can explain the difference between the measured values and the predicted ones. The variations in the total porosity and pH value were, however, relatively low except at the distances below 2.5 millimetres from the surface. It seems that deeper in the specimen both values remained constant in practice, which might result from the stability of the cement hydrates there.

Similar trends of the distributions of the pH value and total porosity in the solution-stored specimens were observed in the air-stored SR04 specimens (Figure 7 and Figure 10). The change in the total porosity in the air-stored specimens from its initial value was less than in the solution-stored specimens, whereas the pH value was reduced slightly more as a result of aerial carbonation.

Figure 13. Total porosity and pH value after 13 years of exposure; experiments vs. model (Publication 3).

Chloride penetration

The distributions calculated for the concentrations of chlorides are presented in Figure 14. The chlorides can be free in the pore solution, including the EDL layer, or they can be bound in cement paste. The sum of those gives the total amount of chlorides. The experimental results for free chlorides and the total

amount of chlorides are given in the same figure. The total predicted concentration of chlorides agreed with the measured results. The adsorption of chlorides seemed to be strongest in the middle part of the specimen. The calculations and the experiments suggested that chlorides are only physically adsorbed as neither the aluminium nor ferrite type of Friedel's salt nor any other similar compounds were clearly detected. The calculated concentration of free chlorides in the solution, which were divided into chlorides within the EDL layer and in the free solution (marked as EDL + free solution), corresponded with the experimental results for the free chlorides. However, the calculated concentration of chlorides in the free solution only was lower than the water-soluble concentrations obtained experimentally, which are generally considered as free chlorides. On the other hand, it is also possible that at least a part of the chlorides in the EDL layer can be removed by water (Beaudoin et al. 1990).

Figure 14. Chloride concentrations after 13 years of exposure; experiments vs. model (Publication 3).

5.3 Concluding remarks of the comparison

The conclusion from the comparison between the natural carbonation and the prediction given by the accelerated tests and the methods based on Equations 3.1-3.3 was that the long-term carbonation cannot be estimated reliably by combining a typically used linear diffusion equation and the results of the accelerated carbonation tests. The carbonation as a phenomenon was confirmed to be more complicated than was assumed by the diffusion equation. It is obvious that in the simulation, it is also necessary to model altering physical and chemical phenomena.

Similar conclusions can be drawn from the diffusion model for chloride ingress. As the result included a relatively high degree of uncertainty and is based directly on the constant values for the diffusion coefficient and surface

chloride content, which are both time-dependent by nature, the error-function method cannot be considered reliable.

The models based only on Fick's second law do not include the time-dependent change of the whole system by checking the thermodynamic equilibrium of the system. Furthermore, the diffusion into concrete happens in a concentrated pore solution and not in an infinite dilute solution as Fick's law presumes. The phenomena directly affecting the diffusion of ions are also neglected. The drawbacks limit the applicability of Fick's second law to predict carbonation and the penetration of ions during exposure periods exceeding the periods covered experimentally.

The thermodynamic model showed a plausible correlation with a large variety of long-term experimental data. The results also confirmed the importance of multi-ionic transport with ion-ion and ion-solid interactions for the evaluation of the long-term diffusion of harmful substances such as chlorides into concrete or the carbonation phenomenon. Therefore, as the thermodynamic model is able to handle variable time-dependent phenomena of physical chemistry in concrete, its use in the long-term simulations of ageing facilities is justified.

Generally, as in both exposure tests with the exposure time of 13 years the alteration of the SRO4 concrete mix took place only in the boundary zone with a thickness of 10 millimetres at most, the performance of the mix in the tests can be considered at least satisfactory. The changes in the pH value and porosity distribution were also relatively low compared to the initial values, improving its ability to resist deterioration phenomena.

