Chapter 2
Materials and Properties

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Abstract Various cementitious materials are used in nuclear applications covering a broad range of environmental conditions and time scales. The characterisation of cementitious materials and the determination of their properties are a key issue for assessing the evolution of nuclear infrastructures. This section gives in first place an overview of blended cements, low pH-cementitious materials and fiber reinforced and advanced cement-based materials. Degradation of cement-based materials in their environments is to a significant extent controlled by their transport properties. For this purpose, reactive transport models are being developed integrating multiple coupled phenomena. The scientific assessment basis needed for the development of these models is discussed. In particular, leaching, carbonation and oxidation of cementitious materials are dealt with. Besides chemical processes, desiccation and pre-cracking play also an important role in determining the transport properties of cementitious materials. Scaling to realistically-sized engineered systems under field conditions is a challenging issue.

Keywords Transport properties · Hydration · Carbonation · Leaching · Desiccation · Pre-cracking · Coupled phenomena

2.1 Introduction

Cementitious materials are used in reinforced concrete for structural components, as well as in grouts and wasteforms in nuclear applications. The context for use is also varied including nuclear power facilities, used fuel interim storage and final
repository disposition, nuclear-chemical processing, facility closure and waste management. Extensive use of blended cements is anticipated in the various components of future nuclear facilities to achieve improved performance characteristics such as higher strength, durability, and radionuclide retention. This initiative is also guided by the global need to optimise the use of raw materials in the near future and to limit the CO₂ foot-print of industrial activities. It is notable that Roman cement is still performing well in many structures after a couple thousand years. As such, large quantities of coal fly ash, ground granulated blast furnace slag (GBFS), and/or silica fume may be used as supplemental cementitious materials along with reduced quantities of Portland cement. Current performance assessment tools, however, have been developed for systems composed mostly of Portland cement. There is, therefore, a critical need for tools that can predict the properties and performance of systems composed of a broad range of cementitious materials. This is a key issue when integrating the long-term aspect for nuclear infrastructure.

2.2 Blended Cements and Hydrated Phase Prediction

Prediction of properties and system performance at longer ages is handicapped by the lack of data with which to implement and to validate the predictive modelling. In particular, the decline in pH over time is uncertain and the mineralogical evolution of the system is uncertain. It is, therefore, important to overcome these knowledge deficiencies. An important advance in knowledge would be the ability to define the hydrated phases produced during the hydration reactions of blended cements, and their associated physical, chemical, thermodynamic and kinetic characteristics and along with the pore solution composition as they play a critical role in the mechanical strength, buffering capacity and radionuclide retention properties, and, thus, impact the overall system performance.

Recently, Snyder et al. (2009) proposed a phase development model in which standardised materials characterisation techniques are used in conjunction with the thermodynamic hydration model developed by Lothenbach et al. (2008) to validate the hydrate phase prediction. Snyder et al. (2009) found X-ray powder diffraction (XRD) with Rietveld analysis and thermo-gravimetric analysis (TGA) to be two very useful techniques in identifying and quantifying hydrated cementitious phases for a range of cementitious binder mixtures anticipated for nuclear applications. Arnold et al. (2012) evaluated the use of Portland cement hydrated phase definitions for predicting solid-liquid partitioning of major constituents from a fly ash, slag, and Portland cement mortar after 30 months of curing and also carried out quantitative scanning electron microscopy—energy dispersive x-ray (SEM-EDX) characterisation of the material. Results indicated that earlier phase definitions provided a useful starting point but modelling of the observed behaviour was challenging for silica at pH above 12 and for aluminium at pH less than 12. Only fractional reaction of GBFS and fly ash was observed experimentally and phyllosilicates, likely introduced with the sand fraction, appeared to play an important
role in partitioning of some constituents. Further research is needed to quantify the reaction rate of fly ash and slag and their respective hydration products. Independent validation of the resulting phase quantification is needed by a combination of approaches such as XRD, TGA and SEM-EDS.

