FORMULATION AND DURABILITY OF TAILORED CEMENTITIOUS HOSTS APPLIED TO TRU WASTE GENERATED AT THE ROCKY FLATS PLANT

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FORMULATION AND DURABILITY OF TAILORED CEMENTITIOUS HOSTS APPLIED TO TRU WASTE GENERATED AT THE ROCKY FLATS PLANT. J. H. Kessler, G. C. Rogers, L. R. Dole, and M. T. Morgan, Oak Ridge National Laboratory, P. O. Box X, Bldg. 3508, Oak Ridge, TN 37830.

This paper discusses the development of cementitious grout formulations at the Oak Ridge National Laboratory which immobilize up to 50% of Rocky Flats Building 374 startup TRU waste. Trial grout mixes were tested in order to minimize the water content and maximize the waste loading. The effects of water reducers and set regulators on these trial mixes were also examined.

Durability and physical-property measurements were performed on formulations which are compatible with standard processing equipment. The densities, porosities, and compressive strengths of these solids are reported. Compressive strengths of the samples were found to increase by as much as 69% after the samples had been exposed to leachants for 28 days at 90°C.

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The Oak Ridge National Laboratory's Cement and Concrete Applications Center (ORNL/CCAC) has produced tailored concretes which have successfully incorporated a wide spectrum of radioactive wastes. This spectrum included TRU, high-, intermediate-, and low-level wastes which are produced throughout the defense and commercial sectors. These concretes have the long-term durability required for the permanent isolation of the incorporated waste. This paper discusses the development of cementitious grout formulations that incorporate up to 50% by weight of the Rocky Flats Building 374 startup TRU waste containing Pu and Am isotopes. A curing process was also established for the solidification of these grouts and the resulting solids' physical properties were measured. The Rocky Flats Building 374 waste processing system involves increasing the pH of an acidified liquid waste stream, treatment with flocculating agents, filtering on a rotary drum vacuum filter, and partial drying in a steam heated sludge dryer. The resulting waste is soft, granular, chemically inhomogeneous, and contains a water content between 10 and 15%.

Initially, criteria were developed for a successful grout/concrete formulation incorporating this waste. These criteria are based upon minimizing transportation and disposal requirements, maximizing waste host durability, and the ease and safety of waste host processing. Therefore, the following criteria were established:

1. waste loading of >30 percent by weight;
2. use the waste "as-is", without pre-conditioning;
3. the mixed grout should have adequate mixability, such that standard grout mixing and transfer equipment may be utilized;

4. the final mixed grout should also remain mixable for at least 30 minutes to facilitate a minimum amount of time to remove any grout from the mixer/transfer system in the event of equipment failure;

5. the grout formulation should have the lowest water/cement ratio possible to improve not only the concrete quality, but also to reduce alpha radiolysis;

6. the grout solidification process should be fast, and at low temperatures to reduce overall cost and risk; and

7. the compressive strength of the resulting solid should be maximized.

Based on the above constraints, the project was divided into four phases. The first phase was to develop the waste host formula incorporating the Rocky Flats Building 374 waste. The second phase focused on establishing an accelerated curing/dewatering process to quickly solidify and reduce the water content of the grout. The third phase identified the physical properties of the resulting solid. The fourth phase, MCC-1 leach tests in brine and deionized water at 90°C were performed using samples containing the Rocky Flats waste spiked with Pu-239. These leach tests are just now nearing completion so that the results are not yet available.
PHASE I: FORMULATION DEVELOPMENT

During these formulation studies, over 80 trial grout mixes were prepared. Individual grout components were varied to determine their effect upon the ease with which the grout could be stirred. These components included: cement (both the type and amount were varied), sand, water, water reducers and set regulators, Fe₂O₃ (added as a radiolysis product recombination catalyst), and the Rocky Flats Building 374 TRU waste.