6. Simulation of the ageing of concrete in facilities for low- and intermediate-level nuclear waste

Long-term simulations of the deterioration of the concrete were performed with the thermodynamic model introduced here, covering the assumed length of the operational phase of 100 years and the post-closure period of 400 years (Publication 5). In the calculations, the composition of the concrete was the same SRO4 as in the experimental work. The composition can be considered as a typical choice for the concrete mix of the facilities. The simulated concrete structure represents a section of the massive wall of the nuclear waste silo as presented conceptually in Figure 15. In the simulations the mass transport was analysed by means of a one-dimensional model. The lengths of the cells are dependent on the period analysed. Concrete carbonation, chloride ingress, and the stability of the cement matrix were considered in the analysis. The input values for the simulation are given in Table 10.

Figure 15 Conceptual model for long-term simulations. The length of the cells and the whole model are given in Table 10.

Table 10. Input values for the long-term simulations.

Parameter	Values	
Composition of SR04 concrete mix	Table 5	
Properties of the solid phases investigated	Table 2	
Surface reactions considered	Table 3	
Diffusion coefficients in the pore solution	Table 4	
Initial solid phase compounds	Table 7	
Initial pore solution composition and pH	Table 8	
Initial porosity and tortuosity	0.124; 0.052	
Ratios of air, capillary, and gel pores	0.20;0.65;0.15	
Specific surface area of C-S-H	30 m ² /g	
Surface site density	4.878 sites/nm ²	
Exposure time of the periods	100 years (operational)	400 years (post-closure)
Time step	7 hours	13 days
Cell length	3 mm	10 mm
Total length	30 mm	300 mm
Boundary values	CO ₂	0.06%
	RH	70%
	Temp.	12 °C
Boundary condition	constant, closed	

6.1 Carbonation during the first 100 years

The results indicate that the carbonation-related alteration in the concrete microstructure has clearly taken place to a depth of approximately 15 millimetres from the exposed surface, as presented in Figure 16 and Figure 17. As a typical installation depth of the reinforcement is more than 25 millimetres, the alterations in the concrete are not expected to reduce the alkalinity of the concrete at the depth of the reinforcement. The main impacts of the carbonation on the deterioration of the concrete are that the material properties are changed from their initial values by the carbonation before the structures become submerged during the post-closure period. A pH value lowered by carbonation will affect the stability of the cement hydrates in the long term compared to the situation without carbonation. Decalcifying and the decomposition of the C-S-H reduce the physical adsorption of substances penetrating into the exposure solution. At the depths up to 15 millimetres from the concrete surface, the variation in the porosity is also significant. The results correspond with the experimental and calculated values in Chapter 5.2.1, only being more pronounced. As a matter of fact, the results indicated that the condition of the SR04 concrete after 100 years is similar to the condition of the SR05 at an exposure period of 13 years (Figure 8 and Figure 10).

Figure 16. Composition of cement hydrates after operational period of 100 years according to calculations with thermodynamic model (Publication 5).

Figure 17. Total porosity and pH value after operational period of 100 years according to calculations with thermodynamic model (Publication 5).

6.2 Chloride ingress during the post-closure period of 400 years

For the initiation of corrosion of the steel reinforcement the threshold value of the chloride content given in the literature is usually 0.05% by mass of concrete. The total chloride concentration obtained by means of the thermodynamic model is presented in Figure 18. The concentration exceeds the limit of 0.05% only near the exposed surface, but is still close to that limit within the whole boundary zone. The threshold content has a large scatter in the literature, depending on numerous parameters, which may also lead to contradictory values.

The method based on the Cl^-/OH^- ratio may offer a theoretically better basis for a threshold value than different mass ratios, as it also considers the other time-dependent phenomena affecting the pH value. The Cl^-/OH^- ratios for the total chloride concentration, and for chlorides in the electrical double layer (EDL) and free solution or the free solution alone after 400 years of the post-closure period, are presented in Figure 19. The ratios between the chlorides and hydroxyl ions are high for all types of chlorides in the whole specimen, if the ratio is compared to the threshold value given in the literature for the case which is between 0.3 and 6 (Angst et al. 2009, Diamond 1986, Taylor et al. 2000). Since the chlorides are mainly bonded physically with calcium ions in the case (Publication 3) and can be released by environmental conditions, such as carbonation, the total amount of chlorides needs to be considered. As a result of the analysis based on the Cl^-/OH^- ratio, the initiation of corrosion is possible at all the depths investigated (0-300 millimetres).

