Research Article

Evaluation of the Properties of Cemented Liquid Scintillator Wastes under Flooding Scenario in Various Aqueous Media

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Experiments simulating flooding scenario in various aqueous media for a long period were carried out to determine the adequacy of cement-clay composite for solidification/stabilization of spent organic radioactive liquid scintillator wastes. The final cement waste form blocks were immersed in three aqueous media, namely, seawater, groundwater, and tapwater. The immersion process lasted for increasing periods up to 540 days. Following each predetermined interval period, physical and mechanical evaluations of the immersed blocks were determined. In addition, the change in the hydration products was followed by X-ray diffraction and infrared spectroscopy as nondestructive analyses to recognize the deterioration in the microstructure that may occur due to the flooding event. Thermal analysis and scanning electron microscopy were performed to confirm the data obtained.

1. Introduction

To determine the radioactivity contents in any specimen based on liquid scintillation technique, the sample under quantification is dissolved or suspended in a cocktail containing an aromatic solvent (e.g., benzene, toluene, and dioxan) and predetermined amounts of other additives known as flours, that is, scintillator. The particles emitted from the radioisotope in the sample transfer their energies to the solvent which in turn transfers that energy to the flours’ molecules that dissipating the energy by emitting light. After this quantification, the spent liquid scintillators are counted as a hazardous organic radioactive waste and should be managed safely [1–3]. This waste could be classified as problematic waste for further processing because of the specific radioactive contamination and the organic nature of this waste. Special treatment options should be developed to address both these characteristics of that waste [4].

The practice of immobilizing radioactive waste with ordinary Portland cement began during the early years of the nuclear industry. This was primarily due to its low cost, availability, and compatibility with aqueous waste. It was soon realized, however, that specific wastes, like scintillator liquid, interact with the cement components causing inhibition or retarding the hydration reaction. To overcome these drawbacks, one or more selected additives were added to the Portland cement mixtures. Several of the more successful mixtures such as sodium silicate, reactive silica, lime, clay, and slag have been identified and commercialized [5].

Solidification/stabilization (s/s) using cement is a chemical treatment process aiming at either binding or incorporating the compounds of a hazardous waste stream into a stable insoluble form (stabilization) or to trap the waste within a solid cementitious matrix (solidification) [6]. The efficiency of s/s treatment of organic contaminants may be improved using adsorbents for the organic components. These adsorbents can be incorporated as additives in the cement mix, or they can be used as a pretreatment prior to conventional cement-based solidification. Several materials have been investigated as adsorbents for organic wastes during s/s treatment. These additives include metal oxide, clays, natural materials (zeolites, fly ash, organic polymers, etc.), and activated carbon [7]. The best method for evaluating the properties and predicting the behavior of cemented wastes during long-term storage is to studying under conditions close to the actual conditions, that is, in experimental near-surface repositories with periodic sampling of the material being tested and groundwater [8]. The pore system governs
the most important properties of the hard cementitious matrix, namely, its strength [9, 10].

A very little researches dealt with the behavior of that category of the waste form under prolonged flooding in various aqueous media, so that the objective of the present work is to evaluate of the suitability of cement-clay composite to solidify and stabilize this waste and to confirm the conformance of cemented liquid scintillator waste to the regulatory requirements during long-term storage.

2. Materials and Methods

Experimental studies were undertaken on a laboratory scale, aiming at the determination of the influence of prolonged flooding in various aqueous media on the physicochemical properties of the final waste form (FWF). Physicochemical properties were evaluated by measuring the most important parameters the strength under compression, mass loss, bulk density, and porosity. Likewise, water absorption, volume of open pores, volume of impervious portion, and apparent specific gravity were, also, determined at the end of predetermined immersion time intervals.

2.1. Materials. The chemical composition of spent liquid scintillation waste (LSW) varies largely and it is based on its origin and applications. The chosen LSW for this study is a widely used one in very large volumes, as waste, resulting from liquid scintillation counting applications, was collected and segregated at Nuclear Research Center, Egyptian Atomic Energy Authority. LSW simulate was prepared and used for formulation of the FWFs subjected to all studies. The simulated waste was composed of Bray’s cocktail and 1,4-dioxan. Bray’s cocktail contains 5 g PPO (2,5-diphenyloxazole), 0.5 g POPOP 1,4-bis(5-phenyloxazol-2-yl) benzene, 30 g naphthalene, and 20 mL ethylene glycol. For preparation of one liter of LSW simulate 5.5 g from Bray’s cocktail was completed to the determined volume with 1,4-dioxan as a solvent in a dark glass bottle.

