Chapter 2
Cementitious Materials and Their Sorption Properties

Abstract The cementitious materials considered here include hydrated cement grout, concrete, and mortar. These materials may be used for waste conditioning, as waste container, and for backfilling. Dry cement (clinker) is a hydraulic binder; concrete is a mixture of hydrated cement, water, and coarse and fine aggregates; mortar and grout are a mixture of water, hydrated cement, and fine aggregates. Clinker is a mixture of several anhydrous minerals, mainly calcium silicates. Ordinary Portland cement (OPC) consists of finely ground clinker plus a small amount of gypsum. Hydration results in the formation of portlandite $\text{Ca(OH)}_2$, largely amorphous calcium silicate hydrates (CSHs), and minor crystalline phases containing aluminium, iron, and sulphate (e.g. ettringite, monosulphate, hydrogarnet, and hydrotalcite). Solutions in equilibrium with fresh hydrated cement are hyperalkaline ($\text{pH} \geq 13.2$) with correspondingly high Na- and K-concentrations. It follows that hydrated cement systems are not in equilibrium with infiltrating water, which leads to dissolution and re-precipitation reactions. It is well established that the degradation of hydrated cement follows a pattern of several different, more or less distinct states, characterised by progressively lower pore water pH and Ca/Si ratio. Hydrated cement solid phases provide a variety of potential sites for different uptake reactions for dissolved elements, ranging from surface adsorption to incorporation and solid-solution formation (these processes are termed sorption henceforth). At low sorbate concentration (below the respective solubility limit), use of a single distribution coefficient for quantifying uptake under a defined set of conditions (e.g. a specific degradation state) is a defensible approach.

2.1 Cementitious Materials

The cementitious materials considered here include hydrated cement grout, concrete, and mortar. These materials may be used for conditioning the waste, as waste container and for backfilling containers in the repository. Cement is a hydraulic binder and can bind other materials together through hydration reaction
Cement itself is a mixture of several anhydrous minerals, mainly calcium silicates, which form in the reaction of calcium carbonate with silica-bearing minerals. Cement is normally produced by heating limestone with clay to about 1450 °C in a kiln. The resulting hard cement clinker is then ground with a small amount of gypsum into a powder to make ordinary Portland cement (OPC), the most common cement type. Portland cements normally comprise four main components: 50–70 % alite, 20–30 % belite, 5–12 % aluminates, 5–12 % ferrite, and small amounts (~2 %) of the added gypsum (Chen et al. 2008; Taylor 1997).

- Alite is tricalcium silicate, $\text{C}_3\text{S}$ (where $\text{C} = \text{CaO}$ and $\text{S} = \text{SiO}_2$) or $\text{Ca}_3\text{SiO}_5$, which reacts with water to form calcium silicate hydrate (CSH) gel and portlandite (Ca(OH)$_2$). Alite is considered to be the most significant constituent phase with respect to strength development at the early stage of cement hydration up to 28 days.
- Belite is dicalcium silicate, $\text{C}_2\text{S}$ or $\beta$-$\text{Ca}_2\text{SiO}_4$. Belite reacts with water to produce also CSH and portlandite but at a slower rate. The strength development by belite hydration is only fully attained after about 1 year.
- Aluminate in unhydrated cement is present partly as ferrite and tricalcium aluminate $\text{C}_3\text{A}$ (where $\text{A} = \text{Al}_2\text{O}_3$) or $\text{Ca}_3\text{Al}_2\text{O}_6$. $\text{C}_3\text{A}$ reacts with water in the presence of sufficient amount of gypsum to yield AFt (calcium aluminosulphate, $\text{F} = \text{Fe}_2\text{O}_3$), e.g., ettringite or AFm (calcium monosulphoaluminate) if the availability of gypsum is limited.
- Ferrite is a calcium aluminoferite, $\text{C}_2(\text{F,A})_5$ with high substitution of Fe for Al; it reacts with water in a similar way as aluminate $\text{C}_3\text{A}$.
- Finally, gypsum is added to slow the setting time and permit a period of workability. A too rapid setting is caused by an immediate hydration of aluminates and because of that, the subsequent strength development of cement becomes poor.

