Research Article

Bitumen Coating as a Tool for Improving the Porosity and Chemical Stability of Simulated Cement-Waste Forms

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Coating of simulated cement-based waste form was investigated by performing physical and chemical experimental tests. Moreover, X-ray diffraction, Fourier transform infrared spectroscopy, and electron microscope examination were applied on coated and noncoated simulated waste forms. Experimental results indicated that coating process improved the characterizations of cement-based waste form such as porosity and leachability. Diffusion coefficients and leach indices of coated specimens were calculated and showed acceptable values. It could be stated that by coating cemented-waste form by bitumen emulsion, the radioactive contaminants were isolated, thus reducing the back release to surrounding environment during flooding by groundwater and consequently, saving the environment.

1. Introduction

A process of solidification/stabilization (s/s) has a very important role in handling, transportation, interim storage, and final disposal of radioactive wastes. For environmental safety, the release of hazardous radioactive materials from the disposal site into the environment should be prevented or delayed.

Cement and bitumen have been used individually as immobilization matrices for the radioactive wastes from the beginning of the nuclear industry in the 1960's [1]. Cement materials are currently the preferred ones for embedding most of low- and intermediate-level radioactive wastes due to the acceptable strength characterizing a cemented-waste form and hence could be handled, transported, and disposed safely [2–4].

Bituminized waste form resists the water penetration exhibiting very low leachability of radio contaminants because of it was considered as impervious matrix with smooth surface. Bituminization, accompanied by both mixing and evaporation processes, can lead to high-volume reduction. In addition, bitumen has good coating properties resistant to attack by microorganisms; consequently, more optimal characterization of the immobilized waste form was achieved. However, bituminized waste forms, prepared by using especially straight-run distillation bitumen, are mechanically and dimensionally unstable [5]. This instability is closely related to the long-term mechanical stability of waste forms at the disposal site.

The aim of this study was to obtain waste form specified by sufficient strength and high mechanical integrity as cemented-waste form and, in the same time, having relatively, high leaching stability, low fracturability, and more elasticity.

In the present work simulated cement waste forms were prepared by mixing water with cement then bituminized by immersion in bitumen emulsion. Mechanical integrity and porosity characterizations of the obtained product were evaluated under chemical and physical investigations. The chemical stability of the coated waste forms was compared with the noncoated ones to evaluate the leachability of radionuclides in different leachants. Besides, X-ray diffraction, infrared spectroscopy, and electron microscope investigations were performed for the final waste form.

2. Materials and Methods

2.1. Materials

2.1.1. Cement Material. Portland cement (PC) CEM1 (N/42.5) used in the present work was the available local
Table 1: Chemical composition (wt.%). Table 2: Elemental analysis of the bitumen used in the coating process, (%).

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>%</th>
<th>Compounds composition</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>19.84</td>
<td>C₃S</td>
<td>53.11</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>4.74</td>
<td>C₂S</td>
<td>16.89</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>4.0</td>
<td>C₃A</td>
<td>5.81</td>
</tr>
<tr>
<td>CaO</td>
<td>61.01</td>
<td>C₄AF</td>
<td>12.16</td>
</tr>
<tr>
<td>MgO</td>
<td>2.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K₂O</td>
<td>0.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO₃</td>
<td>2.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Insoluble residue</td>
<td>0.95</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Loss on ignition = 3.96%.
Lime saturation factor = 96% by wt.

<table>
<thead>
<tr>
<th>Carbon (%)</th>
<th>Hydrogen (%)</th>
<th>Sulphur (%)</th>
<th>Nitrogen (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>89.34</td>
<td>7.07</td>
<td>0.140</td>
<td>0.178</td>
</tr>
</tbody>
</table>

2.1.2. Bitumen. The bitumen used in this study was the commercially available straight-run distillation bitumen, having the elemental analysis described in Table 2.

2.1.3. Leaching Solutions. Three types of water, namely, tapwater, groundwater, and seawater, were used either in leaching experiments or for immersion tests.