One hundred gram batches were prepared for the formulation screening studies. The dry solids (waste, sand, Fe₂O₃, cement, and some of the water reducers or set regulators) were weighed and mixed by hand shaking. The water and some of the water reducers or set regulators were then weighed and mixed. The mixed dry solids were added to the liquid and hand stirred for 5-10 minutes to near constant stirring resistance. These samples were then transferred to capped, plastic storage vials and vibrated to remove any large air bubbles. Periodically, the grouts were probed with a spatula until they were qualitatively determined to have achieved initial set. The α-activity levels of this waste precluded the use of standard techniques for the quantitative determination of workability, slump, and set time.

The Rocky Flats waste is alkaline, very porous, and water demanding (able to absorb nearly 1/2 of its dry weight in added water). These properties made the development of a high quality cement containing an acceptable waste loading difficult. Early formulations indicated that
waste loadings up to 40 wt % made acceptable host solids. Although acceptable grout formulations could be prepared using up to 50 wt % waste, the resulting concrete product properties are considered unreliable due to the inhomogeneity of the Rocky Flats 374 waste stream.

Since excess water in a grout formulation produces a low compressive strength product, it was necessary to investigate the effects of water reducers and set regulators. These components act to reduce the water demand of the grout and still allow adequate mix workability. Table I lists the water reducers and set regulators which were found to be effective. These screening tests showed that Reax-LP and Plastiment are the most effective in reducing water demand and mixing resistance. D-65 and CFR-1 were found to be less effective. The addition of 0.25 to 0.50 wt % Reax-LP immediately reduced mixing resistance, however these mixes tended to become unstirrable shortly after mixing was completed. One to two weight percent of Plastiment resulted in mixes that were initially very stiff, but significantly improved after a few minutes of mixing. A combination of Reax-LP and Plastiment proved to be an effective solution. The combined effect of Reax-LP and Plastiment also reduced the grouts' water demand by 20% to 25%.

Because of its wide availability, Portland Type I cement was chosen as the reference cement for formulation development. Ideal Type I cement was used in this study. However a few formulations were tested using two other cement types substituted for Type I: Lumnite (a high alumina cement produced by Universal Atlas), and Portland Type II
Table I. Effective water reducers and set regulators*

Reax-LP (Westvaco Co., a sodium lignosulfonate)
D-65 (Dowell, water soluble water reducer)
CFR-1 (Halliburton, deltagluconolactone)
Plastiment (Sikamix, hydroxylated carboxylic acid)

*These are proprietary additives produced by the companies listed. This does not constitute an endorsement of these additives.
(produced by Atlas Cement Co.). The Lumnite cement required more water than Atlas Type I to achieve similar grout stirrability. This Type II cement did appear to be slightly better than the Type I. The Type II required 1-2% less water than the Type I to obtain a similar stirrability. Additional studies also suggested that concretes prepared with Type II rather than Type I had compressive strengths approximately 20% higher and weight losses, which were approximately 1-2% lower after dewatering at 250°C.

Based on the criteria for the grout properties and compressive strength, trial mix number 86 was chosen for additional study. Table II describes the mix number 86 formulation.

**PHASE II: MIX SOLIDIFICATION PROCESSING**

A simple, rapid, low temperature solidification process for the Rocky Flats Building 374 waste was developed to achieve reduced processing costs and complexity. Previous experience at the ORNL/CCAC has shown that cementitious grouts can be rapidly cured and dewatered, using such simple, low temperature processes.²⁻⁴ Based on this experience, a 24 hour cure at 90°C at 100% relative humidity followed immediately by a 24 hour dewatering at 250°C in dry air was chosen. For instance, the drums filled with the mixed grout could be put in a closed, 90°C water bath for 24 hours. After 24 hours, the water bath could be drained and the drums heated at 250°C for 24 hours. This would drive off most of the free water, which is not chemically bound in cementitious phases, reducing the drum weight and the consequences of alpha radiolysis.
Table II. Trial mix number 86

