**Waste Form Development for use with ORNL
Waste Treatment Facility Sludge**

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under Subcontract No. 19X-ST305V
with
Oak Ridge National Laboratory
managed by
LOCKHEED MARTIN ENERGY RESEARCH CORP.
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and
William D. Bostick

May 1996

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K/TSO-7A

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This document has been approved for release
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CONTENTS

	Page
LIST OF TABLES	iv
FOREWORD	v
ABSTRACT	vi
1. INTRODUCTION	1
2. OBJECTIVES	2
3. EXPERIMENTAL APPROACH	2
3.1 PREPARATION OF WSS #5 SURROGATE SLUDGE	2
3.2 THERMAL ANALYSIS OF THE SLUDGE	3
3.3 WASTE VOLUME REDUCTION BY CALCINATION	4
3.4 COMPACTION OF THE CALCINED AND UNCALCINED WASTES	4
3.5 COMPRESSIVE STRENGTH ANALYSIS	5
3.6 SURFACE AREA MEASUREMENTS	5
4. RESULTS AND DISCUSSION	5
5. SUMMARY AND CONCLUSIONS	9
6. REFERENCES	10

LIST OF TABLES

Table	Page
1. Composition of WSS-5 Surrogate Sludge	3
2. Compactions and dimensional changes for the calcium oxide produced by calcination of calcium carbonate and the surrogate sludge	6
3. Dimensions of the surrogate sludge containing 35% parafin compressed at 8000 psia	7
4. Compressive strengths of selected parafin-containing samples	8
5. Surface areas of the CaO and the calcined surrogate sludge	8

FOREWORD

This document represents the final report for the project titled "Waste Form Development for use with ORNL Waste Treatment Facility Sludge", awarded to Clark Atlanta University under Lockheed Martin Energy Research contract number 19X-ST305V.

The information presented in this text is complimentary to that contained in the Lockheed Martin Energy Systems report K/TSO-7, "Treatment Options for Low-Level Radiologically Contaminated ORNL Filtercake." The data support a waste treatment/stabilization option proposed by a private sector vendor (Scientific Ecology Group). Calcination of surrogate sludge results in significant reduction of sludge mass and volume, but yields dispersible fine particulate. Compression of the solids at pressures of >4,000 pounds per square inch (psi) produces a poorly consolidated waste form that demonstrates variable dimensional stability (attributed to uptake of atmospheric moisture and carbon dioxide by the excess calcium oxide in the calcined waste). Stabilization of the resulting solids by admixture with parafin wax and consolidation of the mixture by compression is demonstrated to yield a monolithic waste form having adequate dimensional and physical integrity for on-site interim waste storage, and the resultant waste form is anticipated to meet the requirements for off-site disposal.

ABSTRACT

A sludge that simulates Water Softening Sludge #5 (WSS #5 filtercake) at Oak Ridge National Laboratory was prepared and evaluated for its thermal behavior, volume reduction, stabilization, surface area and compressive strength properties. Thermogravimetric analysis and calcination of the filtercake showed that it contained about 44% moisture and other volatile materials.

Compaction of the surrogate waste and the calcium oxide (produced by calcination of calcium carbonate, the major waste constituent) in the presence of parafin resulted in cylindrical molds with various degrees of stability. The most stable product was the calcined surrogate-35% parafin mixture that was compressed at 8000 psi. This sample expanded by 3% after 14 days and it also gave the highest compressive strength of 172 lb/in². In contrast, dimensional expansions of 8.3 to 40.6% occurred in compressed CaO-parafin and surrogate-parafin mixtures after three (3) days of exposure to laboratory conditions. The surface areas of selected samples were ~0.1 to 13 m²/g. The low surface areas will have the advantage of reducing moisture uptake and promote binding of the filtercake with polymeric materials such as parafin. Similar benefits can be obtained by removing the moisture by calcination prior to stabilization in polymeric binders.

This work has demonstrated that surrogate water softening sludge #5 at ORNL can be successfully stabilized by blending it with about 35% parafin and compacting the mixture at 8000 psi. The compressive strength of the waste form is sufficient for temporary storage of the waste while long-term storage waste forms are developed. Considering the remarkable similarity between the surrogate and the actual filtercake, the findings of this project should be useful for treating the sludge generated by the waste treatment facility at ORNL.

1.0 INTRODUCTION

The potential use of grout as a stabilization/solidification medium for hazardous and radioactive wastes has been extensively investigated by Bostick, Gilliam and co-workers (1-5). Bostick et al. (1) have shown that strong-base anion exchange resins derived from polyvinylpyridine are more effective in removing soluble pertechnetate ion (TcO_4^-) from aqueous solution than standard quaternary ammonium resins. They have also shown that the sorbed technetium forms a strong bond with the resin and can only be desorbed to an appreciable extent by very strong reagents such as perchloric acid. Solidification in grout has been suggested as a possible final waste form for the disposal of the spent resin. Similar studies on the application of ion-exchange resins and grout to nitrate ion disposal have been conducted by Morgan and Bostick (2). Addition of granulated blast furnace slag to portland cement has been shown to enhance the integrity of the solidified waste forms containing nitrogen.