The tapwater used was the normal tapwater in Giza district and was used for sake of comparison with the other two types of leachants. The groundwater was obtained from Abu-Zaabel well (no. 202) which is one of the nearest groundwater wells to Inshas-Reactor site. Since the seawater in the world has mainly similar composition, therefore, seawater was supplied from Alexandria, on the Mediterranean Sea. The concentration of some ions of interest in the three media is shown in Table 3.

2.1.4. Radioactive Isotopes. Cesium-137 and cobalt-60 are two of the most famous radionuclides found in numerous types of low- and intermediate-level radioactive wastes and were used in this study to trace the leaching characterization of the final coated waste form.

2.2. Experimental Methods

2.2.1. Preparation of Coated Cement Form. Cylindrical blocks of cement materials were prepared by mixing cement powder with water at the ratio of 0.35 (w/c) and poured into cylindrical plastic molds till hardening. For leaching experiments, water spiked by (Cs-137 + Co-60 ≈ 831 Bq/mL) was used for producing radioactive specimen that will be subjected to chemical resistance tests. After the curing period of 28 days, solid cemented waste forms having dimensions of 60 ± 2 mm height and 31 ± 0.5 mm diameters were obtained and immersed in soft hot bitumen at 90°C then left out to cool and harden for one week before performing the following different investigating tests. It was noticed an increase in the weight of waste form of 10 ± 1% due to coating process, related to the original weight of the blocks before coating.

Figure 1 represents the photo image of noncoated cement blocks and that coated with bitumen.

2.2.2. Characterizations of the Final Waste Forms

(a) Compressive Strength. Mechanical integrity was studied by measuring the compressive strength of solid cement blocks and the coated and noncoated ones. The compressive load required to cause damage were determined for 3–5 cylindrical blocks. A hydraulic press from Ma test, (Italy), model, E 159 SP was used for this test.

(b) Immersion Test. Immersion test was carried out for noncoated and the coated cement blocks by immersing these specimens in tapwater, groundwater, and seawater for 90 days. Visual examinations, compressive strength, and the weight of solid blocks were measured periodically.

(c) Porosity Test. According to saturation technique ASTM C-642, for the permeable pores of samples, a cold water saturation method, (CWS) was performed to calculate the porosity according to the following equation [8–10]:

\[
\text{Porosity (\%)} = \frac{\text{Wet mass (g)} - \text{Dry mass (g)}}{\text{Volume of the block (cm³)}} \times 100. \ (1)
\]

(d) Freezing-Thawing Test. Freeze-thaw cycling test was performed for solid samples of noncoated cement blocks and coated groups. The resulting free standing coated and noncoated blocks after curing period of 28 days were subjected to successive cycles every 24 hours of cooling in a fridge at −50°C and heating in an oven at 60°C up to three months. Mechanical integrity and weight changes due to freeze-thaw were evaluated.

(e) Leaching Test. The chemical resistance of coated and noncoated solid cement blocks was evaluated by following the leaching of radionuclides from specimens immersed in
3.1. Compressive Strength and Porosity Properties. Quality process was appeared. that inherited from cement, so as the necessity for coating bitumen reflected these advantage characterizations beside conditions. Therefore, coating the cemented waste form by low solubilities and compatible with most environmental. Bitumen is virtually impermeable to water and has very energy agency [11] with only one different. Table 4 showed the compressive strength of cemented forms prepared by mixing cement powder with different water/cement (w/c) ratios from 0.25 up to 0.50 (wt/wt). Clearly, the compressive strength was increased gradually till 0.35 w/c ratio due to completing the hydration reaction with increasing water. Then mechanical integrity was decreased gradually with increasing w/c ratio according to the excess of water. Therefore, the optimum w/c ratio is at 0.35, which is similar trend with that recorded in the literature [13].

In this study, the high values of apparent porosity for cemented blocks of rough surface were decreased from 31.5 ± 0.1% to 9.7 ± 1.1% for the bituminized ones, while the compressive strength values decreased in case of coated blocks (from 44.79 MPa for noncoated cement-waste form to 23.15 MPa for coated ones). This may be due to the elasticity inherited by the waste form after the coating by the bitumen emulsion. The cement blocks were flowed rather than fractured. The elasticity gained by bituminization was considered as advantage to avoid the dispersion of the hazardous components in case of their damage.

