CEMENT WASTE MATRIX EVALUATION AND MODELLING OF THE LONG TERM STABILITY OF CEMENTITIOUS WASTE MATRICES

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Abstract

Cement based materials are often used as a solidification matrix for wet radioactive waste from nuclear power plants such as ion exchange resins, sludge and evaporator concentrates. The mechanical and chemical properties of the cement-waste matrix are affected by the type and the concentration of the waste. For this reason the recipe used in the solidification process has to be carefully adjusted to respond to the variations of the waste. At the Ringhals Nuclear Power Plant (RNPP) an evaporator was to be taken into operation during the mid 2005. As a result of this process an evaporator concentrate containing boric acid was expected. The aims of the present study were to develop a recipe for the solidification of artificial evaporator concentrates, (AEC), containing H$_3$BO$_3$ and measure the compressive strength of the waste/cement matrix over a period of 4 years. The confirmation of the previously reported retarding properties of H$_3$BO$_3$ and the studies of AEC without H$_3$BO$_3$ were also included as a part of this work. Finally, thermodynamic calculations were used as a tool in order to predict the evolution of the mineralogy and integrity for the different cement-waste specimens over very long periods of time, i.e. up to about 100 000 years. The most important finding was that when an optimized waste/cement matrix recipe was used the compressive strength increased during the entire 4 year period and no signs of degradation were noticed. It was also found that the long-term performance of the waste matrices is to a large extent site-specific. In general, the composition of the infiltrating water is more influential than the waste matrices, both on the degradation of the waste matrices itself as well as on the engineered barriers.

1. INTRODUCTION

Cement based materials are often used as a solidification matrix for radioactive waste from nuclear power plants for solidification of ion exchange resins, sludge and evaporator concentrates. Further, cement is also used as a construction material for low- and intermediate level waste repositories as well as a backfilling material.

The mechanical and chemical properties of the cement-waste matrix are affected by the type and the concentration of the waste. For this reason the recipe used in the solidification process has to be carefully adjusted to respond to the variations of the waste.

At the Ringhals Nuclear Power Plant an evaporator was to be taken into operation during the mid 2005. As a result of this process an evaporator concentrate containing boric acid was expected.

As shown in figure 1, (redrawn form /Koenne/) boric acid is a strong retarder for the solidification of waste/cement matrices and especially when the concentration of H$_3$BO$_3$ is about 4 weight% of the content of dry cement. The theoretical explanation for this observed feature of boron-containing waste has been attributed to calcium diborate, which is assumed to form coating layers upon unhydrated cement surfaces /van Eijk et al 2001/.

The importance of this work is further emphasized by that this waste type is finally deposited in the silo in the Repository for short lived low- and intermediate level waste, SFR, in which more than 40
moulds are stacked on top of each other. This puts very high demands on the long-term mechanical properties of the waste/cement matrix and especially on the compressive strength of this material.

2. AIMS OF STUDY

The aims of the present study were to develop a recipe for the solidification of artificial evaporator concentrates, (AEC), containing H₃BO₃ and measure the compressive strength of the waste/cement matrix over a period of 4 years. The confirmation of the previously reported retarding properties of H₃BO₃ and the studies of AEC without H₃BO₃ were also included as a part of this work.

Finally, thermodynamic calculations were used as a tool in order to predict the evolution of the mineralogy and integrity for the different cement-waste specimens over very long periods of time, i.e. up to about 100 000 years. It is in this context important to assess both the long-term chemical stability of the waste matrix per se as well as its influence on surrounding engineered barriers by the release of anions.

3. EXPERIMENTAL DETAILS

3.1. Laboratory experiments

Seven different specimens were prepared according to table 1 (samples that contained H₃BO₃ but no AEC), table 2 (reference AEC without H₃BO₃) and table 4 (AEC with H₃BO₃). The composition of the AEC is shown in table 3. After careful mixing, the specimens were cast in moulds with a size of 70*70*70 mm or 40*40*160 mm.