It has also been shown that mixed low-level radioactive and hazardous wastes can be stabilized by solidification in cement-based grout. Hydrolyzable metals such as cadmium, lead, nickel and uranium have been shown to be effectively retained in grouts formulated from portland cement and fly-ash. However, the ability of the grouts to retain technetium is low due to the existence of the radioactive metal (^{99}Tc) as highly mobile pertechnetate anion. Significant improvement in the retention of technetium was achieved by addition of blast furnace slag to the grout. This enhancement has been attributed to the ability of the slag to reduce Tc(VII) to the less aqueous soluble Tc(IV) species. Cement-based waste forms have also been suggested as viable media for final disposal of sludge.

McDaniel et al (6) have shown that the leach rates of cesium-137 can be significantly reduced by the addition of various inorganic substances to the cement. It has been shown that incorporation of conasauga shale into cement reduced the Cs-137 release rates by almost three orders of magnitude after leaching in distilled water for 120 days. Indian red pottery clay reduced the leachability by about two orders of magnitude. Grundite also reduced Cs-137 extraction from the cement, although the effect was less than those for conasauga and pottery clay. The mechanism for the improved retention of cesium is attributed to ion-exchange and sorption to the inorganic media.

2.0 OBJECTIVES

The above discussion shows that there are several methods of treating radioactive wastes for disposal and the selected treatment option will depend on the nature of the waste. The main objective of this project is to evaluate treatment options for safe storage or disposal of water softening sludge (WSS # 5, filtercake) generated at ORNL. However, for safety, a nonradiological sludge that simulates WSS #5 sludge at ORNL was used in this project to help define and demonstrate several treatment options. The waste form performance undertaken included: water elimination, radionuclide stabilization, volume reduction relative to the reference surrogate material, leachability of nonradiological cesium (Cs) and strontium (Sr) from the waste forms prepared from the surrogate material and waste form compressive strength.

3.0 EXPERIMENTAL APPROACH

3.1 Preparation of WSS #5 Surrogate Sludge

Simulated ORNL water softening sludge No. 5 (WSS #5) was prepared from in-house precipitated CaCO_3 and other ingredients shown in Table 1:

Table 1. Composition of WSS #5 Surrogate Sludge

<u>Chemical used</u>	<u>Chemical Formula</u>	<u>Amount, g</u>	<u>Nominal Conc'n, %wt.</u>
Calcium carbonate	CaCO_3	240.5	63.3
Hematite	Fe_2O_3	20.85	5.5
Magnesium carbonate	MgCO_3	59.0	15.5
Aluminum hydroxide	$\text{Al}(\text{OH})_3$	11.8	3.1
Diatomaceous earth	SiO_2	48.0	12.6

Calcium carbonate, the major constituent of the filtercake, was prepared by slow addition of equimolar solution of sodium nitrate (NaNO_3) to calcium chloride (CaCl_2) solution. The pH of the slurry was checked periodically until the final pH was 8.9. The sample was then filtered and rinsed with five volumes of tapwater to remove the excess sodium chloride. The wet sample was then weighed and dried in an oven at about 100°C . The dry solids (380.2g) were blended and 234.5g of water was added to yield a wet filtercake (614.7 g) which contained 38.2 %wt. moisture. The water was spiked with 75 mg/L of strontium (using nonradiological $\text{Sr}(\text{NO}_3)_2$) to obtain 92 μg Sr/g of dry solids.

3.2 Thermal Analysis of the Sludge

The effects of thermal treatment on the surrogate waste was determined using a Seiko Thermogravimetric/Differential Thermal Analyzer (TG/DTA 320). Approximately 3.36 mg of the filtercake was placed in a platinum pan of the instrument and the sample was heated in ultra pure nitrogen to a maximum

temperature of $\sim 1200^{\circ}\text{C}$. A thermogram of the changes in the sample weight was obtained.

3.3 Waste Volume Reduction by Calcination

To determine the volume reduction of the calcium carbonate and the surrogate sludge as a result of heat treatment, samples of these materials were placed in a Coors ceramic boat and calcined at 850°C for 4 hours in a Lindbergh tube furnace with an Eurotherm 818S controller. A heating rate of $20^{\circ}\text{C}/\text{min.}$ was used to raise the temperature from $\sim 25^{\circ}\text{C}$ to 850°C . The samples were allowed to cool to 100°C and then removed from the furnace and cooled to room temperature in a dessicator. The initial weight of the calcium carbonate used was 1.2221g and the weight after the calcination was 0.6793g, giving a weight loss of 44.4%.