3.2. Immersion in Different Types of Water. The immersed coated and noncoated cement blocks in three different types of water were followed for time intervals of 30, 60, and 90 days to evaluate the long-term stability of the final waste forms. The compressive strength values of each group at the end of each interval were measured and the data reached are shown in Table 5. The main trend indicates that, the compressive strength values of coated and noncoated cemented waste forms were decreased by progress in immersion time for 30 days in the three different immersion media tested. The mechanical integrities were increased again after 60 and 90 days of immersion. It is worth mentioning that these values of groups at the different immersion time intervals do not exceed those values of nonimmersed ones. The first decrease in compressive strength of coated and noncoated cement blocks may be due to the diffusion of water into the pores of the specimens and hence, induces the release of lime and calcium sulphate components which leads the loss in the mechanical strength of the blocks [14]. While the second increase in compressive strength after 60 and 90 days could be contributed to the carbonation process that occurred where the calcite claim to be formed due to the reaction of Ca(OH)2 of cement and CO2 of surrounding environment and filling the pores of immersed blocks [15].

Figure 2 describes the change in weights of noncoated cement blocks which increased by immersion in seawater with more than 6% compared to that in tapwater and groundwater where 4% increase in weight was only recorded. This may be due to the salinity of the seawater which leads to accumulation of more salt layers on the block surface compared to that immersed in the other media. On the

\[
\text{Table 3: Chemical analysis of some ions of interest in different types of leachants.}
\]

<table>
<thead>
<tr>
<th>Leachants</th>
<th>pH</th>
<th>K+</th>
<th>Na+</th>
<th>Mg2+</th>
<th>Ca2+</th>
<th>Cl−</th>
<th>SO42-</th>
<th>HCO3-</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tapwater</td>
<td>6.90</td>
<td>0.086</td>
<td>1.07</td>
<td>1.2</td>
<td>1.4</td>
<td>0.77</td>
<td>0.7</td>
<td>1.8</td>
</tr>
<tr>
<td>Groundwater</td>
<td>7.20</td>
<td>22.0</td>
<td>149</td>
<td>13</td>
<td>74</td>
<td>137</td>
<td>317</td>
<td>272</td>
</tr>
<tr>
<td>Seawater</td>
<td>7.93</td>
<td>8.4</td>
<td>652.6</td>
<td>96.9</td>
<td>28.06</td>
<td>496.9</td>
<td>60.8</td>
<td>183</td>
</tr>
</tbody>
</table>

ppm = mg/L.

\[
\text{Table 4: Compressive strength of the cement waste forms of different water/cement (w/c) ratios.}
\]

<table>
<thead>
<tr>
<th>Water/cement (w/c) ratio (wt/wt)</th>
<th>Compressive strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>38.97</td>
</tr>
<tr>
<td>0.30</td>
<td>41.72</td>
</tr>
<tr>
<td>0.35</td>
<td>44.79</td>
</tr>
<tr>
<td>0.40</td>
<td>39.47</td>
</tr>
<tr>
<td>0.45</td>
<td>35.9</td>
</tr>
<tr>
<td>0.50</td>
<td>32.07</td>
</tr>
</tbody>
</table>

different leachants. Leaching tests were performed according to the method recommended by the International Atomic Energy Agency [11] with only one difference that the whole solid blocks were immersed completely in the leachant solutions. The radionuclides content of the leachates were measured using multichannel analyzer, PCAP, USA.

(f) Spectroscopic Analyses. FT-IR analyses were carried out by FT-IR-Jasco, 460 plus equipment, spectra and were usually recorded in the range of 4000–400 cm^{-1} with 2 cm^{-1} resolution. On the other hand, X-RD analyses were performed by using a Philips Analytical X-Ray B.V. operating with Cu tube anode.

(g) Electron Microscope. Jeol JXA-840A Electron Probe Microanalyzer scanning electron microscope (Japan) was employed with stage magnification of ×2,500. The actual pretreatment of preparation consisted only of gold plating of the samples in S150A Sputter Coater Edwards (England) before examination.