Hidalgo López et al. (2008) also demonstrated the usefulness of SEM and infrared spectroscopy for phase definition in blended cements. Nuclear magnetic resonance (NMR) spectroscopy has been shown as a useful tool in evaluating silicate polymerisation (Cong and Kirkpatrick 1996; Colombet et al. 1998; Ramachandran and Beaudoin 2001). While the proposed approaches show promise, important remaining issues include the determination of phases that should be included in the predictive model and the confidence that should be placed in the selection of these phases. Furthermore, the inclusion of GBFS in the material formulation imposes chemical reducing properties within the cement matrix (often used to reduce mobility of technetium), which may slowly oxidize with the ingress of atmospheric oxygen. Under these conditions, the changes in speciation of several important constituents within the cement matrix, such as sulphur and several radionuclides, remains uncertain.

2.3 Characterisation of Low pH-Cementitious Materials

Underground repositories for long-term disposal of high-level radioactive waste are based on the concept of a multiple-barrier system to ensure waste isolation for tens or hundreds of thousands of years. Several designs include a clay-based engineered barrier such as bentonite in contact with large amounts of cementitious materials. Pore waters originating from Portland cement-based materials have a high alkalinity (pH > 13) and are able to react with and modify the mineralogy and properties of the bentonite barrier (Fernández et al. 2009). The alteration of bentonite is characterised by montmorillonite dissolution at the early stage and by the substitution of zeolites presumably by cement phases such as calcium silicate hydrates (C–S–H) on the long-term (Fernández et al. 2009). The use of low pH cementitious materials (pH < 11) is an accepted method to ensure bentonite stability over long periods of time. Calcium aluminate cements (CAC) are thus an interesting alternative to Portland cement-based materials to prevent reaction with bentonite barriers. However, CAC suffer from hexagonal calcium aluminate hydrate phase conversion, generally resulting in an increase in porosity and loss of strength.

Addition of high silica content admixtures such as silica fume has shown to be effective in reducing the hydrate conversion process, increasing the stability of the microstructure, and slightly decreasing further the pore water pH of the cementitious material (Hidalgo López et al. 2008; Garcia Calvo et al. 2009). The microstructure of the new binder is characterised by the development of new phases such as strätlingite (C$_2$ASH$_8$) and siliceous hydrogarnet. While these new binders show promise for use in the underground facility of a nuclear waste repository, little is known on their properties and impact on long-term performance.
2.4 Fiber Reinforced and Advanced Cement-Based Materials

Randomly oriented nano/microfiber (steel, carbon, polymeric, and glass) reinforced cement-based materials are an important class of composite materials that can be tailored for specific applications and can open the door for new applications in nuclear waste containments. The use of these fibers improves the post cracking load bearing capability of cement-based materials by controlling the growth of cracks, limiting the crack width, and improving the material energy absorption performance, resulting typically in an increase in strength, toughness, impact resistance, fatigue strength, and durability as well as a reduction in plastic shrinkage cracking (Banthia and Sheng 1996; Katz 1996; Lange et al. 1996; Banthia and Nandakumar 2003; Shah et al. 2004). Fiber reinforcements provide additional, unique properties, including low electrical resistivity, electromagnetic field shielding, self-sensing capabilities (carbon and steel) (Chung 2000, 2002; Reza et al. 2003), high ductility and self-control of cracks (polymer) (Li 2003), making them attractive for applications where the long-term performance and advanced monitoring of the structure is critical. Whereas, a large number of studies have been conducted to examine the direct structural, mechanical, and electrical properties provided by the fibers (Wang et al. 1987; Katz and Bentur 1994; Toutanji et al. 1994; Fu and Chung 1995; Banthia and Sheng 1996; Lange et al. 1996; Torrents et al. 2000; Nelson et al. 2002), the long-term chemical and structural stability of these materials in response to severe conditions such as thermal and radiation environments and environmental weathering has received little attention.

Among the various properties that influence the composite material, the interfacial bond between cement paste and fiber is the most important. Stress (and thus load) transfer between the cement-based material and the reinforcement takes place through the interface and interfacial zone. It is the efficacy of adhesion that determines the load that can be distributed to the fibers, ultimately determining the maximum load-bearing capacity of the composite structure. Over its lifetime, the material is subjected to a multitude of physical, chemical, and mechanical degradation processes, causing internal chemical changes and stresses that directly affect the interfacial bond between the reinforcing fibers and cement (Sanchez and Borwankar 2010). Pull-out of fibers during cracking can result in exposed fibers in cracks during degradation. Prediction of the long-term performance of fiber reinforced cement-based composites requires, therefore, understanding how the fiber-cement interface changes as a function of material weathering and resultant chemistry.

