# Solidification Testing for an Oak Ridge National Laboratory Wastestream Using Grouts and Radiation Shielding Materials - 9379

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## ABSTRACT

This paper describes results for the solidification grout testing using a surrogate waste that simulates an Oak Ridge National Laboratory (ORNL) low-level radioactive aqueous wastestream. The low-level waste was generated at the Radiochemical Engineering Center (REDC) during several organic separation processes. Samples were generated at bench-scale using the REDC aqueous surrogate and Portland and ceramic cement with and without Gamma Guard I and Gamma Guard II radiation shielding materials. The radiation shielding materials chosen for this application were made up of newly patented, specially formulated materials from Science & Technology Applications, LLC. Column samples were also generated using the REDC aqueous surrogate and Portland cement with and without Gamma Guard I and Gamma Guard II. The 20.3 cm diameter column samples were designed to produce samples with the same height as a 208 L drum to determine if the dense radiation shielding materials could be evenly incorporated into the grouted wasteforms. The samples were made with and without the inclusion of the radiation shielding materials to determine the shielding material's effectiveness to attenuate gamma radiation. The samples were sent to ORNL for gamma bombardment and sliced samples of the solidified wasteforms were placed in front of a collimated cesium-137 (Cs-137) source, to measure the degree of gamma radiation attenuation. This paper presents the results of the testing.

## INTRODUCTION

The U.S. DOE tasked MSE to evaluate various sorbents and grouts to solidify the radioactive liquid organic and aqueous wastestreams from the REDC located at ORNL. REDC recovers and purifies heavy elements (berkelium, californium, einsteinium, and fermium) from irradiated targets for research and industrial applications. Both aqueous and organic wastestreams are discharged from REDC. Organic waste is generated from the plutonium/uranium extraction (PUREX), Cleanex, and Pubex processes. The PUREX waste derives from an organic-aqueous isotope separation process for plutonium and uranium fission products, the Cleanex waste derives from the removal of fission products and other impurities from the americium/curium product, and the Pubex waste is derived from the separation process of plutonium from dissolved targets. An aqueous wastestream is also produced from these organic REDC separation processes. MSE was tasked to test grouting formulations using a surrogate REDC aqueous formulation with and without radiation shielding materials.

ORNL provided MSE with a surrogate recipe for the aqueous waste generated during the organic aqueous separation processes. Surrogate and grout formulations with and without radiation shielding materials were tested at bench-scale and column scale. Grouted samples were sent to ORNL for radioactive bombardment after developing several grouting formulas.

## TEST OBJECTIVES

The project objective was to develop grouting formulations for the aqueous REDC surrogate that contained radiation shielding materials.

Specific objectives for the ORNL REDC aqueous surrogate grout testing and evaluation were:

- develop several grout formulations at bench scale using the aqueous surrogate for Portland and ceramic cements with and without the incorporation of radiation shielding materials;
- verify the absence/presence of free liquid by observing the solidified surrogate wasteforms at bench-scale;
- visually and by weight and volume measurements determine the bulk density of the surrogate wasteforms at bench scale;
- generate column samples at a selected grout formulation;
- visually and by weight and volume measurements determine the density distribution for the surrogate wasteforms at the column scale;
- bombard the surrogate wasteforms to determine the radiation shielding material's effectiveness to attenuate gamma radiation; and
- perform a cost analysis for each radiation shielding material at the selected column grout formulation.

## MATERIAL DESCRIPTIONS

### Surrogate Formulation

The recipe for the aqueous surrogate was provided by ORNL in 2006. The surrogate recipe is presented in Table I. Note that the addition and mixing of surrogate ingredients was conducted within the laboratory hood for small-scale testing and inside the walk-in laboratory hood for larger scale applications.

**Table I. REDC aqueous surrogate recipe.**

| Chemical Name | Molarity (M) |
|---|---|
| Sodium chloride ($NaCl$) | 0.071 |
| Sodium nitrate ($NaNO_3$) | 0.357 |
| Sodium hydroxide ($NaOH$) | 0.357 |
| Sodium carbonate ($NaCO_3$) | 0.238 |
| Sodium aluminate ($NaAlO_2$) | 0.040 |

### Grout Descriptions

Portland and ceramic cement were the grout materials used to generate the bench-scale samples using two different radiation shielding materials. Neat cement samples (samples without radiation shielding materials) were also generated for comparison with the shielded samples (samples containing the radiation shielding materials). During bench-scale testing, it was determined that Portland cement samples provided a better grout matrix to incorporate the dense radiation shielding materials and provided superior attenuation results. Therefore, no column samples were generated using the ceramic cement and this paper focuses on the grout testing performed with Portland cement.