The cement used for immobilization in the present study was supplied by Al Masria Cement Company, Suez, Egypt. It is local ordinary Portland cement (OPC), 42.5N Cement (I), manufactured according to the Egyptian Standard Specifications, EN 197-1/2000.

Natural clay was used as additive material to cement. It was obtained from Belbeis desert, El Sharkia, Egypt. Chemical and phase compositions of both cement and clay materials used are given in Table 1. The data of cement oxide percentage analysis were nominated by the manufacturer. On the other hand, the cement phase compositions were calculated based on Bogue’s equations [11]. Consequently, the clay composition was reported based on X-ray fluorescence analysis.

Three types of water, namely, seawater, tapwater and groundwater were applied as immersion aqueous media for evaluation of the physicochemical characterization of solid waste forms that subjected to flooding test. The groundwater was collected from Inshas, East of Cairo, Egypt, well number 202, which is the nearest groundwater container to Egyptian Nuclear Facility where a disposal site is constructed. The source of tapwater was from Giza district while the seawater was obtained from Alexandra on the Mediterranean Sea. The concentrations of some salts of interest in tapwater, groundwater, and seawater are represented in Table 2.

2.2. Methodology. Cement-clay composite with LSW simulate as a (FWF) was prepared by adding the natural clay to cement paste then LSW simulate was dispersed into the cement-clay composite. The components were mixed entirely until homogeneous slurry was reached and then poured into polyethylene cylinder molds. The paste was packed manually for few minutes to remove any air bubbles. The

Table 1: Chemical composition of ordinary portland cement and natural clay used.

<table>
<thead>
<tr>
<th>Composition</th>
<th>OPC, wt%</th>
<th>Natural clay, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>20</td>
<td>59.54</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>6</td>
<td>22.24</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3</td>
<td>9.47</td>
</tr>
<tr>
<td>CaO</td>
<td>63</td>
<td>0.56</td>
</tr>
<tr>
<td>MgO</td>
<td>1.5</td>
<td>2.21</td>
</tr>
<tr>
<td>SO₃</td>
<td>2</td>
<td>0.19</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.5</td>
<td>—</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.5</td>
<td>1.29</td>
</tr>
<tr>
<td>Chloride</td>
<td>—</td>
<td>0.63</td>
</tr>
<tr>
<td>Ignition loss</td>
<td>2.0</td>
<td>10.50</td>
</tr>
</tbody>
</table>

Figure 1: Compressive strength and mass-loss values of the FWFs under different immersion environments.


Table 2: Concentrations of some salts of interest in tapwater, groundwater, and seawater.

<table>
<thead>
<tr>
<th>Composition g/L</th>
<th>Seawater</th>
<th>Tapwater</th>
<th>Groundwater</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium chloride</td>
<td>27.32</td>
<td>0.0615</td>
<td>0.0923</td>
</tr>
<tr>
<td>Magnesium chloride</td>
<td>3.807</td>
<td>0.021</td>
<td>0.041</td>
</tr>
<tr>
<td>Magnesium sulphate</td>
<td>1.658</td>
<td>0.0010</td>
<td>0.0011</td>
</tr>
<tr>
<td>Calcium sulphate</td>
<td>1.260</td>
<td>0.00028</td>
<td>0.0006</td>
</tr>
<tr>
<td>Potassium sulphate</td>
<td>0.863</td>
<td>0.00015</td>
<td>0.0002</td>
</tr>
<tr>
<td>Calcium carbonate</td>
<td>0.123</td>
<td>0.0510</td>
<td>0.102</td>
</tr>
<tr>
<td>Magnesium bromide</td>
<td>0.076</td>
<td>0.00</td>
<td>0.048</td>
</tr>
<tr>
<td>Conductivity</td>
<td>—</td>
<td>370</td>
<td>850</td>
</tr>
<tr>
<td>pH</td>
<td>7.9</td>
<td>6.8</td>
<td>8.0</td>
</tr>
</tbody>
</table>

Figure 2: Bulk density and specific gravity values of the FWFs under different immersion environments.

Figure 3: Volume of open pores and impervious portion of the FWFs under different immersion environments.

X-ray diffraction (XRD) and infrared spectroscopy (FT-IR) tests as nondestructive analyses. Furthermore, Thermal analysis (DTA and TGA) and scanning electron microscopy (SEM) were performed to evaluate the deterioration in the microstructure of the FWF due to the immersion process and to confirm the data reached from XRD and FT-IR analyses.