Decalcification is of critical concern in structures used for radioactive waste disposal and is closely associated with various types of concrete deterioration. A study of the effect of decalcification on the fiber-cement interface and in turn the mechanical properties of carbon microfiber reinforced cement-based composites has been performed by Sanchez et al. (2009), Sanchez and Borwankar (2010). Results showed a strong coupling between calcium leaching at the fiber-cement interface
and the mechanical degradation of the composites. Prior to decalcification, the fiber cement interface in Portland cement pastes was characterised by the presence of a thin layer rich in calcium hydroxide. During exposure to ammonium nitrate solution, preferential leaching around the fibers occurred resulting in debonding of the fibers and a greater loss of strength. However, as the composites leached, the fibers increasingly contributed to an increased ductility. Decalcification changed the failure mode from brittle cracking to slow ductile load dissipation, which was more pronounced for the Portland cement pastes with the fibers. Addition of silica fume to the mix slowed the degradation process, stabilised the fiber-cement interface during decalcification, and reduced the loss of strength. Research is needed, however, to investigate the effect on the fiber integrity of high shear rates to homogenise samples with silica fume.

The use of nano-sized (e.g., nano-silica, nano-calcium carbonate, and nano-iron) and nanostructured (e.g., nanoclay) particles and also nanotubes and nanofibers have been shown to enhance the performance of cement-based materials, providing higher compressive and flexural strengths, improved hydration and internal curing characteristics, early cracking resistance, and higher durability compared to conventional cement-based materials (Raki et al. 2010; Sanchez and Sobolev 2010; Kawashima et al. 2013; Pacheco-Torgal et al. 2013). These innovative concretes are thus promising for the containment of radioactive wastes, and research is needed to evaluate their long-term performance under environmental conditions relevant to nuclear waste storage. Recent efforts in this area include a study of the effect of decalcification on the chemo-mechanical behaviour of cement pastes containing carbon nanofibers (CNFs) (Brown et al. 2012b). Results showed a strong correlation between the CNF dispersion state, the microstructural evolution of the cement paste during decalcification, and the material mechanical properties.

### 2.5 Transport Properties

Description of the degradation of cement-based materials subjected to exposure to air, water, and saline solutions requires consideration of the rate-limiting mass transfer processes that control the distribution of reactants within the material, chemical speciation, equilibrium, and reaction kinetics between the different phases (henceforth referred to as reactive transport modelling). An initial step in developing a reactive transport model for performance of a cement-based material is the definition of a conceptual model of the material and its associated system, including important transport mechanisms and pathways (e.g., liquid and vapour phase diffusion, percolation, capillary transport, cracking and preferential flow pathways), system chemistry (e.g., aqueous-solid and aqueous-vapour partitioning, mineral phases, local equilibrium vs. kinetic representation), and system initial and boundary conditions (e.g., water contact and infiltration, relative saturation, vapour, liquid and solid interfaces). One example for system definition and interactions is provided in Fig. 2.1. Reactive transport modelling then requires either direct
measurement or simulation-based quantification of key reactive transport parameters that are related to the specific material composition and physical structure, as well as saturation and temperature. Extensive reviews of conceptual models, constituent transport, and degradation mechanisms for cement materials used in nuclear applications are available (CBP 2009; Pabalan et al. 2009; Weiss 2012).

Research associated with transport and reaction of constituents through or from concrete can be considered as (i) providing an improved microscale understanding of various phenomena leading to improved conceptual and mathematical models, (ii) providing needed parameter estimates using measurement or simulation based approaches (Garboczi et al. 1999; Martys and Hagedorn 2002; Arns et al. 2004; Ukrainczyk et al. 2012), and (iii) model scaling and simplification to evaluate engineering-scale applications and scenarios.

