STUDY OF THE CONDITIONING MATRICES FOR ALUMINIUM RADIOACTIVE WASTES

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Embedding of radioactive waste in Portland cement matrix is the most used method applied worldwide, but not all the radioactive waste types are compatible with the normal cement matrix because of negative effects of some chemical reactions developed during the hydrolysis and curing steps of cement paste. The radioactive aluminium, one of the as called “hazardous wastes” generated by the decommissioning of research nuclear reactor as VVR-S – IFIN-HH, or other nuclear techniques applications like irradiation/activation techniques, is a type of radioactive waste which can not be conditioned by this method, due to behaviour of the metallic aluminium in contact with normal cement products. The studies and preliminary results of the work presented in the present paper is part of a research project developed to identify a proper management of this special type of radioactive waste from the storage phase up to final disposal. To obtain a conditioning matrix for radioactive aluminium in accordance with the international disposal requirements and respecting the waste acceptance criteria of the National Radioactive Waste Repository – Baita-Bihor, is necessary to study new formulas of low basicity binding agents, in order to minimize the alkaline attack of cement hydrolysis products on metallic aluminium.

Key words: Aluminium radioactive waste, conditioning matrix, XRF, XRD.

1. INTRODUCTION

Cementitious materials used for radioactive waste encapsulation usually include substantial amounts of Ordinary Portland Cement (OPC) in their formulation. Wastes produced as result of nuclear activities are very diverse and, under certain circumstances, they react chemically with cement phases or mixing water, thus reducing the quality of the product. For example, dismantling of nuclear reactors generates a large volume of LLW and ILW wastes, some of them containing aluminium, which must be carefully managed in the conditioning process, in order to obtain a stable matrix with a proper behaviour in time, due to the disposal constrains.

Aluminium is a reactive amphoteric metal, readily forming a protective oxide layer in contact with air or water. This layer is generally regarded as stable in the pH range 4.5-8.5 [1]. However, in a strong alkaline medium, such that encountered in conventional cementitious materials based on OPC, this layer is soluble, leading to a continuous corrosion associated with hydrogen release and subsequent formation of expansive metal hydroxides, in addition to calcium-based aluminosilicate hydrates. As a result, using Portland cement or a composite cement (OPC blended with blast furnace slag and/or fly ash) to encapsulate wastes containing aluminium is prohibited.

Some alternative cementitious systems have different chemistries that may be more compatible with aluminium. There is no commercial “ready to use” cement formulas for this radioactive waste types, at least for magnesium cements and calcium phosphate cements. There is clearly a need for R&D work to develop such binders, taking into account the requirements for waste conditioning, and to characterize their properties at early age, but also in the long term [2].

Phosphate cements, such as magnesium phosphate or calcium phosphate binders, may also be potential candidates [3-5]. The process for MKP is based on a reaction between burnt MgO and potassium dihydrogen phosphate KH₂PO₄, leading to the precipitation of the main reaction product which is magnesium potassium phosphate hexahydrate (k-struvite: MgKPO₄·6H₂O) [6].

The acid-base reaction involved is highly exothermic. One characteristic of magnesium phosphate cement is that a significant amount of MgO remains unreacted in the system depending on MgO/KH₂PO₄ ratio [7].

This paper presents and evaluate the characterization results obtained from analyzing two potential magnesium phosphate cement formulations and compare these with results obtained from the reference composite cements (CEM III-A and CEM V-A).

2. EXPERIMENTAL PART

2.1. MATERIALS

All variables apart from the water/solid ratios (w/s) were kept constant between the two magnesium phosphate cement formulations investigated. Theoretically, a water/solid ratio (i.e. H₂O/MgO+KH₂PO₄) of 0.25 is required for paste saturation. For convenience, the two formulations are noted “MKP I” and “MKP II”. The investigated cement systems are:

- CEM III-A – water, w/c = 0.4 (reference system);
- CEM V-A – water, w/c = 0.4 (reference system);
- 1 mol MgO – 1 mol KH₂PO₄ – H₂O (w/s = 0.25), with 2 wt-% boric acid addition (MKP I);
• 1 mol MgO –1 mol KH₂PO₄ – H₂O (w/s = 0.3), with 100 wt-% fly ash and 2 wt-% boric acid addition (MKP II).

The Fly ash and boric acid weight loadings were calculated from the combined weight value of MgO and KH₂PO₄.

2.2. PREPARATION OF SAMPLES

The solid materials content of the samples is presented in weight with respect to the total solid content. The pastes (MKP I) were obtained by mixing MgO powder, KH₂PO₄ powder and boric acid powder and in a later stage was added water (w/s = 0.25) [8]. For the preparing of the pastes (MKP II) the adding water at a ratio of w/s = 0.25 gave insufficient workability due to the additional solid fly ash component. Therefore was necessary an addition of water to give an overall water/solids ratio of 0.3 based on total weight. The water contents should be approximate to the required molar ratios to form the alkali metal analogue of k-struvite in the formulated products. Thus the water that is necessary for the mixing of components may rapidly become chemically bound in the system. After the mixture slurry was stirred for 15 min and it was kept for curing inside plastic bags laboratory conditions (25±2°C and 45±5% of relative moisture).