After casting the specimens were wrapped in plastic foil and stored on a shelf in the lab for about one week. The plastic foil was then removed and the specimens transferred to a cabinet and stored under a controlled atmosphere with a relative humidity of 95% and a temperature between 19°C and 21°C. The compressive strength of the samples was measured one week, 6 months, 1 year and 4 years after casting.
**TABLE 1. EXPERIMENTS IN WHICH BORIC ACID WAS ADDED TO THE CEMENT PASTE. THE W/C RATIO WAS 0.35 IN ALL EXPERIMENTS**

<table>
<thead>
<tr>
<th>Specimen #</th>
<th>H$_3$BO$_3$/dry cement* (wt.%)</th>
<th>Additive**</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.6</td>
<td>Ca(OH)$_2$</td>
</tr>
<tr>
<td>2</td>
<td>3.8</td>
<td>NaOH</td>
</tr>
<tr>
<td>3</td>
<td>4.2</td>
<td>NaOH</td>
</tr>
<tr>
<td>4</td>
<td>6.0</td>
<td>Ca(OH)$_2$</td>
</tr>
<tr>
<td>5</td>
<td>7.4</td>
<td>Ca(OH)$_2$</td>
</tr>
<tr>
<td>6</td>
<td>7.8</td>
<td>NaOH</td>
</tr>
<tr>
<td>7</td>
<td>9.1</td>
<td>NaOH</td>
</tr>
</tbody>
</table>

* H$_3$BO$_3$ is a solid compound which was dissolved in water prior to the mixing with the cement paste.
** The amount of Ca(OH)$_2$ and NaOH was adjusted so that the pH in the H$_3$BO$_3$ solution exceeded 11.

**TABLE 2. REFERENCE EXPERIMENTS WITH ARTIFICIAL EVAPORATOR CONCENTRATE WITHOUT H$_3$BO$_3$**

<table>
<thead>
<tr>
<th>Specimen #</th>
<th>[salt] wt% (salt/dry cement)*</th>
<th>W/C ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>0.40</td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>0.35</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>0.44</td>
</tr>
</tbody>
</table>

* The salts were added to the cement as a solution. The composition of that solution is shown in Table 3 below.

**TABLE 3. COMPOSITION OF THE ARTIFICIAL EVAPORATOR CONCENTRATE. FOR THE EXPERIMENTS SHOWN IN TABLE 2, H$_3$BO$_3$ WAS EXCLUDED**

<table>
<thead>
<tr>
<th>Salt</th>
<th>Amount (g/dm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCl$_2$</td>
<td>1.2</td>
</tr>
<tr>
<td>KCl</td>
<td>1.8</td>
</tr>
<tr>
<td>NaCl</td>
<td>3.2</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>7.9</td>
</tr>
<tr>
<td>Na$_2$CO$_3$</td>
<td>22.2</td>
</tr>
<tr>
<td>NaNO$_3$</td>
<td>0.2</td>
</tr>
<tr>
<td>Na$_3$PO$_4$</td>
<td>0.8</td>
</tr>
<tr>
<td>MgCl$_2$*6$H_2$O</td>
<td>4.1</td>
</tr>
<tr>
<td>H$_3$BO$_3$</td>
<td>178.0</td>
</tr>
<tr>
<td>$\Sigma$</td>
<td>219.4</td>
</tr>
</tbody>
</table>
TABLE 4. RECIPES FOR THE SAMPLES WITH AEC AND H₃BO₃

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Total salt: dry cement (wt. %)</th>
<th>H₃BO₃:dry cement (wt. %)</th>
<th>Ca(OH)₂ (g)*</th>
<th>Cement (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9,4</td>
<td>7,7</td>
<td>30</td>
<td>1388</td>
</tr>
<tr>
<td>2</td>
<td>9,4</td>
<td>7,7</td>
<td>60</td>
<td>1388</td>
</tr>
<tr>
<td>3</td>
<td>9,4</td>
<td>7,7</td>
<td>60</td>
<td>1388</td>
</tr>
</tbody>
</table>

* The Ca(OH)₂ was added to the AEC solution before mixing with the cement paste.