To produce concrete or mortar, the cement clinker is mixed with the appropriate amount of water and aggregate material (Taylor 1997). Aggregate material typically consists of sand (quartz) and gravel form silicate or calcareous rocks. In the present case (near-surface disposal of low- and intermediate-level radioactive wastes at Dessel, Belgium), it is specified that all aggregate material consists of calcite grains.
2.3 Cement Hydration

Upon interacting with water, the anhydrous cement clinker undergoes hydration reactions and develops binding properties and strength. Hydration results in the formation of portlandite Ca(OH)$_2$, CSHs, and other minor phases containing aluminium, iron, and sulphate:

- calcium hydroxide Ca(OH)$_2$, or portlandite;
- amorphous (or microcrystalline) CSH phases with an initial Ca to Si molar ratio (C/S) at around 1.8 (this ratio will decrease as cement degrades);
- AFt phases (aluminoferite trisulphate)—a group of calcium sulphaaluminate hydrates, such as ettringite with [Ca$_3$(Al,Fe)(OH)$_6$·12H$_2$O]X$_3$·H$_2$O as general formula, where X denotes a double-charged anion (typically sulphate) or two units of a single-charged anion; and AFm phases (aluminoferite monosulphate)—with [Ca$_2$(Al,Fe)(OH)$_6$]X·H$_2$O as general formula;
- Hydrogarnet (3CaO·Al$_2$O$_3$·6H$_2$O); and
- Hydrotalcite, a layered double hydroxide of the general formula (Mg$_6$Al$_2$(CO$_3$)(OH)$_{16}$·4(H$_2$O).

2.4 Sorbing Minerals in Cementitious Materials

The concrete to be used for the ONDRAF/NIRAS disposal facility in the municipality of Dessel is mainly a mixture of Portland cement (slag-free for CEM I and slag-containing for CEM III), and calcareous aggregates of different grain sizes (Tables 2.1 and 2.2). Solid phases in the concrete therefore comprise hydrated cement solids and calcite aggregates. The major cement solid phases

Table 2.1 Concrete composition for the modules and the containers, Gens (2008). CEM I defined according to EN 197-1:2000 (2000)

<table>
<thead>
<tr>
<th>Component</th>
<th>Content (kg/m$^3$)</th>
<th>Content (weight %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEM I 42.5 N LA HSR LH$^a$</td>
<td>350</td>
<td>15</td>
</tr>
<tr>
<td>Calcitec$^{TM}$ 2001 MS (ground calcium carbonate)</td>
<td>50</td>
<td>2.1</td>
</tr>
<tr>
<td>Sand 0/4 (limestone)</td>
<td>708</td>
<td>30</td>
</tr>
<tr>
<td>Calcareous aggregates (2/6)</td>
<td>414</td>
<td>17.5</td>
</tr>
<tr>
<td>Calcareous aggregates (6/14)</td>
<td>191</td>
<td>8</td>
</tr>
<tr>
<td>Calcareous aggregates (6/20)</td>
<td>465</td>
<td>19.7</td>
</tr>
<tr>
<td>Water</td>
<td>175</td>
<td>7.4</td>
</tr>
<tr>
<td>Water/cement ratio</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>Superplasticiser (Rheobuild$^{TM}$ 1100 conc. 30 %, NS type)</td>
<td>6.46</td>
<td>0.3</td>
</tr>
</tbody>
</table>

$^a$LA low alkali, HSR High sulphate resisting, LH low heat (hydration). Values in () are size range in mm. NS napthalene sulphonate
are crystalline portlandite (Ca(OH)$_2$) and amorphous CSH. Minor phases include ettringite (aluminoferrite trisulphate, AFt), monosulphate (aluminoferrite monosulphate, AFm), hydrogarnet, and hydrotalcite. All these solids provide potential sorbing surfaces for dissolved radionuclides. CSH phases display non-specific sorption; that is, both cations and anions can be sorbed although the mechanism may not always be known. Examples for anion immobilisation onto hydrotalcite, AFm, and AFt phases may be obtained from Wieland and Van Loon (2002). Calcite, initially present as aggregates and/or generated as a newly formed phase owing to cement carbonation, may also sorb radionuclides (Zachara et al. 1991). Although co-precipitation of radionuclides with calcite has been considered in the literature as a particularly relevant sorption process (Curti 1997; Meece and Benninger 1993; Komarneni and Roy 1981), in this review clear distinction is to be made between true sorption and solubility control leading to precipitation. Therefore, data on precipitation and co-precipitation associated with calcite will not be considered as true sorption.