At the microscale, recent research has emphasised the relationships between microstructure, sand fraction, and effective diffusivity as a function of water to cement ratio relative the importance of the interfacial transition zone (ITZ) in understanding observed aqueous diffusion processes (Larbi et al. 2012). Results suggest that the more porous ITZ around individual aggregate particles becomes more connected at sand volume fractions greater than approximately 50%, resulting in significantly increased aqueous phase and gas phase (under unsaturated conditions) diffusivity.

Fig. 2.1 One example of system definition and interactions for evaluation of cementitious materials performance in nuclear applications
Another consideration is the potential influence of the electric double layer (EDL) that forms around the negatively charged cement hydration products to restore electroneutrality. The EDL has been reported to have a non-negligible effect on the transport of ionic species (Chatterji 1994a, b; Revil 1999; Yu and Page 1991; Castellote and Llorente 2006). It has been reported that the effect of the EDL is more significant at low water/cement ratios than high water/cement ratios (Chatterji 1994a). Elakneswaran et al. (2009, 2010) investigated the influence of the EDL properties on chloride ingress in cement-based materials and proposed an integrated thermodynamic modelling approach that incorporates phase equilibrium and surface complexation models in addition to multicomponent diffusion in charge free pores and diffuse double layer of hydrated cement pastes. C–S–H, Portlandite, ettringite, and monosulfate phases were considered for the equilibrium reactions and the surface complexation reactions were limited to C–S–H. Blended cements were used in the study, including a hydrated cement paste, a slag cement paste, and a fly ash cement paste. The sorptive properties of the cement pastes were explained on the basis of the classical Freudlich theory. The diffusion through the EDL was modelled considering the linearised Poisson-Boltzmann equation for symmetric electrolytes. Results showed that the EDL properties of the hydrated cement pastes had a significant effect on the adsorption and transport of chloride through the gel pores (diameter less than 10 nm), which occupied more than 30% of the total pore volume of the pastes. The slag cement paste had the lowest porosity and the greatest amount of gel pores and showed the greatest ability of chloride to bind both chemically and physically, resulting in the greatest influence on the ingress of chloride as compared to the other pastes.

Arnold et al. (2013) used a solution of the full non-linear Poisson-Boltzmann equation for symmetric and asymmetric electrolytes and illustrated that use of the linearised Poisson-Boltzmann equation results in approximation errors on the order of 10% for symmetric electrolytes and up to 50% for asymmetric electrolytes with the greatest effect of the EDL in gel pores. In summary, while it is recognised that ionic transport in cementitious materials is affected by the intercoupling of physical and chemical phenomena, detailed transport mechanisms of ionic species are still not well understood and the known effect of the EDL is generally not accounted for in reactive transport models. As a result, calculated diffusion coefficient values determined only based on Fick’s law without consideration of other ionic effects, increases the uncertainties in predicting long-term aggressive substance ingress into cementitious materials.

Development of simulation-based approaches for estimating relevant effective transport parameters has been on-going (Garboczi et al. 1999; Martys and Hagedorn 2002; Arns et al. 2004; Ukrainczyk et al. 2012). Efforts in this area have been focused on developing appropriate three-dimensional digital images or virtual representations of pore structure, either from direct imaging or through rule-based hydrated microstructure assemblage formation. This latter modelling approach provides information of fundamental importance in terms of mechanistic understanding of transport parameters such as porosity, pore interconnectivity, and...
tortuosity; however, how these parameters change with time during exposure needs to be considered. Efforts are also needed with respect to parameter identification and their degree of certainty to ensure representation of the reality.

2.6 Coupled Phenomena and Materials Behaviour

As illustrated earlier in Fig. 2.1, understanding performance of cementitious materials in realistic engineered applications\(^1\) requires integration of multiple phenomena, many of which are inextricably coupled, and assumed scenarios regarding the expected environment in which the materials are used. Among the materials challenges for cementitious materials that have been identified for the next decades, optimisation of material properties and durability, extension of the service life of civil engineering structures, reduction of CO\(_2\) emissions, and sustainable use and management of resources are certainly the most important ones. Addressing these issues is essential when considering the long-term functioning and durability requirements for nuclear construction (e.g., reinforced concrete confinement building) and waste management components (e.g., waste containers, wasteforms, disposal systems). Three aspects of coupled phenomena and application are cross-cutting amongst most applications: (i) carbonation, (ii) leaching, and (iii) scale-up and integration for evaluation of realistic engineered systems.