3.2. Thermodynamic calculations

Reactive-transport modeling has become a standard tool for quantitative predictions of long-term properties of cementitious materials. Several thermodynamic databases encompass cement-specific mineral phases as calciumsilicahydrate (CSH), portlandite, ettringite etc and several computer programs can combine the thermodynamic equilibrium calculations with transport calculations. Whilst the reactive component has been refined further with the introduction of various solid solution models, the transport component has embraced multi-component diffusion models including a mutual electric interaction between ions as formulated in the Nernst-Planck equation;

\[
J_i = -d_i \left( \frac{\partial \ln(y_i)}{\partial \ln(c_i)} + 1 \right) \frac{\partial c_i}{\partial x} + \sum_{j=1}^{n} d_j z_j c_j \left( \frac{\partial \ln(y_j)}{\partial \ln(c_j)} + 1 \right) \frac{\partial c_j}{\partial x} \sum_{j=1}^{n} d_j z_j^2 c_j
\]

The coupling between the reactive component and the transport component is supplied by various porosity-diffusivity-relations, where porosity, \( \varphi \), parameterized in terms of volume changes

\[
\varphi = \frac{V_{\text{void}}}{V_{\text{tot}}} = \frac{V_{\text{void}}}{V_{\text{mineral}} + V_{\text{void}}}
\]

However, it is emphasized that the evaluation of the porosity is often exclusively based on global averages of the mineral phases volume occupancy in each cell, not a micro-structural interpretation. Although several relation addressing the coupling between the effective diffusivity, \( d_e \), and the porosity are available, such as Archies law

\[
\frac{d_e}{d_0} = \beta \varphi^m
\]

or the relation proposed by Benz-Garboszi /Benz et al 1992/, where the Heaviside function, \( H \), assess the percolation threshold;

\[
\frac{d_e}{d_0} = 0.01 + 0.07 \varphi^2 + H(\varphi - \varphi_c)1.8(\varphi - \varphi_c)^2
\]

the major challenge might reside in the evaluation of the porosity itself.

A prerequisite for assessing the long-term stability is a characterization of the engineered barriers as well as the waste matrix in terms of mineral composition, pH and porosity distribution. Cement based materials are characterized by equilibrium between different mineral phases, primarily amorphous to
crypto-crystalline CSH and crystalline portlandite, but also the water-rich minerals AFm, as monosulphate and monocarbonate, and AFt, as ettringite. The names AFm and AFt denote minerals with three (tri) and one (mono) molecules of anhydrite (CaSO₄). Since CSH is not a mineral phase with unequivocal stoichiometry and congruent dissolution, the gradual alteration/aging during calcium loss is described by a selection of distinct structures (CSH₁.₈, CSH₁.₁, CSH₀.₈ or CSH₁.₆, CSH₁.₂, CSH₀.₈) with different log k values. Alternative techniques to describe the successive degradation include methods based on solid solution. Although the methods are better equipped to capture the continuity in the degradation of CSH, the dependence on experimental data is equally strong and the results may not necessarily be as conservative as the method based on discrete log k values.

The dominating mechanism behind aging of the material is determined by the inward and outward transport of ions, which displaces the prevailing equilibriums and enables dissolution and precipitation of various mineral phases. The leaching of ions and the accompanied mineral changes can be monitored by successive pH-drops. While alkali hydroxides initially maintain the high pH at 13.5, their leaching will lower the pH to 12.5, where it is mainly controlled by portlandite. The subsequent pH drops between 12.5 and 10.5 is characterized by the incongruent dissolution of CSH. Figure 2 shows the typical degradation scheme as predicted by the Thermoddem database /Blanc et al 2007/ for concrete when exposed to leaching by carbonate containing water. For each leaching step a fraction of the water is replaced with fresh water, which displaces the equilibrium and degrades the material by changing the mineral composition. However, the ideal degradation scheme shown in Figure 2 may not necessarily be reproduced in a full-scale model where diffusion processes controls the supply of certain ions and thereby regulates the dissolution and precipitation of the corresponding mineral phases. In reality the dissolution of CSH and the accompanying pH drops is a gradual process. The time scale is highly sensitive to the water composition, especially at late stage degradation where non-cementitous mineral phases dominates the precipitation.