<table>
<thead>
<tr>
<th>Component</th>
<th>wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rocky Flats Building 374 Startup Sludge</td>
<td>40</td>
</tr>
<tr>
<td>Portland Type I Cement</td>
<td>22</td>
</tr>
<tr>
<td>Ottawa Sand</td>
<td>11.25</td>
</tr>
<tr>
<td>Reax-LP</td>
<td>0.5</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.25</td>
</tr>
<tr>
<td>Water</td>
<td>24</td>
</tr>
<tr>
<td>Plastiment</td>
<td>2</td>
</tr>
</tbody>
</table>
PHASE III: PHYSICAL PROPERTIES

Samples were prepared using mix number 86 and the curing/dewatering procedure, developed in Phases I and II, respectively. These samples were used for compressive strength, density, and porosity measurements. Mix number 86 batches, weighing 2.4 Kg, were prepared in a Hobart mixer at a low speed for five minutes. Stainless steel two inch cube molds coated with a thin layer of vacuum pump oil (to prevent sample sticking) were then filled with the mixed grout. During filling, a vibrating table was used to remove any large bubbles. These filled molds were immediately placed in a 90°C steam cabinet for 24 hours. After curing, the specimens were removed and put in a 250°C oven for 24 hours.

Porosity measurements were done by evacuating the sample cubes for at least 1 hour followed by refilling the pores with toluene. Porosity was then determined by the buoyancy weight difference.

Compressive strength measurements were made using a Tinius-Olsen Universal Testing Machine, using a sample loading rate of 600 lb/min. A summary of the physical properties is found in Table III.

An additional series of two inch cubes were used to determine the compressive strength changes after exposure to MCC-1\textsuperscript{5} static leach conditions. Four replicate specimens were leached in MCC-1 deionized water, silicate water and brine for 28 days at 90°C. In this static leach test, the leachant volume to sample surface area was approximately 2.3:1.
Table III. Bulk physical properties of trial mix number 86

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cured Density</td>
<td>1.75 g/cm³</td>
</tr>
<tr>
<td>Dewatered Density</td>
<td>1.23 g/cm³</td>
</tr>
<tr>
<td>Porosity</td>
<td>56%</td>
</tr>
<tr>
<td>Initial Water/Cement Ratio</td>
<td>1.1</td>
</tr>
<tr>
<td>Compressive Strength: After Curing</td>
<td>3.95 ± 0.16 MPa</td>
</tr>
<tr>
<td>Compressive Strength: After Dewatering</td>
<td>7.30 ± 0.24 MPa</td>
</tr>
<tr>
<td>Final Sample Volume vs. Initial Waste Volume:</td>
<td>~1.2:1</td>
</tr>
<tr>
<td>Final Sample Weight vs. Initial Waste Weight:</td>
<td>~1.8:1</td>
</tr>
</tbody>
</table>
Afterwards, these samples were dried at 250°C for 24 hours, cooled, and tested for compressive strength. As shown in Table IV, the compressive strengths of these specimens increase after leaching. In the case of the MCC-1 brine, the compressive strength increased by 69%.

**SUMMARY**

A cement-based product has been developed which successfully incorporates 40 wt % Rocky Flats Building 374 waste with only a 20% volume increase. This formula's mix properties make it compatible with inexpensive, standard mixers. The curing and dewatering steps represent a fast, simple and low temperature process. The compressive strength of this product is adequate and improves upon exposure to potential repository environments.
Table IV. Compressive strength of mix 86 before and after leaching in MCC-1 leachants

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Compressive strength (MPa)</th>
<th>% Increase of compressive strength after leaching</th>
</tr>
</thead>
<tbody>
<tr>
<td>90°C, 24 hr cure; 250°C dewater, before leaching</td>
<td>7.30 ± 0.24</td>
<td></td>
</tr>
<tr>
<td>28 days in 90°C deionized water; 250°C dewater</td>
<td>8.55 ± 1.88</td>
<td>17</td>
</tr>
<tr>
<td>28 days in 90°C silicate water; 250°C dewater</td>
<td>8.24 ± 1.55</td>
<td>13</td>
</tr>
<tr>
<td>28 days in 90°C brine; 250°C dewater</td>
<td>12.32 ± 0.78</td>
<td>69</td>
</tr>
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REFERENCES