3. Results and Discussions

Bitumen is virtually impermeable to water and has very low solubilities and compatible with most environmental conditions. Therefore, coating the cemented waste form by bitumen reflected these advantage characterizations beside that inherited from cement, so as the necessity for coating process was appeared.

3.1. Compressive Strength and Porosity Properties. Quality of Portland cement (PC) aggregate, such as shape and surface roughness, is one of degree of porosity factors [12]. Clearly, the compressive strength was increased gradually till 0.35 w/c ratio due to completing the hydration reaction with increasing water. Then mechanical integrity was decreased gradually with increasing w/c ratio according to the excess of water. Therefore, the optimum w/c ratio is at 0.35, which is similar trend with that recorded in the literature [13].

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Table 5: The compressive strength values of coated and non-coated cemented blocks at different periods of immersion in various media.

<table>
<thead>
<tr>
<th>Immersion time, (days)</th>
<th>Tapwater</th>
<th>Compressive strength (MPa)</th>
<th>Groundwater</th>
<th>Seawater</th>
<th>Groundwater</th>
<th>Seawater</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Non-coated</td>
<td>Coated</td>
<td>Non-coated</td>
<td>Coated</td>
<td>Non-coated</td>
<td>Coated</td>
</tr>
<tr>
<td>0</td>
<td>44.79</td>
<td>21.4</td>
<td>44.79</td>
<td>21.4</td>
<td>44.79</td>
<td>21.4</td>
</tr>
<tr>
<td>30</td>
<td>31</td>
<td>18.7</td>
<td>29.0</td>
<td>23.3</td>
<td>27.4</td>
<td>18.6</td>
</tr>
<tr>
<td>60</td>
<td>32.5</td>
<td>27.7</td>
<td>30.8</td>
<td>25.1</td>
<td>30.87</td>
<td>23.05</td>
</tr>
<tr>
<td>90</td>
<td>35.4</td>
<td>28.8</td>
<td>32.8</td>
<td>26.2</td>
<td>33.1</td>
<td>24.8</td>
</tr>
</tbody>
</table>

Figure 2: Weight change during immersion of coated and non-coated blocks in different waters with time.

Table 6: Compressive strength values of coated and non-coated cement blocks subjected to freezing thawing treatment.

<table>
<thead>
<tr>
<th>Freezing thawing cycles</th>
<th>Compressive strength, (MPa)</th>
<th>Non-coated samples</th>
<th>Coated samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>44.79</td>
<td>21.4</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>33.42</td>
<td>18.42</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>29.1</td>
<td>16.91</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>29.1</td>
<td>14.6</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>18.2</td>
<td>12.7</td>
<td></td>
</tr>
</tbody>
</table>

3.3. Freezing Thawing Test. Table 6 represents the data obtained from the freeze-thaw test performed on both coated and noncoated blocks after 7, 14, 30, and 90 cycles. Decrease in the compressive strength of coated samples was recorded and reached 8.7 MPa after 90 freezing thawing cycles, compared to 12.09 MPa that lose in the mechanical integrity of noncoated samples that obtained. This indicated that coating of cement waste form by bitumen enhances its resistance to the disposal site climatic changes.

3.4. Chemical Characterizations. The mathematical theory of transport by diffusion from solid matter based on Fick’s law can be used as analytical solution for the leaching of radionuclides from waste forms [16, 17].

Cumulative leach fraction of radioactivity released from the solidified forms is derived as

\[
\sum a_n = 2 \left( \frac{S}{V} \right) \left( D_e \cdot \frac{t}{\pi} \right)^{1/2},
\]

where \( \sum a_n \) = total amount of substance released in all leaching periods up to time \( t \), \( A_0 \) = initial amount of substance of interest originally present, \( S \) = specimen surface area, \( V \) = specimen volume, cm\(^3\), and \( D_e \) = effective diffusion coefficient.

Also, the leachability index \( L_x \), as a figure of merit [18], can be calculated using the following equation:

\[
L_x = \frac{1}{i} \sum_{n=1}^{i} \log \left( \frac{1}{D_e} \right),
\]

where \( i \) = the number of leaching periods.