3. Results and Discussion

The data obtained from the immersion of the hard blocks were compared to that of non-immersed samples, which were prepared by the same way and exposed to the same conditions. The results from various experiments for the blank samples as well as those immersed in various water media for increasing periods are given in Figures 1, 2, 3, and 4.

For gathering, the obtained data revealed the following.

(i) In general, an increase in compressive strength, bulk density, specific gravity, and volume of impervious portion values was recorded; on the other hand, decrease in mass loss, volume of open pores, water absorption, and apparent porosity values with the increase of immersion time up to 18 months were detected.

(ii) The Nuclear Regulatory Commission (NRC), USA, recommended a minimum compressive strength...
samples in seawater may be due to the formation of CaCO$_3$ and the elevation in the mechanical durability for the immersed FWFs under different immersion environments.

Elevation in the mechanical durability for the immersed samples in seawater may be due to the formation of CaCO$_3$ (calcite) as a result of the reaction of lime liberating during hydration of cement paste with CO$_2$ present in seawater. Calcite can act as filler for pore cement matrix and also accelerate the hydration of tricalcium aluminate (C$_3$A) to form calcium carboaluminate hydrates, that is, filling up the empty pores inside the FWF blocks; therefore, the durability of the FWF blocks was enhanced [12]. Filling up the empty pores inside the FWF blocks increased the strength and water resistance of the hardened cement block [13–15]. Also, the formation of secondary minerals, primarily calcite, can suppress the migration of radionuclides [16], which decreases their leaching. Consumption of Ca(OH)$_2$ (lime) by the reaction with pozzolans materials, such as clay, and/or carbonation can result in greatly enhanced durability strength [17], where portland-pozzolana cements gain strength slowly and may require curing over a comparatively long period and the long-term strength is high [18].

Migration of moisture through pore structure of the cement matrix can induce buildup of internal hydraulic pressure, which causes cracking in the composite and consequently can affect negatively on the physicomechanical properties. The refinement of pore structure in the FWF by adding clay leads to reduce the permeability of the hardened cement composite and can dispose retardation in moisture migration through a cement matrix so that physicomechanical properties would be enhanced [19]. Additional changes in the cement structure can occur due to crystallization processes within a pore system by adding clay as admixture leading to enhancement of the physicomechanical properties [20].

FT-IR analysis data for the FWF that incorporating liquid scintillator waste simulates after subjecting to flooding treatment are represented in Figures 5, 6, 7, and 8. These comprised comparable spectra for 28 days cured FWF, non-immersed, aged FWF, and the immersed ones for increasing periods. The main characteristic features of all these sets can be summarized as follows [21]:

(i) sharp absorption bands at 3641 cm$^{-1}$ which refer to bending vibration of the free O–H group coordinated to the Ca$^{2+}$ in the Ca(OH)$_2$;

(ii) the broad absorption stretching band near 3445 cm$^{-1}$ that attributed to the –OH group bonded to hydrogen and may also to the molecular water of calcium silicate hydrates gels (C–S–H);

(iii) the shoulder assigned in the region 1641–1647 cm$^{-1}$ characterizing water H–OH deformation vibration;

(iv) the presence of calcite CaCO$_3$, formed due to the carbonation of Ca(OH)$_2$, was identified at two absorption bands in the region of 1452–1461 cm$^{-1}$ and characterizing the stretching vibration in CO$_3^{−2}$ group as well as near 875 cm$^{-1}$ and 713 cm$^{-1}$ that refers to the bending vibration of the carbonate group in the calcite;

(v) the broad medium band appeared close to 980 cm$^{-1}$ in all analyzed specimens is due to Si–O–Si asymmetric stretching vibration while the deformation of SiO$_4^{−4}$ in the anhydrous C–S–H was appeared in the region of 450–463 cm$^{-1}$ as a weak sharp peak.

Collectively, it should be notified that no essential differences were detected between the IR data for the various FWFs subjected to variable leachants for increasing immersion periods existed up to 18 months. Moreover, the addition of simulated scintillator imposed no effect on the chemical
configurations of the FWF subjected to the immersion treatment; this indicated that the candidate cement-clay composite can immobilize the spent liquid scintillator fairly even under accidental flooding of the disposal site.