### Radiation Shielding Material Descriptions

The radiation shielding materials chosen for application in this testing sequence are made up of newly patented, specially formulated materials from Science & Technology Applications, LLC called Gamma Guard I and Gamma Guard II. The radiation shielding materials were designed to attenuate gamma radiation from within the grouted wasteforms.

## BENCH-SCALE TESTING

The aqueous surrogate grout combinations were tested at bench scale to determine several weight-based waste-loading ratios (solid to surrogate) for each of the cement mixtures with and without radiation shielding materials. ORNL was concerned that the dense radioactive shielding material contained in the grout mixtures would settle during the curing period, causing an uneven distribution of the shielding materials within the grouted wasteforms. The bench-scale testing was designed to determine if the shielding materials were compatible with the surrogate grout mixtures and if they could be evenly incorporated into the grouted surrogate wasteforms. Bulk densities were determined during the bench-scale testing and then the samples were cut into two smaller sample sections: one from the top section of the sample and one from the bottom section. The bench-scale sample sections were then sent to ORNL for radioactive bombardment from a collimated cesium-137 (Cs-137) source to determine the samples ability to attenuate gamma radiation.

### Density Testing

Initial weight-based waste-loading ratios of 2:1, 2.5:1, 3:1, and 4:1 (total solids to surrogate) and weight-based loading ratios of 3:1, 4:1, and 5:1 (radiation shielding material to cement) were used during bench-scale testing for the Portland cement mixtures based on early small scale compatibility testing. The bench-scale samples were generated in square plastic gallon-sized containers and checked daily for the presence of free liquids and settling for a period of one week. The samples were then removed from the containers, checked visually for settling, and then weighed and measured to determine a bulk density for each of the samples.

Table II presents the sample ratios, the bulk density readings, and the volumetric increase after mixing the surrogate samples generated with Portland cement and the Gamma Guard I and Gamma Guard II shielding materials. The Gamma Guard I shielding material produced samples with a uniform density

**Table II. Bench-scale data collected during and after sample generation for Portland cement samples with and without Gamma Guard I and Gamma Guard II shielding materials.**

| Weight-Based Waste Loading Ratio (Total Solids to Surrogate) | Weight-Based Loading Ratio (Gamma Guard Formulation to Cement) | Volumetric Increase, (Final Volume /Surrogate Volume) | Measured Bulk Density (g/mL) |
|---|---|---|---|
| **Neat Grout Samples** | | | |
| 2:1 | NA | 1.72 | 1.81 |
| 2.5:1 | NA | 1.92 | 1.90 |
| 3:1 | NA | 2.14 | 1.98 |
| 4:1 | NA | 2.66 | 2.10 |
| **Gamma Guard I Samples** | | | |
| 2:1 | 5:1 | 1.58 | 2.13 |
| 2.5:1 | 3:1 | 1.63 | 2.27 |
| 3:1 | 3:1 | 1.75 | 2.43 |
| 4:1 | 3:1 | 2.01 | 2.63 |

| | | | |
|---|---|---|---|
| **Gamma Guard II Samples** | | | |
| 2:1 | 3:1 | 1.46 | 2.15 |
| 2.5:1 | 3:1 | 1.48 | 2.50 |
| 3:1 | 3:1 | 1.66 | 2.56 |
| 4:1 | 3:1 | 1.45 | 2.60 |
| **Gamma Guard II – Duplicate Samples** | | | |
| 2.5:1 | 3:1 | 1.47 | 2.59 |
| 4:1 | 3:1 | 1.45 | 2.94 |

NA=not applicable since no radiation shielding materials were added to the neat cement samples

distribution of shielding materials within the grouted wasteforms. The samples generated with the Gamma Guard II shielding material showed that settling had occurred in the samples during the curing time, and because of that, two duplicate Gamma Guard II bench-scale samples were generated. The duplicate samples were mixed using a different mixer, and the radiation shielding materials appeared to be evenly incorporated into the grouted matrix after the samples were removed from the containers. Notice the difference in density values for the duplicate samples compared to the initial Gamma Guard II samples. The duplicate samples have much higher density values than the initial samples because all of the Gamma Guard II shielding material was incorporated into the grouted wasteform.