3.4 Compaction of the Calcined and Uncalcined Wastes

To further reduce the volume of the wastes, samples of the calcined and the uncalcined calcium oxide and the surrogate wastes were compressed at 4000, 6000 or 8000 psi for 10 minutes using a Buehler Specimen Mount Press. The effects of parafin addition on the strength of the compressed wastes were also studied. The weight of each sample before compression was 14.0 g. The dimensions of the cylindrical molds produced were measured shortly after the compaction and repeated for several days to determine the stability of the compressed wastes.

3.5 Compressive Strength Analysis

The compressive strengths of selected samples were determined by Quantachrome Corporation, Boynton Beach, Florida, using a Quantachrome Crush Strength Analyzer and the ASTM standard test procedure D4179. A copy of the analysis is attached. The samples were compressed diametrically since the compressed test samples were too large to fit into the instrument grips for the commonly applied axial crush strength tests.

3.6 Surface Area Measurements

The BET surface area of the calcined calcium carbonate was measured using nitrogen as the adsorbate and a Micromeritics Gemini 2360 Surface Area Analyzer. The surface areas were determined using five N₂ adsorption values.

4.0 RESULTS AND DISCUSSION

The results of the TGA studies are shown in Figure 1. The initial rapid weight loss (indicated by A) up to about 100°C is attributed to loss of moisture. Beyond this temperature, changes in the TGA profile are also noted at about 197, 347 and 637°C, as shown by B, C, and D, respectively. The slight weight loss around 200°C could be due to loss of water of hydration. The changes in the thermogram at 347°C and 637°C are ascribed to the decomposition of MgCO₃ and Al(OH)₃, respectively, and was confirmed by literature data (6,7). The total weight loss due to the thermal treatment to 1200°C was approximately 44 % and it is in good agreement with the value of 44.4% obtained when the sample was calcined at 850°C. This confirms the moisture content of the sample to be about 44%. Since the amount of water added to

the synthetic sludge constituted 38.2%, the difference in moisture content (i.e., 38 versus 44%) is attributed moisture in the starting materials used to prepare the surrogate waste. The thermogram for the CaCO_3 indicated that this sample decomposed at $\sim 900^\circ\text{C}$ and it is in agreement with the decomposition temperature of 898.6°C for calcium carbonate reported in the literature (6).

The compaction results and the dimensional changes of the molds after three days of exposure to atmospheric conditions are summarized in Table 2.

Table 2. Compaction and dimensional changes for the calcium oxide produced by calcination of calcium carbonate and the surrogate sludge.

<u>Waste</u>	<u>Parafin Added, % wt.</u>	<u>Compaction Pressure, psi</u>	<u>Dimensional Change, %.</u>
CaO	0	4000	31.3
CaO	0	6000	40.6
CaO	0	8000	15.6
CaO	15	8000	16.7
CaO	50	8000	25.0
Uncalcined Surrogate	15	8000	16.7
Calcined Surrogate	15	8000	8.3

The initial diameter of the CaO compressed at 4000 psi was 3.2 cm and the height was 1.2 cm. However, after 3 days, the diameter of the cylindrical mold expanded to

4.2 cm and it started to disintegrate. The diameters of the CaO samples that were pressed at 6000 and 8000 psi expanded from 3.2 cm to 4.5 and 3.7 cm, respectively after 3 days of exposure to laboratory conditions. Like the sample that was compressed at 4000 psi, the latter two samples were also unstable, although the specimen that was compressed at 8000 psi was slightly more stable. The diameters of the samples compressed at 4000, 6000 or 8000 psi expanded by 31.3, 40.6 and 15.6 %, respectively. After 3 days, the height of the uncalcined surrogate-15% parafin cylinder was 1.4 cm, while that of the calcined surrogate-15% parafin mold was 1.3 cm. These values represent expansions of 16.7 and 8.3 % , respectively. Compared to the parafin-based samples, more crumpling occurred in the parafin-free CaO after about one week of exposure to the atmosphere.

Addition of 35% parafin to the surrogate sludge increased the strength of the compacted material as shown in Tables 3. The stability of this sample was monitored for 39 days.

Table 3. Dimensions of the surrogate sludge containing 35% parafin compressed at 8000 psi.

<u>Time, Days</u>	<u>Diameter, cm</u>	<u>Height, cm</u>
0	3.2	1.50
14	3.2	1.50
21	3.2	1.55
28	3.2	1.55
35	3.2	1.55
39	3.2	1.55

As the results in Table 3 show, the dimensions of this sample were essentially constant within the time period investigated and indicates insignificant moisture uptake by the sample. However, a slight increase of 3% in the height of the sample was noted after 14 days of exposure to the laboratory environment.

