Durability of Cement Stabilized Low-Level Wastes

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Westinghouse Hanford Company Richland, Washington

Management and Operations Contractor for the
U.S. Department of Energy under Contract DE-AC06-87RL10830

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DISCLM-2.CHP (1-91)
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Date Published
December 1995

Presented at
1995 Fall Meeting of the Materials Research Society
Boston, Massachusetts
November 27, 1995

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DURABILITY OF CEMENT STABILIZED LOW LEVEL WASTES
Durability of cement stabilized wastes

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Abstract
Cementitious materials containing high proportions of slag and fly ash have been tested for suitability to immobilize simulated alkaline and carbonated off-gas waste solutions after vitrification of low-level tank wastes stored at Hanford. To assess their performance, long-term durability was assessed by measuring stability of compressive strength and weight during leaching and exposure to sulfate and carbonate solutions. The important parameter controlling the durability is pore structure, because it affects both compressive strength and susceptibility to different kinds of chemical attack. Impedance spectroscopy was utilized to assess the connectivity of the pore system at early ages. Mercury intrusion porosimetry (MIP) and SEM were utilized to assess development of porosity at later ages. Phase alterations in the matrix exposed to aging and leaching in different media were followed using XRD.

Mixtures were resistant to deterioration during immersion in solutions containing high concentrations of sulfate or carbonate ions. Mixtures were also resistant to leaching. These results are consistent with microstructural observations, which showed development of a finer pore structure and reduction in diffusivity over days or months of hydration.

Keywords: Durability, permeability, diffusion, deterioration, cement, wastes.

1 Introduction

Immobilization of tank wastes at Hanford is expected to utilize a vitrification process. It is assumed that there will be an off-gas waste produced during vitrification, and the objective of our studies is to explore stabilization of this off-gas waste using cementitious materials. For these studies, two off-gas waste compositions were used, one with a composition similar to the tank waste but more dilute, and the other with added carbo-
nate CO₂ to simulate waste from a gas–fired melter, where CO₂ levels will be high.

There are two important issues to consider in designing a durable cement–stabilized waste form. One is microcracking due to thermal stresses resulting from the temperature rise during early hydration. Therefore it is important to design the material such that excessive temperature rise does not occur. The other important issue is that the material be resistant to leaching and chemical attack. If the material is free of microcracks and low in permeability, it is likely to resist these processes. Because the waste form is to be buried underground, any chemical attack would likely involve sulfate or carbonate solutions.

It is known that pozzolans improve the durability of cementitious materials. They reduce heat evolution, and they increase the resistance of concrete to deterioration by aggressive chemicals such as chlorides, sulfates, etc. [1]. Much of this increase in durability is attributed to decreased permeability and reduced ion diffusivity resulting from a finer pore structure. Therefore the waste materials in this study contained ~60 weight % of fly ash and slag. Attapulgite clay (~10% by weight) was used to prevent excessive bleeding.

In order to assess the durability of waste materials, they have been exposed to leaching solutions and to solutions containing high concentrations of sulfate or carbonate ions, and their pore system development has been studied.

This paper describes the durability of the off–gas wasteforms developed for Hanford. A companion paper [2] deals with the chemical evolution of these materials.

2 Experimental procedure

To prevent excessive heat evolution during hydration of cementitious mixtures combined with a highly alkaline liquid waste, high proportions of slag and fly ash were utilized. The mix design was adjusted to meet the requirement that temperature on adiabatic curing not exceed 90 °C. The temperature rise was measured using an adiabatic calorimeter constructed in our laboratory. The mixtures tested are designated by their percent (by weight) of cement¹, fly ash², slag³ and clay⁴. For example, the material 3:3:3:1 contains 30% cement, 30% fly ash, 30% slag and 10% clay. Two types of waste solutions were tested: alkaline (A) and carbonated (C). Table 1 shows their chemical compositions. The proportion of solid to liquid was 1 kg to 1 liter. The materials were cured adiabatically for 4 days (reaching the temperatures shown in Table 2); after that they were sealed in tubes and cured isothermally at 70 °C for 10 months. Additional details are provided in Ref. [2].