The addition of fly ash and boric acid was deemed necessary to retard the cement set and also to potentially reduce the heat of hydration [9].

The setting time (initial and final set) of the wet cement pastes was investigated using a Vicat apparatus using a free drop according to Standard EN 196-3.

The pH of bleeding water for the wet cement pastes was measured simultaneously using a combined pH/temperature probe and the measurements were repeated at 30 minute intervals up to 48 h.

Also, the conductivity of the same wet cement pastes (reference cements and MKP) was measured up to 48 h.

Powder X-ray diffractions (XRD) were performed at 2 days cure time, using a D8 – Advance diffractometer with Ni-filtered Cu Kα radiation (λ = 1.5418Å), diffraction angles 2 theta ranged between 10° and 70°, a step size of 0.02° and an acquisition time of 4 sec/step. A criterion for the analysis precision is the sample preparation. In order to obtain a reproducible result, the samples were grounded to a specific particle size for analysis by X-ray diffraction [10].

The raw materials used for preparation of the investigated cementitious systems have been chemically characterized by XRF. The XRF measurements were performed with a spectrometry Xenemetrix EX-6600 SDD model, equipped with a X-ray generator EG 60 with Pmax = 300 W, HVmax = 60 kV, Imax = 4.9 mA, detector type SDD (Silicon Drift Detector) with area of 25 mm² and analog digital pulse processor (ADDP). The spectral analyses were performed with nEXt software, version 2.0.q.6. The chemical composition of raw materials is indicated in Table 1.
Aluminium plates were inserted in the fresh paste cubes for the visual inspection after 7 days.

3. RESULTS

The basic informations on the matrices used were obtained by X-ray diffraction, elemental chemical analysis, setting time and determination of pH in the pore solution matrix.

Table 1
Chemical composition (weight %) of blends components

<table>
<thead>
<tr>
<th></th>
<th>CEM III/A</th>
<th>CEM V/A</th>
<th>KH₂PO₄</th>
<th>CaSO₄</th>
<th>MgO</th>
<th>Fly Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>61.21</td>
<td>54.65</td>
<td>–</td>
<td>45.03</td>
<td>4.49</td>
<td>4.39</td>
</tr>
<tr>
<td>SiO₂</td>
<td>25.18</td>
<td>27.12</td>
<td>0.2</td>
<td>0.34</td>
<td>6.17</td>
<td>2.52</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5.68</td>
<td>9.45</td>
<td>–</td>
<td>–</td>
<td>0.42</td>
<td>26.19</td>
</tr>
<tr>
<td>MgO</td>
<td>3.82</td>
<td>2.81</td>
<td>0.17</td>
<td>0.58</td>
<td>85.82</td>
<td>–</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.37</td>
<td>4.14</td>
<td>–</td>
<td>–</td>
<td>2.76</td>
<td>15.93</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.74</td>
<td>0.96</td>
<td>43.49</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.40</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.32</td>
<td>0.56</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1.67</td>
</tr>
<tr>
<td>MnO</td>
<td>0.23</td>
<td>0.22</td>
<td>–</td>
<td>–</td>
<td>0.16</td>
<td>–</td>
</tr>
<tr>
<td>SrO</td>
<td>0.05</td>
<td>0.05</td>
<td>–</td>
<td>0.23</td>
<td>68ppm</td>
<td>–</td>
</tr>
<tr>
<td>ZnO</td>
<td>–</td>
<td>0.02</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>–</td>
<td>0.01</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>–</td>
<td>–</td>
<td>55.65</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>SO₃</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>53.81</td>
<td>0.17</td>
<td>–</td>
</tr>
</tbody>
</table>

The results of pH, the conductivity and the setting time are summarized in Table 2.

Table 2
Processing parameter results

<table>
<thead>
<tr>
<th>Formulation</th>
<th>1 h</th>
<th>24 h</th>
<th>48 h</th>
<th>pH</th>
<th>Conductivity (mS/cm)</th>
<th>Initial setting time, h</th>
<th>Final setting time, h</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEM III/A - water</td>
<td>13.4</td>
<td>13.5</td>
<td>13.6</td>
<td>25.2</td>
<td>2h 15min</td>
<td>3h 45min</td>
<td></td>
</tr>
<tr>
<td>CEM V/A - water</td>
<td>13.3</td>
<td>13.4</td>
<td>13.51</td>
<td>21.3</td>
<td>2h30min</td>
<td>4h</td>
<td></td>
</tr>
<tr>
<td>MKP I</td>
<td>7.5</td>
<td>7.67</td>
<td>7.94</td>
<td>93.5</td>
<td>1h</td>
<td>1h 30min</td>
<td></td>
</tr>
<tr>
<td>MKP II</td>
<td>6.4</td>
<td>6.55</td>
<td>6.6</td>
<td>93</td>
<td>2h</td>
<td>2h 45min</td>
<td></td>
</tr>
</tbody>
</table>
4. DISCUSSION OF RESULTS

The setting times of the two formulations of MKP given in Table 1, show that both formulations had a comparable initial set time and both achieved final set within 10 h. The results for a reference grout of CEM III/A and CEM V/A at a 0.4 water/solids ratio is also given for comparison.