The neat grouted samples showed the largest increase in volume when compared to the samples that contained the shielding materials. The Gamma Guard I samples had the second largest increase in volume, while the Gamma Guard II samples had the smallest volumetric increase.

**Radioactive Bombardment Testing**

After all of the volumes were calculated for the bench-scale samples, the samples were cut into two 4-inch by 4-inch by 1-inch samples and placed in specially made sample boxes and sent to ORNL for radioactive bombardment. Figure 1 shows the 3:1 waste-loading ratio with a 3:1 shielding material to cement ratio top and bottom REDC surrogate samples made with Gamma Guard I and Portland cement and the neat Portland cement sample. The samples were bombarded by placing them in front of a collimated Cs-137 source to determine the ability of the sample to attenuate gamma radiation. The bench-scale sample set was bombarded with the planned source strength of 50 roentgens per hour (R/hr). An empty samples box was bombarded to determine the actual radiation reading provided by the 50 R/hr source, and that value was 50.9 R/hr. Therefore, the percent attenuation for each sample was calculated using a radioactive source strength of 50.9 R/hr. The results from the ORNL gamma attenuation testing are presented in Table III.

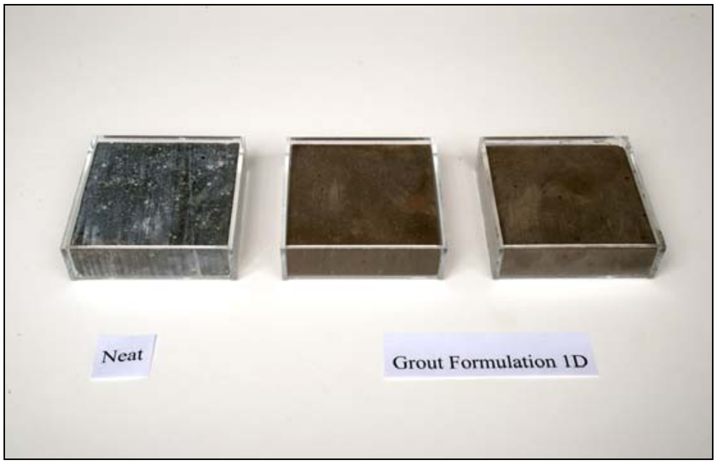


***Figure 1. Grouted samples generated using Gamma Guard I and Portland cement and the neat Portland cement sample.***

After examining the attenuation data values in Table III, it is apparent that Gamma Guard II is a superior radiation shielding product when compared to Gamma Guard I. The neat cement samples had percent attenuation values ranging from 25.2 to 26.1%, the Gamma Guard I samples had percent attenuation values ranging from 24.8 to 29.9% while the Gamma Guard II samples had percent attenuation values that ranged from 33.8 to 46.0%. When comparing the per cent attenuation for the 4:1 to 3:1 shielded samples compared to the corresponding neat sample, samples generated using the Gamma Guard I provided attenuation values that were 6 to 6.5% better than the neat sample and Gamma Guard II sample provided samples that were 20 to 26% better than the neat samples. The measured densities for the 4:1 to 3:1 Gamma Guard I sample was 2.63g/mL, and 2.60 and 2.94g/mL for the Gamma Guard II Portland cement formulations. Even though the measured bulk density value for the Gamma Guard I sample was slightly greater than the initial Gamma Guard II sample, the percent attenuation values for the Gamma Guard II samples were approximately 11 to 17% better than for the Gamma Guard I samples.