Impedance spectroscopy was utilized to observe changes in electrical conductivity of the tested materials during the first few days of hydration. As described elsewhere [3], the measured sample conductivity (σ) was normalized by the measured conductivity of the pore solution (σ₀). The resulting normalized conductivity (σ/σ₀) is a microstructural parameter that characterizes the capillary pore network. It is directly related to the diffusivity through the Nernst–Einstein equation, and can be used to compute permeability through the Katz–Thompson equation.

1. Type I/II, Ash Grove, Durkee, OR
2. Type F, Centralia, Ross Sand and Gravel Co., Portland, OR
3. Koch Minerals Co., Chicago, IL
4. Engelhard Co., Iselin, NJ
I. Composition of solutions

<table>
<thead>
<tr>
<th></th>
<th>Alkaline</th>
<th>Carbonated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(NO₃)₃·9 H₂O</td>
<td>7.03 g/l</td>
<td>7.03 g/l</td>
</tr>
<tr>
<td>Na₃(PO₄)·12 H₂O</td>
<td>24.53 g/l</td>
<td>24.53 g/l</td>
</tr>
<tr>
<td>NaN₃</td>
<td>12.17 g/l</td>
<td>12.17 g/l</td>
</tr>
<tr>
<td>NaOH</td>
<td>53.76 g/l</td>
<td></td>
</tr>
<tr>
<td>NaN₃</td>
<td>32.73 g/l</td>
<td>32.73 g/l</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td></td>
<td>39.97 g/l</td>
</tr>
</tbody>
</table>

\[ k = \frac{1}{220} d_c^2 \frac{\sigma}{\sigma_0} \]  \hspace{1cm} (1)

where \( k \) is the coefficient of permeability and \( d_c \) is the threshold pore diameter (obtained by mercury intrusion porosimetry).

Mercury intrusion porosimetry was utilized to assess the changes in pore size distribution and porosity at ages up to 10 months. This method was also used to measure \( d_c \) used in equation (1). Prior to measurement the samples were immersed in methanol for 3 days and subjected to drying at 105°C to reduce damage to microporosity during drying. The minimum intruded pore diameter was 3 nm.

The leaching test was designed to simulate leaching by ground water percolating through the burial vault. The test was based on the ANSI/ANS-16.1-1986 test. Four leaching agents were used: deionized water, simulated ground water, 5.3 mmole/L solution of magnesium sulfate, and 5.3 mmole/L solution of sodium bicarbonate. Table 3 shows the composition of the simulated ground water, which was based on analyses of the ground water at Hanford [4]. The experiment was performed on cylinders (50 mm

Table 2. Adiabatic curing temperatures

<table>
<thead>
<tr>
<th>Materials</th>
<th>Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>3:3:3:1C</td>
<td>60</td>
</tr>
<tr>
<td>3:0:6:1C</td>
<td>65</td>
</tr>
<tr>
<td>3:4:2:1A</td>
<td>54</td>
</tr>
<tr>
<td>3:5:1:1A</td>
<td>52</td>
</tr>
</tbody>
</table>

Table 3. Simulated ground water composition

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Quantity, μg/mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium</td>
<td>50.7</td>
</tr>
<tr>
<td>Magnesium</td>
<td>15.2</td>
</tr>
<tr>
<td>Sodium</td>
<td>28.4</td>
</tr>
<tr>
<td>Sulfate</td>
<td>51.2</td>
</tr>
<tr>
<td>Total Carbon</td>
<td>32.0</td>
</tr>
</tbody>
</table>
in length, 26 mm in diameter) at 45°C. All samples were immersed in 250 mL bottles containing the leach medium. The leach medium was changed at 1, 2, 3, 7, 14, 28, 56, 84, and 112 days. Compressive strength and weight were monitored periodically.