Figure 18. Total chloride ingress after post-closure period of 400 years according to calculations with thermodynamic model (Publication 5).

Figure 19. Simulated Cl^-/OH^- ratio after post-closure period of 400 years according to calculations with thermodynamic model (Publication 5).

6.3 Stability of concrete during the post-closure period of 400 years

The concentrations of all the ions studied in the pore solution and in the concrete are presented in Figure 20 and Figure 21, respectively. The calcium content is reduced near the exposed surface in both cases. The reduction is mainly due to the dissolving of calcium hydroxide and the sequential decomposition of the C-S-H, which takes place simultaneously (Figure 22 and Figure 23). The leaching of calcium has increased the total porosity as well. The increased porosity speeds up the ingress and accumulation of the harmful substances in the concrete, leading to a faster deterioration of the concrete. The presence of carbonates in the groundwater has further lowered the pH value near the exposed surface after the carbonation that took place in the operational phase. On the other hand, the carbonation also improved the situation by delaying the removal of the calcium.

Magnesium has most probably replaced the calcium in $\text{Ca}(\text{OH})_2$ to form brucite, as suggested by the increased magnesium concentration near the exposed surface. The other magnesium-bearing component, hydrotalcite, has also formed. Even though brucite might protect the interior from dissolution, it is insoluble, which reduces the pH of the pore solution. Further reactions of magnesium with the calcium of the C-S-H gel after the depletion of calcium hydroxide could also result in an increase in the volume and a possible loss of strength of the concrete. Neither this particular phenomenon nor the other harmful reactions of magnesium with sulphates or chlorides was observed in the simulations.

If the calcium hydroxide is leached or the carbonation has progressed enough, the AFm and AFt phases will finally break down. That was observed in the simulation, where the ettringite dissolved slightly near the exposed surface

during the post-closure period. The other detrimental sulphate-related phases, such as gypsum and thaumasite, the formation of which could also be possible, were not deposited in the simulations. Significant reaction and substitution of carbonates with AFt and AFm phases were not detected either.

Figure 20. Concentration of ions in pore solution after post-closure period of 400 years according to calculations with thermodynamic model (Publication 5).

Figure 21. Total concentration of ions after post-closure period of 400 years according to calculations with thermodynamic model (Publication 5).

Figure 22. Composition of cement hydrates after post-closure period of 400 years according to calculations with thermodynamic model (Publication 5).

Figure 23. Total porosity and pH value after post-closure period of 400 years according to calculations with thermodynamic model (Publication 5).

6.4 Evaluation of uncertainties in the simulation of carbonation

The method used for evaluating the uncertainties in the simulated results (Chapter 3.4) was applied to the results of the carbonation after an operational period of 100 years. In this research, the criterion for the depth of the carbonation is defined by the depth of the dissolution front of portlandite, that is, the depth where the amount of portlandite has fully dissolved as a result of carbonation. This criterion for the carbonation is based on the results of the

experimental work and the simulation after 13 years presented in Chapter 5. The altered zone of porosity properties and cement hydrates are dependent on the behaviour of the portlandite. Generally, the criterion for the carbonation depth is obviously case-specific and depends heavily on the type of cement.

In Figure 24 the fragility curves are presented for 5%, 95%, and median levels of confidence after 100 years of exposure, when the dissolution of the portlandite is considered in the SR04 mix. The uncertainties were assumed to be independent of the concrete mixes. For the aleatoric uncertainty β_r a value of 0.2 was obtained from the variation coefficients that were calculated from the phenolphthalein measurements of this study and from the other measurements (Jones et al. 2000, 2001). The epistemic uncertainty β_u was evaluated to be 0.1, covering the variation used in the analysis methods for the cement hydrates and the variation in the control system of the environmental conditions (temperature ± 2 °C and relative humidity $\pm 5\%$) during the exposure period. When the confidence level of 95% is considered, there is a probability of 0.5 that the carbonation remains below 9.5 millimetres. The median value is 11.1 millimetres for the SR04.