**Table III. Results for gamma attenuation testing.**

| Weight-Based Waste Loading Ratio (Total Solids to Surrogate) | Weight-Based Loading Ratio (Gamma Guard Formulation to Cement) | Sample Section or Neat Sample | Radiation Source Strength, R/hr | Radiation Reading, R/hr | Per Cent Attenuation for Each Grouted Sample | Per Cent Attenuation for the Shielded Samples Compared to the Neat Cement Sample |
|---|---|---|---|---|---|---|
| **Empty Sample Box** | | | **50** | **50.9** | | |
| **Gamma Guard I and Portland Cement** | | | | | | |
| 2:1 | 5:1 | Top | 50.9 | 38.1 | 25.2 | 0 |
| 2:1 | 5:1 | Bottom | 50.9 | 38.3 | 24.8 | -0.5 |
| 2:1 | NA | Neat | 50.9 | 38.1 | 25.2 | 0 |
| 2.5:1 | 3:1 | Top | 50.9 | 37.6 | 26.1 | 0.5 |
| 2.5:1 | 3:1 | Bottom | 50.9 | 37.2 | 26.9 | 1.6 |
| 2.5:1 | NA | Neat | 50.9 | 37.8 | 25.7 | 0 |
| 3:1 | 3:1 | Top | 50.9 | 37.4 | 26.5 | 0.5 |
| 3:1 | 3:1 | Bottom | 50.9 | 37 | 27.3 | 1.6 |
| 3:1 | NA | Neat | 50.9 | 37.6 | 26.1 | 0 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 4:1 | 3:1 | Top | 50.9 | 35.9 | 29.5 | 6.0 |
| 4:1 | 3:1 | Bottom | 50.9 | 35.7 | 29.9 | 6.5 |
| 4:1 | NA | Neat | 50.9 | 38.2 | 26.1 | 0 |
| **Gamma Guard II and Portland Cement** | | | | | | |
| 2:1 | 3:1 | Top | 50.9 | 33.7 | 33.8 | 11.6 |
| 2:1 | 3:1 | Bottom | 50.9 | 33.0 | 35.2 | 13.4 |
| 2:1 | NA | Neat | 50.9 | 38.1 | 25.2 | 0 |
| 2.5:1 | 3:1 | Top | 50.9 | 31.7 | 37.7 | 16.1 |
| 2.5:1 | 3:1 | Bottom | 50.9 | 31.2 | 38.7 | 17.5 |
| 2.5:1 | NA | Neat | 50.9 | 37.8 | 25.7 | 0 |
| 3:1 | 3:1 | Top | 50.9 | 30.7 | 39.8 | 18.4 |
| 3:1 | 3:1 | Bottom | 50.9 | 30.0 | 41.1 | 20.2 |
| 3:1 | NA | Neat | 50.9 | 37.6 | 26.1 | 0 |
| 4:1 | 3:1 | Top | 50.9 | 29.8 | 41.4 | 20.7 |
| 4:1 | 3:1 | Bottom | 50.9 | 28.7 | 43.6 | 23.7 |
| 4:1 | NA | Neat | 50.9 | 37.6 | 26.1 | 0 |
| **Gamma Guard II and Portland Cement – Duplicate Samples** | | | | | | |
| 2.5:1 | 3:1 | Top | 50.9 | 30.3 | 40.5 | 19.8 |
| 2.5:1 | 3:1 | Bottom | 50.9 | 30.7 | 39.7 | 18.8 |
| 2.5:1 | NA | Neat | 50.9 | 37.8 | 25.7 | 0 |
| 4:1 | 3:1 | Top | 50.9 | 27.9 | 45.2 | 25.8 |
| 4:1 | 3:1 | Bottom | 50.9 | 27.5 | 46.0 | 26.9 |
| 4:1 | NA | Neat | 50.9 | 37.6 | 26.1 | 0 |

NA=not applicable since the neat cement samples do not include shielding materials

After checking the initial Gamma Guard II attenuation values and the duplicate Gamma Guard II attenuation values, it is apparent that the mixing process not only affected the density values but the attenuation data as well. All of the initial Gamma Guard II samples have better attenuation results for the bottom sample sections than for the top sample sections showing that the initial Gamma Guard II samples did not get sufficient mixing to completely incorporate the dense shielding material. The duplicate sample set has top and bottom sample attenuation values that are within 0.8% of each other while the initial sample set has attenuation values that range from approximately 1% to 2.2%. After consulting with ORNL, it was decided to generate the column samples at the 3:1 total solid to surrogate ratio and a 3:1 radiation shielding material to cement ratio.

## Column Testing

The column samples were generated after calculating the volume necessary for a 20.3 cm diameter column that would represent the height of a 208 L drum sample. A column sample was generated using Portland cement with Gamma Guard I and Gamma Guard II at the 3:1 to 3:1 waste loading and shielding to cement ratios. The samples were mixed in 19 L buckets and poured into the columns to cure. Between 13 and 14 liters of grout were generated for each of the two column samples. After the grouted REDC surrogate was poured into the columns, a temperature probe was placed into the top of the sample to measure the temperature increase of the sample until a maximum value was reached. The initial temperature for the Gamma Guard I sample was 18.5 ºC and reached a maximum temperature of 19.0 ºC after 1 hour while the initial temperature for the Gamma Guard II sample was 17.2 ºC and reached a maximum temperature of 21ºC after 3 hours. Figure 2 shows the Gamma Guard II sample during generation.