The ion transport occurs through diffusion through the pore system of the cement, which consists of capillary pores and gel pores. The capillary pores represent the major pathway, since the diffusivities are assumed to be at least 400 times larger than in the gel pores. Although theoretical results indicate that cement phases with a water/cement ratio (w/c) below 0.4 would not contain any capillary pores, inhomogenities and unhydrated clinker grains will in reality contribute to the pore structure.

![FIG. 2. The degradation scheme of cement when leached by carbonate-containing water as predicted by the Thermoddem database.](image-url)
There are several computer programs available with the capacity of performing thermodynamic equilibrium calculations; some of which include transport processes. Although all programs aim at minimizing the Gibbs free energy of a specific system, there is a distinction, based on the underlying numerical methods, between methods based on Law-of-Mass-Action — Reaction Stoichiometry (LMA) or direct Gibbs Energy Minimisation (GEM).

In LMA the starting point is the master species (usually the aqueous ion) for which no thermodynamic data is specified and log k values for all the product species. The speciation, i.e. equilibrium concentrations of aqueous ions or complexes, surface species and solids, is determined by iteratively solving the balance mass action through the Newton-Raphson method. The GEM approach is based on mass balance for the entire system by specifying chemical elements and charge balance only.

The two codes employed in this study are PHREEQC /Parkhurst and Apello 1999/(which is based on LMA) and GEMS-PSI /GEMS-PSI 2009 / (which is based on GEM). Whereas PHREEQC is a more general-purpose program and has more features regarding transport processes, surface complexing etc, GEMS is more specifically devoted to and has fewer restrictions regarding solid solution models. GEMS has successfully been applied to hydration process of cement (see for instance /Matschei et al 2007a/ and /Lothenbach et al 2006/) and is in this study employed to ensure that appropriate boundary conditions are applied for the reactive-transport modelling by the code PHREEQC. The computer codes and accompanying databases are employed are summarized in Table 5.
TABLE 5. Summary of computer codes employed in the thermodynamic modelling

<table>
<thead>
<tr>
<th>Code</th>
<th>Hydration</th>
<th>Degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>GEMS-PSI /GEMS-PSI 2009/</td>
<td>Phreeqc /Parkhurst and Apollo 1999/</td>
<td></td>
</tr>
<tr>
<td>GEMS, cemdata07 /NAGRA/PSI 2002/</td>
<td>Thermoddem /Blanc 2007/</td>
<td></td>
</tr>
<tr>
<td>Initial mineral composition</td>
<td>Final mineral composition</td>
<td></td>
</tr>
</tbody>
</table>

4. RESULTS AND DISCUSSION

4.1. Laboratory experiments

The compressive strength for the specimens containing boric acid one week, 6 months and 12 months after casting is shown in figure 3. This figure shows (in close agreement with /koenne/, figure 1) a minimum in the compressive strength for specimens containing approximately 4 weight % of boric acid. These specimens collapsed after having being stored for a few weeks and no further measurements could be made. Unfortunately the specimens were scrapped and it was therefore not even possible to determine whether the specimens hardened at all during the first year.

Another interesting finding from figure 4 is that the specimens that contained NaOH instead of Ca(OH)2, i.e. the ones where a concentration of H3BO3 of 3.8, 4.2, 7.8 and 9.1 weight% did not harden during the first week. However, whereas the specimens with a concentration of H3BO3 of 3.8 and 4.2 collapsed during storage the other two reached a very high compressive strength after curing for 6 months in a controlled atmosphere.

![FIG. 3. Compressive strength as a function of the concentration of boric acid.](image)

Figure 4 shows the compressive strength as a function of time for a period of up to 12 months after casting for specimens containing H3BO3 but no AEC, i.e. the same as are shown in figure 3. In this figure, the compressive strength seems to have reached a maximum 6 months after casting after one
year it has again decreased for all specimens. No measurements were obtained after 4 years due to the lack of samples.

![Graph showing compressive strength as a function of time for specimens containing boric acid.](image)

**FIG. 4. Compressive strength as a function of time after curing for the specimens containing boric acid. The concentration of boric acid (weight %) is presented in the index in the right hand part of this figure.**

The compressive strength for the reference AEC is shown in figure 5. Even though the data is somewhat scattered the trend indicates a decrease in compressive strength with increasing concentration of the AEC.