Figure 24. Fragility curves at different levels of confidence when the dissolution of portlandite is considered after 100 years of exposure in SR04 concrete mixes (temperature 12 °C and relative humidity 70%).

7. Conclusions

In the study a thermodynamic model was introduced for estimating the ageing of concrete in the conditions of Finnish rock caverns designed for the final disposal of nuclear waste. The model considers ion-ion and ion-cement hydrate interactions, as well as the properties of the gas phase in multi-ionic transport and reaction phenomena in the concrete during the operational and post-closure periods of the facilities. A large variety of experimental data extracted from the sulphate-resistant Portland cement (SRPC) concretes exposed to natural carbonation in air or the penetration of aggressive substances under submersion for 13 years in controlled environments was used for evaluating the model. The theory of the model was shown to give a plausible basis for estimating the long-term ageing phenomena of concretes, particularly in practical applications where the design period of structures can be as much as hundreds of years. The approach introduced is general and can be applied to different concrete mixes by defining their case-specific initial values. The other improvements the thermodynamic simulation methods provide compared to the methods that are typically used are the possibilities of observing and understanding the latent factors of deterioration during long exposure periods, which makes it possible to influence the selection of materials in the design phase or to find proper corrective measures.

It was also shown that the methods which are typically applied by the construction industry for predicting the long-term deterioration of concrete structures are not able to handle the variable complex physiochemical phenomena in concrete if the exposure periods considerably exceed the periods covered experimentally. Additionally, the time to the initiation of corrosion may be underestimated when the methods based only on Fick's second law with typical threshold contents of chlorides given by the mass of cement or concrete are used. The fact that the methods based on the linear diffusion equation are not able to produce or consider information about the deterioration mechanisms by updating the physical chemistry of the system during the simulations also has a prejudicial impact on the credibility of these methods.

The simulations performed for concrete in the nuclear waste facilities studied here illustrated that the concrete undergoes a complex deterioration process during the service life of the facilities. The two completely different types of long-term environments in the Finnish disposal concept also

emphasise the need for careful simulations as the carbonation of the concrete during the operational period will affect the deterioration during the post-closure period. The sulphate-resistant type of concrete with a water-to-cement ratio of 0.43 used in the simulations performed satisfactorily during the exposure period of 500 years that was investigated. However, the initiation of corrosion of the steel reinforcement during the service life of facilities cannot be excluded.

The threshold concentration of chlorides (based on a Cl^-/OH^- ratio) for the initiation of corrosion of the reinforcement at the typical depths of the reinforcement may be exceeded despite the alkaline conditions maintained inside the concrete. It is, therefore, recommended to use case-specific values for a threshold content and evaluate the method used for estimating the time to the initiation of corrosion of the reinforcement in demanding structures with a long design service life.

The physical adsorption of chlorides most probably affects the total chloride concentration during the long-term exposure. The leaching of calcium-bearing components from the concrete affects the strength of the concrete. However, the main detrimental reactions of the concrete take place at a depth of less than 50 millimetres from the exposed surface, which is typically a relatively small part of the whole structure and, especially, of the total number of multiple technical barriers.

On the basis of the experimental work it can be concluded that the reliability of the thermodynamic model is mainly governed by the uncertainty of the experimental data utilised in the evaluation of the model or used as initial values. Both long-term laboratory and large-scale experimental data are valuable, because of the natural heterogeneity and continuous physical and chemical changes in the concrete. The difficulties are particularly emphasised when the sensitivity of the test methods is remarkable, such as with pore solution analyses. Statistical analyses of the factors and the uncertainty of the simulation result can be used for introducing a more robust basis for decision making. The role of the aggregates in the deterioration of the concrete should be evaluated in the future. More sophisticated models for the alteration of the C-S-H are necessary if the timescale is significantly extended past 500 years.

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