When the cemented waste forms come in contact with water, the hazardous soluble materials, including the radionuclides, moves from the waste form to the surrounding water causing dissolution or chemical reaction with the components of water. Therefore, maintaining stable chemical and physical properties of waste form is a very important task to delay or even to prevent the release of hazardous radionuclides into the environment when it come in contact with water in disposal site.

Bitumen is chemically inert matrix, insoluble in water, and it shows a remarkable lower leach rate of the final waste form when compared to the cemented waste forms.

Figure 3 represents the cumulative fractions of radionuclides leached from coated and noncoated waste form specimens as a function of time.

It is clear from Figure 3, that the leachability after coating process was reduced up to 90% compared to noncoated specimens. This value was in agreement with the results published previously by Matsuzuru et al. [19]. This could be explained in view of low porous surface of coated specimens which retarded break throw of water into cement block specimens and consequently delayed the release of radionuclides [20]. This could be compared to the noncoated other hand, low permeability of bitumen layer is leading to low penetration of water into coated cement blocks causing undetectable weight change in the specimens (not exceed 1%).
Figure 3: Cumulative leach fraction for coated and noncoated cement specimens versus leaching time.

Figure 4: Scanning electron micrographs of fracture surface of cemented waste form (a) and other coated by bitumen emulsion (b).

porous cemented blocks which showed more water penetration inside the specimens. In addition, it is clear from Figure 3 that there is no significant differences in cumulative leach fractions for coated specimens when exposed to the three leachants. On the other hand, in case of noncoated specimens, the releasing of radionuclides into seawater is higher than that for tapwater and ground water. This may be attributed to the high salinity and the high concentration of soluble ions in seawater which enhance the exchange of radionuclides of noncoated specimens compared to that in groundwater or tapwater.

According to the equation of the average effective diffusion coefficient \( (D_e) \) and leachability index \( (L_x) \), the values of \( D_e \) was increased while \( L_x \) decreases and the data are reported in Table 7. The higher leachability index of coated specimens comparing with noncoated ones confirmed the chemical improvement obtained by the coating process.

Figure 4 shows the scanning electron micrographs of cemented-waste form and the coated one. It is clear from Figure 4(a) the rough surface of hydrated cement specimen. On the other hand, the coated block in Figure 4(b) appears as a smooth surface. This figure also illustrates the role of bitumen emulsion in coating the hydrated cement and entering into its pores giving less permeability to the waste form and consequently an acceptable improvement in the chemical criterion as reached from the chemical test data.

3.5. Infrared Spectroscopy. The infrared spectroscopic analysis was performed for coated and noncoated cement blocks after curing period of 28 days and it gave nearly identical peaks assignment for the two samples as shown in Figure 5. Hydrated cement is assigned by more known

<table>
<thead>
<tr>
<th>Leachant solution</th>
<th>Non-coated</th>
<th>Coated</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D_e )</td>
<td>( L_x )</td>
<td>( D_e )</td>
</tr>
<tr>
<td>Tapwater</td>
<td>1.23E−11</td>
<td>9.217728</td>
</tr>
<tr>
<td>Groundwater</td>
<td>1.71E−11</td>
<td>9.052412</td>
</tr>
<tr>
<td>Seawater</td>
<td>1.65E−11</td>
<td>9.165989</td>
</tr>
</tbody>
</table>

Table 7: Effective diffusion coefficient \( (D_e) \) and leachability index \( (L_x) \) of radionuclides for coated and non-coated waste forms.
D-values are typically the same with some differences in the relative intensity percent. The obtained records are in a good agreement with those reported in literature for portlandite and calcite [23]. Basing on the X-ray and infrared analyses, it could be stated that bituminization of cemented waste form has no negative effect.

4. Conclusion

By studying the simulated cement waste form coated by bitumen emulsion, the experimental results indicated that coating process improved their porosity character, resistance to immersion and freezing thawing, and chemical stability. In addition, leachability of bituminized cemented waste form was lowered to about 90% of its value before a coating step. Based on these results and the data obtained from spectroscopic analyses and electron microscopy, it could be concluded that coating of the cemented waste form using bitumen emulsion before the disposal process is a preferable approach to avoid the back release of radioactive components to man’s environment.

References


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