Different sorbing cement minerals have a characteristically high surface area (m$^2$/g solid); for example, hardened cement paste (HCP) has a surface area >50 m$^2$/g, portlandite had a surface area of ~6 m$^2$/g, while CSH phases were reported to have a surface area of 148 m$^2$/g (Tits et al. 2006a, b). Large surface area combined with high-sorption data (mol/g) results in high surface densities of sorption sites (mol/m$^2$ or sites/nm$^2$). Therefore, large masses of cement result in a large sorption capacity for radionuclides and other contaminants. Also, under such circumstances, use of a single $K_d$ or $R_d$ to represent sorption at low radionuclide concentration is a defensible approach. From a qualitative point of view, differences in sorption values for different cement or natural minerals such as calcite may be related to differences in surface area and nature (intrinsic charge) of the surface. From a more quantitative point of view, surface area information may also be used in calculating sorption values, for example by means of surface complexation models (Apello and Postma 2006) or ion exchange models (Tits et al. 2008).

Table 2.2 Proposed composition of backfilling mortar for use in containers, Gens (2008)

<table>
<thead>
<tr>
<th>Component</th>
<th>Content (kg/m$^3$)</th>
<th>Content (weight %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEM III/C 32.5 LA HSR LH</td>
<td>510</td>
<td>23.3</td>
</tr>
<tr>
<td>Silica fume</td>
<td>52</td>
<td>2.4</td>
</tr>
<tr>
<td>Calcareous aggregates (0/4)</td>
<td>1392</td>
<td>63.7</td>
</tr>
<tr>
<td>Water</td>
<td>223</td>
<td>10.2</td>
</tr>
<tr>
<td>Water/cement ratio</td>
<td>0.437</td>
<td></td>
</tr>
<tr>
<td>Superplasticiser (Rheobuild 1100 conc. 30 %, NS$^b$ type)</td>
<td>8.9 maximum$^a$</td>
<td>0.406</td>
</tr>
</tbody>
</table>

$^a$Could be adjusted downwards, depending on seasonal conditions

<table>
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$^b$Naphtalene sulphonate
Portlandite (Ca(OH)$_2$)
Portlandite is rarely studied as a sorbing solid. The hydroxyl functional groups on the surface of portlandite have potential to bind strongly sorbing metal ions, in addition to Ni, or sorb anions such as the halogens Cl$^-$ and I$^-$ through substitution with hydroxyl (Gougar et al. 1996). One of the few experimental studies identified in this review is that of Noshita et al. (2001) which demonstrated that portlandite does not sorb Cs and iodide to a significant extent, but it binds Ni as strongly as CSH phases. The observed Ni sorption was interpreted as being due to surface complexation and co-precipitation. Binding of anions and oxyanions is presumably weak, although it has been reported that some oxyanions may have some affinity to portlandite (Cornelis et al. 2008).

CSH Phases
The CSH phase refers to a CSH, as defined previously. CSH is nearly amorphous to X-ray diffraction and, on that account, is often referred to as “cement gel”. Its low crystallinity suggests a structural resemblance to two crystalline CSH, tobermorite, and jennite. The structures of both are known—they occur in nature and can be made synthetically—and consist of corrugated sheets or layers of alternating (Ca–OH) and silicate units. In tobermorite, the silicate sheets are incomplete and much of the silica is dimeric, whereas in jennite, the dimeric units are bridged by additional silicate tetrahedra forming pentameric or higher molecular weight units. From NMR (nuclear magnetic resonance), it appears that these polymer units are organised into platelets, each with typical maximum dimensions of a few tens of nanometres. The individual platelets adhere strongly giving rise to nanoporous bulk gel. The high surface area measured by gas sorption (e.g. 148 m$^2$/g reported by Tits et al. 2006b) arises from the poor packing of platelet substructures. This nanometre-scale substructure is responsible for the low crystallinity reported by XRD: sharp diffractions typical of a “crystal” are only obtained from crystals bigger than approximately 100 nm. Therefore, the low crystallinity and imperfect “structure” of CSH can be expected to give rise to a high density of sorption sites for both cations and anions (Glasser 1993). The “structure” of CSH also makes it impossible to distinguish in any fundamental way between “surface” and “bulk” processes. No doubt operational criteria could be developed to distinguish “surface” from “bulk” but at present, there are no agreed criteria.