2.7 Carbonation and Oxidation of Cementitious Materials

Carbonation of cementitious materials, from reaction with atmospheric or other sources of carbon dioxide such as biogenic, can result in a decrease in the pore-water pH of cementitious systems to pH \(\sim 9\) which can lead to depassivation of embedded steel and thus to the onset of steel reinforcement corrosion for structural materials and increased leaching of radionuclides or other constituents. The rate of carbonation is a function of the following: (i) material alkalinity and pore structure (including potential crack pathways), (ii) water saturation, and (iii) concentration of external carbon dioxide sources. Several NUCPERF papers focused on improving the understanding of carbonation processes. Brown et al. (2012a) carried out reactive transport modelling sensitivity studies focused on the impacts of concrete formulation and exposure conditions for underground high level waste storage tanks at the U.S. Department of Energy sites. For simulation, Stora et al. (2009) performed numerical modelling of unsaturated accelerated carbonation of CEM I cement-based materials using the DUSS software. The simulations underlined the importance of

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\(^1\)Cementitious materials performance adequacy with their functionality for nuclear engineered applications.
initial mineral phase composition. In particular, the study showed that the reduction of calcium-bearing hydrates due to the substitution of clinker by silica enhances the carbonation propagation, even though the initial porosity slightly decreased. Thouvenot et al. (2012) presented the results of coupled cement drying and carbonation in the context of waste packages for intermediate level waste in deep geologic disposal. Results indicated that the drying period for 11-cm thick concrete components was between 2 and 10 years, and carbonation depths on the order of 2–3 cm are expected over 100 years. Arnold et al. (2009) described the effects of carbonation on constituent retention in a cementitious wasteform and Auroy et al. (2012) described ongoing experimental studies on the impacts of the carbonation process on transport properties of the resultant cementitious matrix.

An analogous reaction is the oxidation of wasteforms through gas phase diffusion of atmospheric oxygen or introduction as dissolved oxygen in water and reaction at the water film-solid interface. Reducing admixtures, such as granulated blast furnace slag, are added to cementitious wasteforms to maintain reducing conditions as a mechanism for increased retention of some important radionuclides, such as technetium-99 (Pabalan et al. 2012). Pabalan et al. (2012) studied the rates of leaching as a consequence of oxidation for one wasteform composition; however, the rate and extent of oxidation, along constituent retention, are not generally well known. For example, it is unclear if release is a function of a rind formation around reduced particles or if oxidation is more uniform.

These studies point to the research and application needs of (i) gas phase diffusivity and reaction as a function of water saturation; (ii) improved definition of the mineral phases and associated thermodynamic solubility parameters for carbonated materials (especially for compositions with supplemental cementitious materials such as fly ash, slags, and silica fume); (iii) clearer understanding of anticipated oxygen, carbon dioxide, and relative humidity boundary conditions under anticipated exposure conditions; and (iv) the need to understand the impact of changes in mineralisation as a result of carbonation and oxidation on transport properties.

2.8 Leaching

Leaching processes and assessment are important because leaching of major material constituents can result in decalcification and decrease in pore solution pH leading to corrosion and degradation of structural or hydraulic properties. Leaching of trace species results in the release of radionuclides and other constituents of potential concern. Recently, the U.S. Environmental Protection Agency has standardised a set of four leaching test methods, developed as part of the Leach Environmental Assessment Framework (LEAF), that are suitable for evaluation of cementitious materials and wasteforms. The goal of the LEAF methods is to describe constituent leaching as a function of one or more release-controlling parameters rather than to simulate leaching under a single set of test conditions.
The LEAF leaching methods have been documented (Kosson et al. 2002; Garrabrants et al. 2010), validated (Garrabrants et al. 2012a, b), and are now adopted as EPA testing methods (USEPA 2013). Tests conducted using the LEAF approach include methods to characterise (i) liquid-solid partitioning (LSP) as a function of pH using EPA Method 1313, (ii) LSP as a function of liquid-to-solid ratio (L/S) using EPA Method 1314 or Method 1316, and (iii) mass transfer parameters as a function of leaching time using EPA Method 1315. These methods not only support U.S. regulatory applications, but also provide a basis for parameterising reactive transport models for concrete and cementitious wasteforms (Sarkar et al. 2010, 2012; Brown et al. 2012a). Currently, these methods are being used to evaluate formulations for secondary and low activity wasteforms as part of waste management at former defense sites in the U.S. (Mattigod et al. 2011; Um et al. 2011; Arnold et al. 2012).