XRD analysis is useful for detecting the hydrates and unhydrates components of the OPC composites. The families of hydrates of calcium aluminate, such as ettringite and monosulphate hydrate, showed the highest peaks on the low angle side of XRD profile. On the other hand, the peaks of aggregate minerals (e.g., alite, belite, etc.) appeared at the high angle side [22]. The qualitative results of the performed XRD for the proposed cement-clay composite immobilizing LSW immersed in different types of water for increasing periods compared with non-immersed ones are represented in Figure 9.

Clearly, portlandite constitutes the main hydration products in all non-immersed and immersed samples in various leachants media even after 18 months; calcite and C–S–H come as minor constituents then gypsum, quartz, and
ettringite present as traces. Any how, the following observations can be also deduced from the XRD spectra for all samples under consideration.

(1) Portlandite is one of the two cement hydration main products responsible to the mechanical integrity of the FWF and recognized at 2θ values equal 18.18°, 34.14°, and 54.39°.

(2) C–S–H is the second principal hydration product of cement and gives the product about 50% of its strength [23]. Due to its low crystallinity [22], it can be hardly detected at 2θ values of 34°, 39°, and 55° [24].

(3) An appreciable amount of unavoidable calcite at 2θ values 29.470°, 39.47°, 43.28°, and 48.61° was also identified. It is obvious that the calcite contents in the FWF immersed in groundwater and seawater were greater than those for non-immersed samples and those immersed in tapwater. The carbonate originated from the reaction of CO2 present in groundwater and seawater with portlandite was according to the following reaction:

\[
\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} \tag{1}
\]

(4) Traces contents of quartz, ettringite, and gypsum, at 2θ values equal 26.68°, 9.42°, and 11.9°, respectively were detected. These components may be attributed to the clay added as admixture.

These data are in a good agreement with the previously published work and confirmed the data obtained from FTIR spectroscopy.

Scanning electron microscopy (SEM) has been used to describe the structure of the hardened FWF component and to evaluate the influence after the immersion in various water solutions.

FWF is characterized by microstructures, which is mainly composed of [25] the following.

(i) Portlandite crystals that are locally embedded in amorphous C–S–H appear as well crystalline plates like structures and exhibit hexagonal habit. They were detected in the samples which subjected to immersion conditions or not, Figures 10(c), 11(a), 12(d), 13(a), and 13(d).

(ii) The clusters of portlandite crystals fill up the pores inside the bulk of the hydrated cement paste for non-immersed samples, Figure 10(c) and those immersed in ground and seawater, Figures 11(a) and 13(d).

(iii) C–S–H and ettringite phases were found collapsed with portlandite for nondipped samples and those exposed to groundwater and seawater as in Figures 10(d), 11(c), 12(b), and 12(d), respectively.

(iv) It was clear that the pores (that look black in SEM graphs) were little for samples immersed in seawater and groundwater as in Figures 12(a) and 13(c) compared with non-immersed samples and those immersed in tapwater, Figures 10(b) and 11(b), respectively.

Hence, the microstructure appeared to be more compacted and contentious for samples immersed in seawater and groundwater followed by those immersed in tapwater and non-immersed ones. This can explain the data reached from the porosity measurement and reported the low porosity values for blocks immersed in seawater relative to that dipped in the two other media. SEM configuration could verify the adequate performance of the proposed cement-clay mixture as an immobilizing composite for organic liquid scintillator waste under exposer to aqueous media during the long-term disposal process.

In order to assess thermal stability of the FWF blocks and the effect of immersion for long periods on the hydration products, thermogravimetric analysis (TGA), differential thermogravimetric analysis (DTGA), and differential thermal analysis (DTA) were performed for composite samples before and after immersion in different leachants. On the basis of DTA and TGA analyses, changing in the properties of the cement mixtures occurred due to mechanical activation that cannot be perceived from X-ray diffraction analysis. Reactivity of the activated mixtures increases by the decrease in melting temperature of certain minerals and the temperatures of the characteristic reactions. The energy received during mechanical activation leads to changes in the crystal structure, which causes reduction in the reaction enthalpy and, therefore, to a reduction of the decomposition temperature [26]. TGA measures the mass changes in the sample as a function of endothermic or exothermic peaks in the DTA thermogram.

TGA and DTGA data obtained for the immersed FWF blocks in various aqueous media and for non-immersed ones were recorded in Table 3 and also in Figure 14. From the data obtained, it could be observed that all TGA diagrams were characterized by four zones [27].

(1) The mass losses at temperatures less than 120°C, were due to the dehydration of pore’s water and release of hygroscopic water.

(2) The loss in the range ≈(120–460°C) was related to the dehydration of water associated with C–S–H, ettringite, monosulphate, and gypsum.