There is also controversy about the limits of composition of CSH. For example, Al can substitute in CSH. But the role of aluminium appears to be twofold: as a genuine substituent and in occluded phases. For example, tetrahedral Al occurs in CSH and there is general agreement from NMR that it preferentially substitutes in bridging positions between adjacent silicate dimmers. However, NMR also records penta- and octahedrally coordinated Al, the structural role of which is less clear. It is probable that octahedral Al is, at least in part, presented as occluded AFm, i.e. a second phase is present (F. Glasser, personal communication).
These complex structural considerations and the possible presence of an occluded second phase or phases cannot, at present, be resolved. But the precursors of CSH, alite and belite, incorporate 1–2 wt% alumina and, since their hydration gives rise to CSH, it is likely that all Portland cements give rise to similar CSH. It is an open question to what extent alumina-free synthetic preparations, as for example those frequently made in the laboratory, will reflect the sorption properties of “real” CSH, i.e. CSH from commercial cements containing Al. Also, the extent to which intercalated phases (if present) will affect the properties is variable. Tentatively, differences between synthetic CSH and the product from commercial cement may occur but are unlikely to be large. This is because in many cases, also some data on the sorption properties of phases are likely to be present as intercalates (AFm and AFt). The main feature, which seems to dominate CSH sorptive properties, is the presence of a relatively high volume fraction, several %, of nanopores.

In this context, CSH also exhibits a zeta potential which affects the balance between “surface” and “bulk” sorption. The zeta potential is dependent on the C/S ratio: CSH with high Ca/Si molar ratio has a positive charge and thus tends to sorb anions. Atkins and Glasser (1992) demonstrated that CSH of high C/S ratio is a better scavenger for I than CSH of lower C/S ratio. As the C/S ratio decreases as a result of cement degradation, the surface charge becomes less positive, passing through the point of zero charge at C/S of about 1.2 and turns to negative at lower C/S ratio. Thus, in terms of electrostatic sorption, CSH with a low C/S ratio is a better sorbent for cationic species.

**AFt**

AFt is calcium aluminosulphate hydrate with some iron substituted for aluminium, with ettringite being the most important AFt phase. It has a very open structure and presents several possibilities for crystal chemical incorporation. Many contaminant ions may substitute for the essential ionic components of ettringite—calcium, aluminium, and sulphate. Gougar et al. (1996) summarised sorption mechanisms on ettringite: divalent cations such as Sr$^{2+}$ and Ni$^{2+}$ may substitute calcium; trivalent metal ions replace aluminium, and anions such as CO$_3^{2-}$, Cl$^-$, IO$_3^-$ exchange with sulphates. Ettringite surfaces exhibit a net negative charge, so incorporation of anions in the bulk is probably more important than surface adsorption (Cornelis et al. 2008). Although our definition of sorption was based on an exclusion rule, i.e. all processes other than precipitation, co-precipitation, and solid solutions are considered as sorption, ettringite is included as a relevant solid phase for selecting sorption values.

**AFm**

This phase forms in the presence of limited sulphate availability or an elevated temperature. Its structure is tolerant of substitution and can sorb many contaminants through ion substitution. AFm is known to sorb di- and trivalent heavy
metal ions and diverse anions. The formation of solid solution with AFm may cause a stronger sorption of oxyanions on AFm as compared to ettringite. AFm phases bind iodide, I\(^-\), better than AFt phase (Atkins and Glasser 1992). Based on anticipated chemically similar behaviour between Cl\(^-\) and I\(^-\), AFm phase should have the potential to sorb Cl\(^-\) as shown by formation of Friedel’s salt (3CaO·Al\(_2\)O\(_3\)·CaCl\(_2\)·10H\(_2\)O), a chloride-containing AFm phase.

**Hydrogarnet**
Sorption may happen on hydrogarnet through ion substitution, e.g., Cr(III) may replace Al in hydrogarnet (Glasser 2002).

**Hydrotalcite**
Hydrotalcite has a layer structure and can incorporate many di- and trivalent cations, e.g. Ni\(^{2+}\), and Co\(^{2+}\) in place of Mg\(^{2+}\), Cr\(^{3+}\) in place of Al, etc. Anions such as CO\(_3^{2-}\), Cl\(^-\), and NO\(_3^{-}\) may also substitute for OH\(^-\) and SO\(_4^{2-}\).

**Calcite**
Calcite will be present as aggregate and newly generated by cement carbonation. Calcite is highly crystalline and has a much smaller reactive surface area [e.g. between 0.2 and 1 m\(^2\)/g (Jacques 2003)] and much simpler structure than the sorbing cement materials. It therefore exhibits lower sorption potential than most other cement phases.