This trend follows the trend shown in Figure 11, which shows that the porosity increases with increasing concentration of AEC in the range 4-10 wt %.
FIG. 5. Compressive strength as a function of concentration of AEC for a period of up to 12 months after casting.

The compressive strength for the different AEC specimens were not affected to any major extent by the storage in a controlled atmosphere of up to one year after casting, figure 6. It was thus decided that these samples could as be used as references to the results presented in figure 7.

FIG. 6. Compressive strength as a function of time after curing for specimens containing different concentrations of AEC.
Figure 7 shows the compressive strength for three samples containing AEC and H$_3$BO$_3$ during a period of 4 years. The compressive strength of these samples are similar to the reference samples after one year; compare figure 6 and 7. However, the compressive strength for the specimens containing both AEC and H$_3$BO$_3$ continues to increase and has reached values between 57 and 78 MPa, four years after casting.

**FIG. 7.** The compressive strength as a function of time for the samples containing AEC and H$_3$BO$_3$.

4.2. Thermodynamic calculations

4.2.1. Waste matrix evaluation

The mineral composition of a cementitious waste matrix is dependent on the composition of the anions in the waste. Carbonates are associated with various carboaluminates, as monocarboaluminate and hemicarboaluminate and, at higher levels, calcite. Sulphates on the other hand promote the formation of mineral phases as ettringite.

Thermodynamic modeling with GEMS2 have been used to predict the mineral composition at higher concentrations of anions in order to gain understanding of some of the features experienced during encapsulation of the waste, but also for attaining appropriate initial conditions as an input for the long-term modeling. Since sulphates and carbonates have somewhat contradicting effects on the cementitious waste matrix, their influence has been assessed separately before assessing a artificial evaporator concentrate.
Figure 8 shows the expected mineral composition at increasing levels of carbonates; hemicarbonates are replaced by monocalcium carbonates and at even higher concentrations of carbonates the evolution is characterized by the formation of calcite. According to results obtained by GEMS-PSI, the final product will consist of, apart from CSH and portlandite, calcite, monocalcium carbonate, ettringite and hydrotalcite. The evolution of carbonate-based mineral phases in cement is regulated by the availability of sulphates and aluminate. The aluminate is initially mainly found in monosulphate whereas at increasing levels of carbonate the aluminate is distributed between hemicarbonate and ettringite, which is in agreement with results obtained by Matschei et al. At even higher concentration of carbonate, the hemicarbonate is subsequently replaced by monocalcium carbonate, while the ettringite remains constant as regulated by the availability of sulphates. The limited supply of aluminate limits the growth of monocalcium carbonate and additional carbonate leads to unrestricted precipitation of calcite. As noted by Matschei et al., hemicarbonate is not stable under calcite saturated conditions.

Throughout the interval the pH changes are not significant, which also is in agreement with the results obtained by Matschei et al. where pH was nearly constant up to 20 g CO₂ per 100 g cement.
Figure 9 show the corresponding mineral evolution at increasing levels of sulphates. Initially, sulphates enter the cement through calcium sulphate (gypsum), which is added to the cement paste to control the setting time. During hydration sulphates initiates the formation of monosulphate and ettringite. At low sulphate concentrations ettringite, destabilizes and react to form monosulphate, whereas at high sulphate concentrations new ettringite is formed /Lothenbach et al 2010/. An increasing supply of sulphates mainly leads to the increasing precipitation of ettringite. The aluminate initially distributed between hemicarbonate and monocarbonate is successively redistributed between monocarbonate and ettringite. At sufficiently high concentrations of sulphates, calcite replaces monocarbonate as the major carbonate containing mineral phase. At even higher concentrations, carbonates together with the excess of sulphates are incorporated in thaumasite, which reduces the content of calcite. The mineral phases associated with chlorides, Friedel’s salt and Kuzel’s salt are to a lesser extent considered to cause volume expansion, however the formation of such chloroaluminates may release sulphates from monosulphate, which in turns may result in expansive ettringite /Matschei et al 2007c/. If on the other hand chlorides are supplied together with sulphates and carbonates, such as in the process of encapsulation of evaporator concentrate, the additional chlorides are assumed to ascertain less influence on the final waste matrix than the sulphates and carbonates.