Within the framework of the development of the LILW disposal facility of El Cabril in Spain, a service life model was developed (Zuloaga et al. 2009). A specific study dedicated to the leaching of concrete barriers of the disposal vaults taking into account the evolution of water content due to seasonal temperature changes was carried out. The experience showed that the engineered barriers behaved as assumed with previous estimation except in the case with the temperature changes. It was concluded that, the life assessment of a real engineered barrier has thus to consider all realistic scenarios and taking into account all the materials and the elements of the multi-barrier isolation system.

Another example of correlations between measures and predictive model development for long-term behaviour of concrete structures subjected to leaching was provided by a study carried out by de Larrard et al. (2009). This work was the opportunity to compare various field measurements achieved during concrete structure building operations (tunnel and bridge), with calculations performed with a finite volume method. Numerical simulation of accelerated leaching test using ammonium nitrate were carried-out with a special focus on the effect of the mesh refinement on the solid calcium concentration profile and the optimisation of computational times. The finite volume modelling method developed within this study was regarded as a very promising approach to provide probabilistic calculations taking in account the variability of calcium diffusion parameters.

Garcia Calvo et al. (2009) investigated the durability of low-pH cementitious materials, specifically their resistance to long-term aggression to groundwater from real repository conditions. Leaching tests at low overpressures (~0.5 bars) and groundwater from the Aspo site (Sweden) with high Cl\(^-\) and Mg\(^{2+}\) content were used. The use of silica fume and fly ash as high silica content admixtures was evaluated. Results showed that the material based on CAC plus silica fume provided a good resistance to groundwater aggression while that based on CAC plus fly ash showed an altered front with decalcification of the C–A–S–H phases and incorporation of magnesium ions. The materials tested had, however, relatively high porosity that could be due to the formation of dense hydrogarnet and the use of a high water to binder ratio.
Other recent work by Dauzères et al. (2010a, b) on clay-rock/cement-based material interaction in the context of geological disposal has provided interesting results through the comparison of the leaching behaviour of CEM I and low pH-pastes. Leaching tests (at the cement/clay interfaces while exerting confining pressure on the solid) were performed for a minimum of one year using synthetic mudstone water at neutral pH and 25 °C under a controlled CO₂ environment (1.3 %). Results showed that the decalcification of the low pH-material was greater than that of CEM I, showing the formation of amorphous silica and an intense capillary porosity opening. It was also observed that the carbonation of the CEM I paste was quite limited with only the formation of a superficial calcite layer. In contrast, the low pH-paste was carbonated over the entire decalcified zone. For this material, a magnesium enriched zone (M–C–S–H) behind the decalcified and carbonated domain was also observed.

The results described above show that there is still significant research needed to understand and predict the long-term behaviour of complex materials in the disposal context. Research would benefit from well described reference cases, use of standardised leaching characterisation methods to allow comparison of results in combination studies designed to elucidate specific ageing mechanisms, and the resultant impacts on constituent release and chemical, mechanical, and transport properties. Additional research is also needed that connects small-scale laboratory results with observations of field test systems over prolonged timeframes.

2.9 Desiccation and Pre-cracking in Cement Pastes and Mortars

During their lifetime, cracking in concrete structures could occur due to mechanical loading (at the service state a limited opening depending on the standards and the environmental conditions is allowed for reinforced concrete structures) or due to physical (autogenous, thermal and drying shrinkage, freeze-thawing, elevated temperatures…) or chemical phenomenon (alkali-aggregate reaction, delayed ettringite formation…) and finally lead to a decrease in durability.