The measured pH of the MKP I/ MKP II are significantly lower than that obtained with the reference system (lying in the stability range for aluminium).

The results obtained as reference sample through XRD on the hydrated cements (CEM III/A and CEM V/A) are presented in figures 1 and 2.

![Fig. 1 – The diffraction spectrum of hydrated cement CEM III/A (color online).](image1)

![Fig. 2 – The diffraction spectrum of hydrated cement CEM V/A (color online).](image2)
The XRD spectrum of the hydrated CEM III/A (Fig. 1) emphasizes the appearance of the crystalline hydrated compounds such as: tricalciumhydroxysulfataluminate similar to the natural ettringite, calcium hydroxide well crystallized from the intergranular solution, the hexagonal calcium hydroaluminate and the compound Ca$_3$(AlO$_2$)$_3$(OH)(H$_2$O). There were also identified compounds which remain unreacted: tricalcium silicate (C$_3$S), dicalcium silicate (C$_2$S), dicalcium aluminoferrite (C$_2$AF) and quartz (SiO$_2$). The formation of these hydrated products is explained through the following mechanism of hydrate-hydrolyze: the reactions of hydrate-hydrolyze occur immediately after the cement-water mixing.

The first process of dissolution - hydrolysis determine the saturation of intergranular solution with Ca$^{2+}$, SO$_4^{2-}$, OH$^-$, from which is subsequently separated the calcium hydroxide.

In the diffractogram obtained on the hydrated sample CEM V/A (Fig. 2) is observed, as in the case of sample hydrated CEM III/A, the appearance of the hydration formations tricalciumhydroxysulfataluminate and the calcium hydroxide. Its characteristic lines are smaller than those obtained in hydrated CEM III/A. The mineralogical compounds tricalcium silicate (C$_3$S), dicalcium silicate (C$_2$S), dicalcium aluminoferrite and quartz, remained unreacted and are emphasized through their specific peaks and are in higher quantities than in case of the hydrated sample CEM III/A.

The powder XRD patterns for the two magnesium phosphate cement formulations (MKP I and MKP II) are given in figures 3 and 4.

![Fig. 3 – The diffraction spectrum of MKP I formulation (color online).](image-url)
The main reaction product of two magnesium phosphate cement formulations was confirmed, by powder XRD, as MgKPO$_4$·6H$_2$O (k-struvite), which was found to dominate the crystalline phase composition (Figs. 3 and 4). A significant amount of unreacted MgO was identified. Other reflections for MgCO$_3$ and KH$_2$PO$_4$ (from the structure of raw materials) were also observed.

The powder XRD pattern for formulation MKP II shows that the main hydration product is k-struvite, as expected. The intensity of characteristic lines are lower than the MKP I formulation, which shows that the occurrence of this phase is smaller. In Figure 4 it is noted that by the addition of fly ash, KH$_2$PO$_4$ is consumed in the forming reaction of specific structure of MKP cement.

In order to perform a preliminary evaluation of the metallic aluminium behavior in cemented matrix, the prepared samples were kept both in tight plastic bags and in an aqueous medium. After 7 days the samples were mechanically destroyed and visually examined (Figs. 5, 6 and 7).
The visual examination allows the observation of the surface metallic aluminum plates, respectively the corrosion of surface due to the formation of hydroxide.

5. CONCLUSIONS

Within this paper are presented the experimental works and the characterization results obtained from analyzing two potential magnesium phosphate cement formulations (MKP I and MKP II) and the comparison of these with results obtained from the reference composite cements (CEM III-A and CEM V-A).

From the experimental results we can draw-up the following conclusions:

- The pH values of both magnesium phosphate cement formulations increased slowly over the 240 min measurements duration, with pH values between 6.4 ÷ 7.94, indicating a significant lower value compared to reference composite cement (pH ≈ 13). The neutral values pH of the wet pastes is due to the formation of this cement through acid-base reaction.
- The decreasing of pH values should be the main parameters for controlling the corrosion of aluminium metallic.
- The addition of boric acid into the two magnesium phosphate cement extended the initial setting times to more convenient timescales (within 1h).
- The XRD results obtained for the reference composite cement (CEM III/A and CEM V/A) indicate the formation of portlandite (Ca(OH)$_2$) which is the main component responsible for the high values of pH.
- The diffraction spectra obtained for both MKP formulations show that the principal reaction product of the cement is MgKPO$_4$·6H$_2$O and dominate the crystalline composition.
Magnesium phosphate cement is a novel material intended to be used for the radioactive aluminium embedding. So, in future other important parameters would need to be considered and evaluated such as compressive strengths, dimensional stability and long-term behaviour in simulated and real disposal conditions.

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REFERENCES