Although boron have well-known retarding effect on the hydration process attributed by the formation temporary coating layers of calcium diborate /van Eijk 2001/,, the corresponding final mineral phases in a hydrated cement matrix are less investigated. According to preliminary results when assessing the cement conditions with higher concentrations of boron with the PCHatches database, there may be a final precipitation of calcium diborate, however further experimental work is required in order to validate the thermodynamic approach for boron species.
While the net effect of increasing levels of sulphates in general is a denser material due to voluminous ettringite, carbonates in general have the opposite effect because of the low molar volume of calcite. However at lower concentrations, before the precipitation of calcite, carbonates also are associated with a decrease in porosity. Thus for an evaporator concentrate containing both carbonates and sulphates, the porosity can initially be expected to decrease, while at higher concentrations, the effects of carbonates and sulphates will have a contrary influence on the final waste matrix. The net effect on the porosity from entirely carbonates and sulphates are shown in figure 10, together with the effect of an evaporator concentrate. A minimum porosity is predicted to occur at approximately 5 wt% g salt/dry cement.

4.2.2. Long-term stability of waste matrices and their influence on engineered barriers

Long-term properties of waste matrices have been evaluated against a reference case with a waste matrix entirely consisting of cement. A failure criterion adopted based on the mineralogical distribution. The chemical integrity has been assessed through the complete leaching of portlandite and a gradual degradation of CSH. It is emphasized that a mineralogical failure is not necessary identical to a mechanical failure, since for instance freezing and fractures may have severe detrimental effects on the barrier and waste matrix considered as a construction material, although it may still be intact from a chemical point of view. The numerical results have been visualized as cross sections of the repository depicting the predicted mineral phases in the engineered barriers as well as the encapsulated waste. As seen in figure 11 and 12 the differences between the reference case and a case with increased concentrations of carbonates are small. Similar results have been seen for numerous waste combinations. Thus, a conclusion would be that the waste composition in general is subordinate to the composition of the infiltrating water regarding the impact on engineered barriers. However, for certain waste load composition and higher concentrations, there may be a need to evaluate the impact on the barriers for a specific waste package.

The long-term effects of boron-containing waste have not been addressed through full-scale simulations. Preliminary results show some precipitation of calcium diborate, which thereby to some extent reduces the concentrations of portlandite and CSH. However, the calcium diborate precipitate appear to be rather resistant to leaching and does not affect long-term mineralogical evolution.
5. CONCLUSIONS

In this study a recipe for the solidification of evaporator concentrates containing $\text{H}_3\text{BO}_3$ has been developed and the compressive strength for different mixtures of artificial evaporator concentrates and $\text{H}_3\text{BO}_3$ solidified in a cement matrix studied over a period of up to 4 years.

The most important finding was that when an optimized waste/cement matrix recipe was used the compressive strength increased during the entire 4 year period and no signs of degradation were noticed.

Other findings of interest were that …

— When the concentration of boric acid is about 4 wt. % in a cement-waste matrix the matrix does not harden and the specimen collapses. This is in good agreement with previous findings presented in the literature.

— When NaOH is used as an additive the hardening of the specimen is retarded as compared to when Ca(OH)$_2$ is used.

— There is a weak trend that the compressive strength for specimens containing artificial evaporator concentrates decreases when the concentration of AEC increases. This can be an indication of an increasing porosity as noted in the thermodynamic calculations.

— The long-term performance of the waste matrices is to a large extent site-specific. In general the composition of the infiltrating water is more influential than the waste matrices, both on the degradation of the waste matrices itself as well as on the engineered barriers.

— According to preliminary results, boron-containing waste appears to have only a minor impact on the long-term stability of the waste matrices and the engineered barriers. However, further experimental and theoretical work is needed.

REFERENCES

[12] Nagra/PSI Chemical Thermodynamic Data Base Version 01/01 (Nagra/PSI TDB 01/01. 2002.)