At early age, in massive structures, if shrinkage is restrained or due to temperature gradients, internal stresses develop and cracks could occur. This is an important problem that could be experimentally tested for instance by means of an active restrained shrinkage ring test (Briffaut 2009). This test allows comparing the effect of different concrete mixes or different reinforcement on the cracking behaviour. In this test, all phenomenon involved (evolution of mechanical properties with hydration, thermal and autogenous shrinkages, creep, mechanical damage and their couplings) are considered. The behaviour of massive concrete structures is actually rather well modelled and applied to the case of nuclear vessels (Benboudjema and Torrenti 2008) or buffers used for the storage of radioactive wastes (Craeye et al. 2009). Note that elevated temperatures at early age could also
be the source of delayed ettringite formation. Cracking due to this reaction affects strongly the transfer properties of concrete (Al Shamaa et al. 2014).

After a long time, cracks are mainly due to drying shrinkage. An extensive literature is available on drying shrinkage and dimensional stability (de Sa et al. 2008; Bissonnette et al. 1999; Saito et al. 1991). As far as desiccation is involved, the permeability and the desorption isotherm and the couplings with cracking should be considered [see an example of model in (Torrenti and Benboudjema 2012)].

The cracking pattern and interconnectivity between micro and macrocracks have been reported to play an important role in the transport properties of the material (Lim et al. 2000). The development of microcracks facilitates the transport of aggressive salts and ions into the material, accelerating its deterioration. Most of the studies performed to evaluate the influence of cracking are based on the measurement of water and chloride permeability of pre-cracked specimens obtained from controlled compression or splitting tensile testing (Lim et al. 2000; Saito and Ishimori 1995; Djerbi et al. 2008; Wang et al. 1997; Ludirdja et al. 1989; Samaha and Hover 1992). A comprehensive review of the effect of mechanical stress on permeability of concrete is provided by Hoseini et al. (2009).

Recently, Rougelot et al. (2009) proposed a new method to investigate the effect of cracks on transport properties in cement pastes and mortars based on measurement of the extent of water vapour desorption and drying kinetics. Results demonstrated the influence of diffuse microcracking over macrocracks on the hydric patterns. Two methods of generating cracks in the material were used: (i) three points bending, leading to localised macrocracks and (ii) thermal shock, leading to more diffuse microcracking. Change in the compressive Young’s modulus was used as an indicator of the damage induced by the thermal shock. Results showed that localised macrocracks did not influence the kinetics of water desorption while diffuse microcracking affected the transport properties of the material, most likely due to an increase in pore connectivity. The more connected porous network led to acceleration in the drying process and removal of water from ink-bottle pores. The Young’s modulus after thermal shock was found to decrease by 15–20 % and was more significant for mortars than cement pastes. While these results clearly indicated the importance of considering the cracking pattern when dealing with durability issues, the rather severe treatment from thermal shock could have affected the paste mineralogy and differential shrinkage between the paste and the aggregate may have occurred.

Additionally, it should be mentioned that in the context of radioactive waste storage and disposal, concrete structures could be subjected to temperatures as high as 80 °C and thus to subsequent desiccation and cracking. The impact of temperature on the water movement and sorption properties of concrete has been poorly studied and results are scarce. Pihlajavaara (1976) had studied this effect and found a great impact of temperature and a reduction of the water content at saturation when temperature increases. Recent studies by Poyet (2009) and Poyet and Charles (2009)
on desorption isotherms of CEM I HPC concrete performed at 30 and 80 °C confirmed these results. The isotherm shape was drastically modified and the water content at equilibrium was strongly reduced at 80 °C. The water content at saturation was significantly lower at 80 °C than at 30 °C. The description of the impact of temperature on concrete sorption properties was achieved using the Clausius-Clapeyron equation and the isosteric heat of sorption. Results obtained allowed for computation of concrete desorption isotherms at any other temperature with a good accuracy. Concrete durability assessment in such hydro-thermal environment should integrate this kind of approach.

Note that concrete carbonation should also influence the desorption isotherms (Auroy et al. 2012) and the transfer properties.