### 2.5 Degradation of Hydrated Cement

#### 2.5.1 Degradation States

Solutions in equilibrium with hydrated cement are hyperalkaline, featuring pH values of about 13.2 or higher, and correspondingly high Na- and K-concentrations. It follows that hydrated cement minerals are not in equilibrium with infiltrating water and will dissolve partly upon contact. Moreover, in particular the amorphous CSH phases are not thermodynamically stable in contact with infiltrating water and tend to degrade over time. Depending on the conditions, cement degradation may arise from a number of processes, but the principal degradation mechanism expected for a near-surface waste disposal facility is leaching of HCP components by infiltrating water.

It is well established in the literature that degradation of hydrated cement follows a pattern of several different, more or less distinct states that are characterised by progressively lower pore water pH (Berner 1992; Neall 1994; Atkinson et al. 1989a). Figure 2.1 shows schematically the degradation of hydrated cement with the corresponding pH decrease as a function of time (or more
specifically, with the number of pore water exchanges). A representative illustration of a detailed modelling analysis of the degradation sequence of cement is given below for the Dessel disposal facility (Jacques 2008; Jacques et al. 2008).

According to scheme shown in Fig. 2.1, four states of cement degradation are typically distinguished.

**State I (13.5 > pH > 12.5)**
Pore fluids in hydrated cement contain high concentrations of free alkali metal ions resulting from the initial dissolution of alkali metal sulphates (and the subsequent uptake of sulphate by AFt and AFm phases). In charge balancing the system, equivalent concentrations of hydroxyl ions are produced. Thus, HCP pore fluid in State I has a very high pH in a range of >12.5–13.5 at 25 °C. The pore fluid composition of this state is dominated by Na, K, and OH. As the solubility of portlandite is low at such pH values, only small amounts of Ca are released from the solids and the C/S ratio is high.

**State II (pH = 12.5)**
When all alkali ions are removed at the end of State I, the pH of the pore fluid will be controlled by the solubility of portlandite at 12.5 (25 °C). The composition of
the pore fluid at this state is essentially a 20 mM calcium hydroxide solution. The duration of this state is proportional to the amount of portlandite in the hydrated cement.

**State III (12.5 > pH > 10)**
This state follows the complete dissolution of portlandite at the end of State II. The pH in this state is regulated by the incongruent dissolution of CSH phases. CSH phases of high Ca/Si ratio (C/S > 1.5) coexist with portlandite at States I and II. The dissolution of CSH with high Ca/Si ratio begins at the end of State II, and the Ca/Si ratio as well as pH begins to decrease. Atkins and Glasser (1992) reported that the pH of the pore fluid controlled by the solubility of CSH phases with a C/S of 0.8–1.5 should be in a range of 11–12.4. Tits et al. (2008) found that the pH of the pore fluid in equilibrium with synthetic CSH phases (C/S of 0.82–1.65) is in a range of 10–12.5. At the end of State III, CSH phases dissolve congruently, fixing the pH at a constant value of about 10 (Jacques et al. 2008). The lower-bound pH is thus set at 10.

**State IV (pH < 10)**
CSH phases and other hydrated cement components are completely dissolved and the pH drops below pH 10. The composition of the pore fluid is governed by the remaining aggregate minerals (only calcite in the present case) and the incoming water.

### 2.5.2 Illustrative Example

As an illustration, the changes in solid phase and pore water composition of the concrete envisaged for the surface disposal facility at Dessel, Belgium, are shown in Fig. 2.2 for the infiltration of typical soil water. The four states of cement/concrete degradation are clearly visible:

- **State I**: The pH is controlled by the dissolution of alkalies. This state ends after approximately 0.35 kg of cumulative leached water. This amount of water correspond to approximately 5 pore volumes assuming a porosity of 7 % (or about 3 years under the assumptions specific for the Dessel site, cf. Jacques et al. 2008).
- **State II**: The pH is controlled mainly by the dissolution of portlandite. The concentrations of all other elements (except Na and K) are controlled by cement phases and remain constant due to the constant pH. This state ends after approximately 3500 years for the same assumptions (Jacques et al. 2008).
State III is the most complex. The pH and element concentrations (except Na and K) are controlled by a sequence of dissolution and precipitation reactions of the CSH, AFm, and AFt phases. This state ends when these phases are no longer present, i.e. after depletion of the last phase characteristic for hydrated cement, the tobermorite-like endmember of the CSH phases. This state ends after approximately 36,400 years for the same assumptions (Jacques et al. 2008).

State IV: After depletion of the hydrotalcite phases, pH is partly buffered by calcite dissolution.

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