The test for sulfate deterioration was based on ASTM C1012, "Standard Test Method for Length Change of Hydraulic-Cement Mortars Exposed to a Sulfate Solution". Beginning at the age of 1 month, cylindrical samples were immersed in a 0.352 mol/L solution of magnesium sulfate and stored at 45°C for 10 months. ASTM C1012 calls for measurement of length change of bars. We were unable to make such measurements due to the low strength of these materials. Instead, weight change and compressive strength were measured periodically.

An analogous test was used for carbonate deterioration. The cylindrical samples at the age of 1 month were immersed in a 0.352 mole/L solution of sodium bicarbonate and stored at 45°C for 4 months. Weight change and compressive strength were measured periodically.

3 Results

Figure 1 shows the normalized conductivity of 3:0:6:1C. The value of normalized conductivity dropped rapidly after 24 hours, reaching 0.001 by 3–4 days. This value is more than an order of magnitude lower than a conventional Portland cement paste with w/c of 0.5 [3].

Table 4 summarizes the MIP measurements at 1 month and 10 months. All samples showed an increase in pore surface area and a decrease in pore size with time. Most samples also showed a small increase in pore volume during this time interval.

Figure 2 presents the evolution of compressive strength during the leaching experiments. The strength values have a scatter due to the stochastic nature of the test and the heterogeneity of the samples. An increase in compressive strength after 1 month was ob-
Table 4. Summary of MIP measurements for off-gas materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Age, month</th>
<th>Porosity, vol.%</th>
<th>Pore area, m²/g</th>
<th>Threshold diameter, µm</th>
<th>Median pore diameter, µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>3:3:3:1C</td>
<td>1</td>
<td>50.6</td>
<td>62.5</td>
<td>1.0</td>
<td>0.009</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>52.4</td>
<td>124.8</td>
<td>0.1</td>
<td>0.007</td>
</tr>
<tr>
<td>3:0:6:1C</td>
<td>1</td>
<td>53.7</td>
<td>94.24</td>
<td>0.3</td>
<td>0.009</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>49.9</td>
<td>134.7</td>
<td>0.15</td>
<td>0.006</td>
</tr>
<tr>
<td>3:4:2:1A</td>
<td>1</td>
<td>58.6</td>
<td>84.6</td>
<td>0.2</td>
<td>0.018</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>63.8</td>
<td>101.6</td>
<td>0.15</td>
<td>0.009</td>
</tr>
<tr>
<td>3:5:1:1A</td>
<td>1</td>
<td>31.8</td>
<td>35.5</td>
<td>1.0</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>52.2</td>
<td>92.0</td>
<td>0.1</td>
<td>0.01</td>
</tr>
</tbody>
</table>

served in 3:4:2:1A, attributed to continuing hydration. All the other materials were reasonably stable in weight and compressive strength when subjected to leaching.

Table 5 presents results of the sulfate test. Samples with carbonate waste (3:3:3:1C and 3:0:6:1C) had a very small increase in weight (2–3%) and small decrease in strength during 10 months. Samples with alkaline waste (3:5:1:1A and 3:4:2:1A) had lower initial compressive strengths, but little strength loss or weight change. In the absence of a predetermined failure criterion for strength loss or weight change on exposure to sulfate solution, we can only conclude that the low changes observed appear to reflect satisfactory performance, especially taking into account the very aggressive, highly concentrated solutions (10^4 times the level of sulfate in the ground water) and the low strength of these materials at the start of exposure. Examination of materials exposed to sulfate attack using SEM showed a dense rim 1–2 mm thick rich in calcium and sulfur; by XRD the prevalent phase was gypsum.

Table 6 presents the results of the carbonate test. Only small changes in weight (1–2%) and strength were observed. Examination of the material using SEM showed that a calcium rich phase was uniformly distributed in pores of the matrix; by XRD the prevalent phase was calcite.