2.10 Understanding Durability and Performance in the Context of Specific Applications

Material performance specifications, formulations, and environmental stresses that challenge long-term durability are strongly a function of specific applications. Thus, there is need for general definition of performance envelopes (e.g., range of conditions and performance requirements) that are important for different applications. The resulting performance envelopes and key information gaps within each performance envelope provide an important framework for guiding future research. For example, reducing conditions and interfaces between cementitious wasteforms and concrete containment structures, are important considerations for grouted low activity waste disposal (Pabalan et al. 2012; Protiere et al. 2012), but not for many other structural applications. Also, specific waste types, such as low activity salt waste at the United States Savannah River Site and ion-exchange resins may impose unique material composition and performance challenges (Lafond et al. 2012; Neji et al. 2012; Pabalan et al. 2012; Protiere et al. 2012). Reactions and leaching with boric acid are of interest specifically for used fuel storage pools (Pabalan and Chiang 2012). Interactions of concrete at interfaces with bitumen, clays and salt formations, as well as bacterially mediated reactions, are important for some geologic repository designs (Fernández et al. 2009; Alquier et al. 2012; Bertron et al. 2012). However, understanding the impact of certain reactions and conditions on performance, such as carbonation (Atış 2003; Khunthongkeaw and Tangtermsirikul 2005; Auroy et al. 2012; Brown et al. 2012a) and temperature effects (Kasami et al. 2012) have very broad applicability.

Additionally, keeping in mind operational aspects, it is essential to consider realistic degradation conditions by considering, for example, the water chemistry, the hydro-thermal environment (temperature/saturation), and the initial state of the material (e.g., carbonation, see recent work by Drouet et al. (2010) on the carbonation of blended cement-based materials).
2.11 Integration for Application to Engineering Systems

Integration of multiple phenomena and scaling to realistically-sized engineered systems under field conditions requires further research. For example, water flow by capillary and condensation processes and in response to temperature changes and thermal gradients is not often considered but was found to be central to understanding the performance of a field test case (Zuloaga et al. 2009). Drying shrinkage has been found to be dependent on the size of structural components (Benboudjema and Torrenti 2012). Denitrifying bacterial activity has also been observed at conditions anticipated for the cement matrix interface for wasteforms with high nitrate content, with important consequences on the understanding of radionuclide retention (Alquier et al. 2012). Probabilistic approach integrating the variability of key parameters controlling physic-chemical and mechanical properties is also a major issue for the long-term prediction of concretes structures stability and durability. These are just a few examples that point to the essential nature of large-scale field testing for validation of both conceptual and reactive transport models and the importance of long-term monitoring of test sites, with the intention of feedback to improve modelling and estimates of long-term performance.

2.12 RILEM TC-226-CNM Recommendations for Future R&D

Priorities for future R&D which should deserve further attention were highlighted during discussion panel sessions held at the end of the workshops:

- Multiple Processes and Properties have to be considered as a function of material composition
  - Processes: evolution of mineralogy and morphology, moisture transport, constituent transport, chemical reactions
  - Properties: thermal, hydraulic, mechanical, chemical properties
  - Constitutive relationships: link between processes and properties
- Need for guidance to establish consistent and complete data sets
- Need for better understanding of coupling (non-linear) of multiple processes and evolution of properties
- Need for better understanding of the interconnection pathways in cementitious materials with aggregates
- Need for better understanding of the effect of microstructure (including ITZ at the cement—aggregate interface) on effective diffusion and other transport properties
- Need to understand ageing and degradation phenomena for new materials (e.g., carbon fiber-cement paste interfaces in bulk material and exposure face, low pH cement)
- Need to be able to describe complex blended systems incorporating complex wasteforms
- Models need to take account of experimental data on real systems so that actual mineral phases and localised microstructure are not omitted
- It is essential that real systems (i.e. not idealised lab tests) need to be well characterised
- Extrapolating short-term data to the long-term is a major problem in a number of technical areas, including cement mineralogy and redox conditions
- The effect of microstructural changes on mechanical properties needs to be evaluated and the links between specific phase changes and mechanical changes needs to be demonstrated

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