**Figure 2. Gamma Guard II and Portland cement sample during the mixing process.**

After a 2-week curing period, the samples were removed from the columns and cut into four sections. Figure 3 shows the Gamma Guard II and Portland cement column sample being cut into sections. The sample sections were weighed and measured to determine the bulk density for each of the column sections. Table IV presents the sample ratios, the volumetric increase for each sample (surrogate volume/final sample volume), the measured sample section weights and volumes, and the bulk densities for each of the sample sections. Sample section #1 corresponds to the top sample section, and sample section #4 corresponds to the bottom sample section.

**Figure 3. Gamma Guard II and Portland cement column sample being cut into sections.**

The bulk density values for the Gamma Guard I Portland cement samples ranged from 2.10 to 2.13 g/mL with the densest sample located in sample section #3 one section above the bottom of the sample. The bulk density values for the Gamma Guard II Portland cement sample sections ranged from 2.84 to 2.93 g/mL with the densest samples located in sample sections #2 and #4. The bulk densities for the Gamma Guard I sample sections were within 0.03 g/mL and within 0.09 g/mL for the Gamma Guard II sample sections. The bulk density values show no significant density distribution fluctuations for the Gamma Guard I Portland cement sample sections. The gamma Guard II Portland cement sample section bulk densities do fluctuate more than the Gamma Guard I sample section densities but do not indicate substantial settling of the radioactive shielding materials within the grouted matrix.

After the sample sections were weighed and measured, they were cut into 4-inch by 4-inch by 1-inch samples and placed in specially made sample boxes for shipment to ORNL for radioactive bombardment. Figure 4 is a photograph of the REDC surrogate, Gamma Guard II, and Portland cement sample sections after being cut and placed in the sample boxes.

**Table IV. Volume increase and bulk density measurements for Gamma Guard I and II Portland cement column samples.**

| Weight-Based Waste Loading Ratio (Total Solids | Weight-Based Loading Ratio (Gamma Guard to Cement) | Volumetric Increase (Surrogate Volume/ Final Sample | Sample Section | Weight (g) | Volume (mL) | Bulk Density (g/mL) |
|---|---|---|---|---|---|---|

| to Surrogate) | | Volume) | | | | |
|---|---|---|---|---|---|---|
| **Gamma I and Portland Cement** | | | | | | |
| 3:1 | 3:1 | 1.77 | 1 | 4631.0 | 2200.8 | 2.10 |
| | | | 2 | 5498.0 | 2602.2 | 2.11 |
| | | | 3 | 6648.5 | 3127.5 | 2.13 |
| | | | 4 | 6035.4 | 2860.4 | 2.11 |
| **Gamma II and Portland Cement** | | | | | | |
| 3:1 | 3:1 | 1.43 | 1 | 8047.5 | 2837.9 | 2.84 |
| | | | 2 | 8226.5 | 2808.9 | 2.93 |
| | | | 3 | 8138.0 | 2837.9 | 2.88 |
| | | | 4 | 8822.5 | 3011.7 | 2.93 |

The samples were sent to ORNL for radioactive bombardment at the same time the bench-scale samples were sent and were bombarded using the same planned source strength of 50 R/hr as the bench-scale samples. Once again, an empty sample box was bombarded to determine the actual radiation reading value used to calculate the percent attenuation for each of the samples. The 50 R/hr planned radiation source gave a value of 50.9 R/hr and that value was used to calculate the percent attenuation values. Table V presents the attenuation results for the Gamma Guard I and Gamma Guard II Portland cement column samples.


**Figure 4. REDC surrogate, Gamma Guard II and Portland cement samples.**

The column attenuation results are consistent with the bench-scale attenuation results for the samples generated with Gamma Guard II and Portland cement. The attenuation results for the shielded samples when compared to the neat cement sample range from 22.1% to 22.9% for the Gamma Guard II column samples and from 2.7% to 2.9% for the Gamma Guard I column samples, indicating good mixing. The volumetric increase for the Gamma Guard II column samples was 1.43% while the volumetric increase for the Gamma Guard I column samples was 1.77%. The Gamma Guard II shielding material provided better attenuation results and produced a smaller wasteform, resulting in a superior product.