The results provided in Table 4 show that the compressive strengths of the waste forms that were evaluated ranged from 49 to 172 lb/in². The data also show that the compressive strength increased with increase in the parafin content of the surrogate wastes.

Table 4. Compressive strengths of selected parafin-containing samples.

<u>Sample</u>	<u>Compressive Strength, (lbs/in²)</u>
15% parafin + calcined surrogate sludge compressed at 8000 psi.	49
35% parafin + calcined surrogate sludge compressed at 8000 psi.	172
15% parafin + calcined CaCO ₃ compressed at 8000 psi	139

The data in Table 5 show that the surface area of the calcined calcium carbonate is 0.1 m²/g. This value is much lower than that obtained for the calcined surrogate sludge which had a surface area of ~13 m²/g. Thus, it appears that the sludge constituents, other than the calcium carbonate, are primarily responsible for the observed surface area results. Due to problems with the surface area instrument which were later detected and rectified, the current results should be more valid than those (which were around 160 m²/g) reported earlier .

Table 5. Surface areas of the CaO and the calcined surrogate sludge.

<u>Sample</u>	<u>Surface Area, m²/g</u>
Calcined CaO	0.1
Calcined surrogate sludge	13.2

5.0 SUMMARY AND CONCLUSIONS

A synthetic sludge that simulates Water Softening Sludge #5 (WSS #5) at Oak Ridge National Laboratory has been successfully prepared and evaluated for its thermal behavior, volume reduction by calcination, stabilization, compressive strength properties and surface area. Thermogravimetric analysis of the filtercake resulted a weight loss of 44%, which occurred between 100 and 640°C. The weight reduction is attributed to loss of moisture and the decomposition of the surrogate constituents, primarily magnesium and calcium carbonates and aluminum hydroxide.

Compaction of the surrogate waste and the calcium oxide (produced by calcination of calcium carbonate) in the presence of parafin resulted in cylindrical molds with various degrees of stability. The most stable product was the calcined surrogate-35% parafin mixture that was compressed at 8000 psi. This sample expanded by 3% after 14 days and it also gave the highest compressive strength of 172 lb/in². In contrast, dimensional expansions of 8.3 to 40.6% occurred in compressed CaO-parafin and surrogate-parafin mixtures after three (3) days of exposure to laboratory conditions. The surface areas of selected samples were ~0.1 to 13 m²/g. The low surface areas will have the advantage of reducing moisture uptake and promote binding of the filtercake with polymeric materials such as parafin. Similar benefits can be obtained by removing the moisture by calcination of the sludge at temperatures around 640°C.

This work has successfully demonstrated that surrogate water softening sludge #5 at ORNL can be sufficiently stabilized by blending it with about 35% parafin and compacting the mixture at 8000 psi. The material has a compressive strength of about 172 lb/in² which is sufficient for temporary storage of the waste while long-term storage waste forms are sought. Since the composition of the surrogate sludge is

similar to that of the real filtercake at ORNL, the results of this project may be extrapolated to the real WSS #5 sludge.

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<Sample>
OAKRIDGE-FILCAK
3.364 mg
(3.364 mg)

<Reference>
EMPTY PT PAN
0.000 mg

<Comment>
FIRST RUN TEST

<Sampling>

0.5 sec

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<Gas>
N2 100.0 ml/min
0.0 ml/min

Seiko Instruments Inc.

Figure 6.1 Thermogravimetric analysis of surrogate filtercake (WSS #5).

Quantachrome Corp.
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January 8, 1996

Dr. Gautam Saha
Clark - Atlanta University
Box 325
Atlanta, GA 30314

Dear Gautam,

Here are the results from the samples you recently submitted to us for crush strength analyses. After our recent discussion, we applied diametral compression to the three samples. We also were able to apply a higher pressure on the samples than during the previous attempts. This means an upper limit of approximately 175 pounds of force, rather than the 135 pounds earlier. The results are:

Sample 1 -- 172 pounds -- 35% parafin + calcined ^{surrogate} sludge
Sample 2 -- 49 pounds -- 15% parafin + calcined ^{surrogate} sludge
Sample 4 -- 139 pounds -- 15% parafin + CaO

I have also enclosed a copy of a paper submitted to the American Ceramic Society Bulletin by Walker and Reed on the testing of pressed compacts. Their work was performed with our *Crush Strength Analyzer*. I hope that this will help you with your work.

I trust these results are to your satisfaction. If so, I think you will agree that the *Crush Strength Analyzer* will be a valuable tool for your laboratory. If I can be of further service, please call me at (407)-731-4999. Thank you for your consideration and continuing interest in Quantachrome Corporation.

Sincerely,

Mark Alper
Southeast Region Sales Manager