4 Discussion

Permeability to water and diffusion of ionic species in cementitious materials are important keys to durability. Therefore the development of porosity in these waste materials was assessed using different techniques. The measurements of electrical conductivity in the first few days of hydration showed a rapid drop in diffusivity of the samples. The estimated permeability of materials at the age of 1 month using eq. (1) was in the range of 10^{-16} m/s. It is known that addition of mineral admixtures such as slag or fly ash leads
Figure 2(a–d). Compressive strength evolution in the leaching experiment:
(a) 3:5:1:1A, (b) 3:4:2:1A, (c) 3:0:6:1C, (d) 3:3:3:1C.
Table 5. Results of immersion in sulfate solution

<table>
<thead>
<tr>
<th>Material</th>
<th>Initial compressive strength, MPa</th>
<th>Compressive strength at 10 months, MPa</th>
<th>Increase in Weight, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>3:3:3:1C</td>
<td>6.2</td>
<td>6.2</td>
<td>3.2</td>
</tr>
<tr>
<td>3:0:6:1C</td>
<td>8.3</td>
<td>5.8</td>
<td>2</td>
</tr>
<tr>
<td>3:5:1:1A</td>
<td>3.0</td>
<td>2.5</td>
<td>7.5</td>
</tr>
<tr>
<td>3:4:2:1A</td>
<td>2.8</td>
<td>2.5</td>
<td>7.8</td>
</tr>
</tbody>
</table>

Table 6. Results of immersion in the carbonation solution

<table>
<thead>
<tr>
<th>Material</th>
<th>Initial compressive strength, MPa</th>
<th>Compressive strength at 10 months, MPa</th>
<th>Increase in Weight, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>3:3:3:1C</td>
<td>6.2</td>
<td>5.8</td>
<td>2.4</td>
</tr>
<tr>
<td>3:0:6:1C</td>
<td>8.3</td>
<td>6.2</td>
<td>2</td>
</tr>
<tr>
<td>3:5:1:1A</td>
<td>3.0</td>
<td>2.9</td>
<td>1</td>
</tr>
<tr>
<td>3:4:2:1A</td>
<td>2.8</td>
<td>5.1</td>
<td>2</td>
</tr>
</tbody>
</table>

to a decrease in pore size and an increase in the fraction of pores in the finer size range of 15 nm or less [5], and the MIP measurements showed this trend. At later ages the pores became smaller in size and formed a pore structure of greater surface area, changes that are expected to reduce permeability.

All the materials showed a resistance to deterioration in concentrated sulfate solution (Table 5). Ingress of sulfate ions is presumed to be controlled by the rate at which sulfate diffuses through the pore structure. Although the direct measurements of diffusivity have not been conducted, the results of the sulfate test suggest that the materials have quite low diffusivities. The diffusivity was likely also reduced by precipitation of calcium sulfate.

Leaching, like chemical attack, involves movement of water and dissolved species due to a concentration gradient. So leaching also depends on the pore structure and permeability of the paste. All the materials showed resistance to leaching. These results correlate quite well with the results of chemical attack, and can be explained by low diffusivities and low permeabilities of the materials.

Phase alterations observed by XRD suggest that a further increase in strength may be expected. In a companion paper [2] it is suggested that calcium silicate hydrate has a tendency to increase polymerization and crystallization, leading to improved strength.
and decreased permeability. The observed low content of calcium hydroxide in these materials is also favorable for durability.

5 Conclusions

It has been the experience that well cured cementitious materials with low water–solid ratios have low permeability and resist deterioration. This study showed that cementitious materials containing a high proportion of slag, fly ash, and alkaline solution and cured at elevated temperatures, despite having very high water–solid ratios, may also have low permeability and resist deterioration.

6 Acknowledgement

The research was funded by grant MTS–SVV–097600 from the Westinghouse Hanford Company. We thank the Ross Sand and Gravel Co., Koch Mineral Co., Engelhard Co., and the Ash Grove Cement Co. for materials.

7 References

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