**Table V. Attenuation results for the Gamma Guard I and Gamma Guard II Portland cement column samples.**

| Weight- | Weight-Based | Sample | Radiation | Radiation | Percent | Percent |
|---|---|---|---|---|---|---|

| Based Waste Loading Ratio (Total Solids to Surrogate) | Loading Ratio (Gamma Guard Formulation to Cement) | Section | Source Strength (R/hr) | Reading (R/hr) | Attenuation for Each Sample Section | Attenuation for the Shielded Samples Compared to the Neat Cement Samples |
|---|---|---|---|---|---|---|
| **Gamma Guard I and Portland Cement** | | | | | | |
| 3:1 | 3:1 | Empty Box | 50 | 50.9 | | |
| | | 1 | 50.9 | 36.6 | 28.1 | 2.7 |
| | | 2 | 50.9 | 36.5 | 28.3 | 2.9 |
| | | 3 | 50.9 | 36.5 | 28.3 | 2.9 |
| | | 4 | 50.9 | 36.6 | 28.1 | 2.7 |
| | NA | Neat | 50.9 | 37.6 | 26.1 | 0 |
| **Gamma Guard 1I and Portland Cement** | | | | | | |
| 3:1 | 3:1 | Empty Box | 50 | 50.9 | | |
| | | 1 | 50.9 | 29.3 | 42.4 | 22.1 |
| | | 2 | 50.9 | 29.1 | 42.8 | 22.6 |
| | | 3 | 50.9 | 29.1 | 42.8 | 22.6 |
| | | 4 | 50.9 | 29.0 | 43.0 | 22.9 |
| | NA | Neat | 50.9 | 37.6 | 26.1 | 0 |

NA=not applicable since the samples are neat cement samples and do not contain shielding materials

## COST PROJECTIONS

The cost projections are based on the weight-based waste-loading ratio of 3:1 total solids to surrogate and the weight-based ratio of 3:1 Gamma Guard shielding material to Portland cement used during the column testing to solidify 100 gal of the aqueous surrogate waste. The costs were calculated based on a 200,000-pound purchase for the Gamma Guard I and Gamma Guard II products and on a 1-ton purchase for the Portland cement without freight charges. The cost projections are presented in Table VI.

**Table VI. Cost projections to solidify 100 gallons of aqueous surrogate waste.**

| Weight-Based Waste Loading Ratio (Total Solids to Surrogate) | Weight-Based Waste Loading Ratio (Gamma Guard Formulation to Cement) | Cost Projection ($/100 gal) | Final Wasteform Volume (gal) |
|---|---|---|---|
| **Gamma Guard I and Portland Cement** | | | |
| 3:1 | 3:1 | $6,784 | 177 |
| **Gamma Guard II and Portland Cement** | | | |
| 3:1 | 3:1 | $10,137 | 168 |

## CONCLUSIONS

The grout testing sequence proved that dense radiation shielding materials could be incorporated into a grout matrix of Portland cement. The bench-scale and column samples generated using the Gamma

Guard II shielding material produced superior attenuation results when compared to Gamma Guard I. As shown in Table III, the Gamma Guard II bench-scale samples at the 4:1 ratio of total solids to surrogate and 3:1 ratio of shielding material to cement attenuated gamma radiation approximately 20% better than the Gamma Guard I sample generated at the same ratios.

Column samples were generated using both Gamma Guard formulations to prove the shielding materials could be evenly incorporated into a grout matrix at a larger scale. The column samples were both generated at the 3:1 total solids to surrogate waste ratio and the 3:1 radiation shielding material to cement ratio. The column samples produced attenuation results comparable with the bench-scale samples with the Gamma Guard II samples, again attenuating the gamma radiation better than the Gamma Guard I samples by approximately 20%.

## RECOMMENDATIONS

MSE recommends the Gamma Guard II shielding material over Gamma Guard I to attenuate gamma radiation. However, the cost of the product is expensive when compared to the cost of radioactive shielding materials currently being used. MSE also recommends testing other radiation shielding materials to compare with the Gamma Guard II material in an attempt to identify less expensive products that may produce acceptable gamma attenuation results.

## ACKNOWLEDGEMENT

Work was conducted through the DOE Environmental Management Consolidated Business Center at the Western Environmental Technology Office under DOE Contract Number DE-AC09-96EW96405.