(3) In temperature range from 460°C to 560°C, the mass losses could describe the dehydroxylation (decomposition of portlandite).

(4) The fourth characterizing zone in TGA diagrams that started approximately at 700°C up to 850°C was attributed to the decarbonization of calcite according to the following reaction:

\[
\text{CaCO}_3(\text{Calcite}) \rightarrow \text{CaO(s)} + \text{CO}_2(\text{g}). \tag{2}
\]
Table 3: Mass loss in the FWF* due to thermogravimetric analysis (TGA) following the immersion in different aqueous media.

<table>
<thead>
<tr>
<th>Immersion media</th>
<th>The mass loss due to heating up to 1000°C</th>
<th>Total mass loss</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&lt;120°C</td>
<td>(120°C–460°C)</td>
</tr>
<tr>
<td>Non-immersed</td>
<td>1.9</td>
<td>5.5</td>
</tr>
<tr>
<td>Tapwater</td>
<td>5.8</td>
<td>12.1</td>
</tr>
<tr>
<td>Groundwater</td>
<td>5.9</td>
<td>13</td>
</tr>
<tr>
<td>Seawater</td>
<td>5.8</td>
<td>13.2</td>
</tr>
</tbody>
</table>

*Cement/water ratio = 0.3, clay = 3%, LSW = 15%.

The mass due to the decarbonization reaction is higher in case of sample dipped in seawater compared to that immersed in both tapwater, and groundwater. To fortify the results, they are depicted through XRD analysis.

Figure 15 shows the DTA thermograms of the immersed FWF in various aqueous media compared with non-immersed one. It is worth mentioning that there were slight differences in thermograms recorded for the four peaks of the immersed samples when compared with non-immersed ones.

Portlandite represented the predominant cementitious products formed due to hydration reaction of the neat cement with water as the following reaction:

\[
\text{CaO(s)} + \text{H}_2\text{O(l)} \rightarrow \text{Ca(OH)}_2(\text{s})
\]

Calcite was formed through a subsequent carbonization process due to the reaction between the formed portlandite...
and the atmospheric CO₂ or that present in groundwater or seawater as following reaction:

\[
\text{Ca(OH)\textsubscript{2}(s)} + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{CaCO}_3(\text{s}) + 2\text{H}_2\text{O}(\text{l})
\]

Correlating the TGA data to the DTA thermogravess, it can deduce numbers of characteristic endothermic peaks, Figure 15 as follows [22, 28]

(i) The first endothermic peak was below 100°C, which indicated the presence of hygroscopic and pore's water.

(ii) The second endothermic peaks up to \(\approx 116^\circ\text{C}\), which could be conducted to the presence of hydration products such as, C–S–H, monosulphate and ettringite.

(iii) The third endothermic effect, at peak \(\approx 484^\circ\text{C}\), that might represent the loss of hydroxyls and hydrogen atoms from portlandite to form of H₂O.

(iv) The fourth effect at peak centered near 770°C showed the loss of carbonate ions in the form of CO₂ from calcite.

The data in Table 3 reveal that the hydration products (C–S–H, monosulphate, ettringite, portlandite, and calcite) were higher in case of FWF immersed in various types of water when compared to the non-immersed ones, and this may be attributed to the enhancement in the durability of the immersed hardened FWF, that is mainly due to the changes in the internal microstructure rather than the alteration in the hydration products compositions; that is, flooding water may favor a little bit more hydration reaction that consequently affects the internal structure of the cementitious waste forms and consequently, their porosity and other parameters describing the final waste forms. These data also confirm the data obtained from XRD and FT-IR analyses.

4. Conclusions

Based on the experimental data obtained, it could be deduced that the candidate cement-clay composite can solidify and
Figure 12: Scanning electron microscope of the FWF immersed in groundwater for 18 months.

Figure 13: Scanning electron microscope of the FWF immersed in seawater for 18 months.
Figure 14: TGA and DTGA thermograms of the FWF immersed in different types of water.

Figure 15: DTA thermograms of the FWF immersed in different types of water.
stabilize up to 15% organic liquid scintillator waste safely and has acceptable resistibility toward the immersion in different aqueous media even under an aggressive prolonged flooding scenario. This waste form composite can optimally comply with the requirements for the disposal process.

References


[22] H. M. Fahmy, Applications of recycled textile wastes in cement composite [Ph.D. thesis], Chemistry Department, Faculty of Science, Cairo University, 2011.


