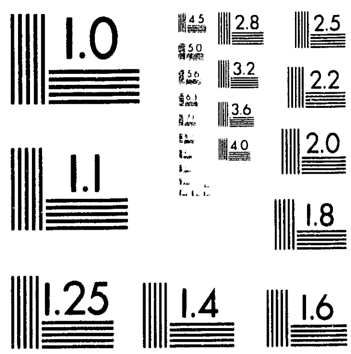
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CRITICAL PARAMETERS AND TCLP PERFORMANCE OF THE RFP MICROWAVE SOLIDIFICATION SYSTEM

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ABSTRACT: Two series of experiments were conducted at Rocky Flats Plant (RFP) to identify the critical operating parameters for microwave solidification and to evaluate the performance of the product against the EPA's Toxicity Characteristic Leach Procedure (TCLP). A surrogate hydroxide coprecipitation sludge spiked with heavy metals was used in the study. The RFP process uses microwave energy to heat and melt the waste into a vitreous final form that is suitable for land disposal. The results of the study indicate that waste loading and borax content in the glass forming frit are critical in the treatment of hydroxide sludge. Also, the product will easily satisfy EPA's limitations for land disposal. These results are very encouraging and support RFP's commitment to the use of microwave technology for treatment of various mixed waste streams at the facility.

KEY WORDS: solidification, microwave solidification, vitrification, hydroxide sludge, TCLP

INTRODUCTION

The Rocky Flats Plant (RFP) has been a major production

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facility in the Department of Energy's (DOE) nuclear weapons complex for over forty years. As such, it has generated, stored and treated a variety of hazardous and radioactive wastes during its functional history. Due to a rapidly changing regulatory environment, there currently exists a large inventory of waste in storage at RFP which cannot be shipped to a permanent internment facility. These materials do not meet Department of Transportation (DOT) shipping requirements nor do they meet the waste acceptance criteria (WAC) for disposal. The WAC typically requires that the waste form pass the Toxicity Characteristic Leach Procedure (TCLP) limitations as required by the Resource Conservation and Recovery Act (RCRA) for land disposal.

To relieve this waste storage situation, research and development engineers at RFP have developed an innovative technology for the treatment of homogeneous, inorganic, solid, mixed wastes. The RFP process uses microwave energy to heat and melt the waste into a vitreous final form that is suitable for land disposal. To verify that the final waste form meets these requirements and to establish preliminary estimates of the operating parameters for the process, wastes were processed through the microwave treatment system and the products analyzed using TCLP methods.

These tests were conducted in support of the process optimization efforts currently underway for the treatment of hydroxide sludge. This sludge is produced during a coprecipitation process in the liquid waste treatment facility and is dewatered using a vacuum drum filter which is precoated with a filter aid media. An experimental matrix was developed with the assistance of the RFP Statistical Applications group to identify the critical parameters for the treatment of this sludge, to provide a first estimate of their optimal value, and to evaluate the performance of the product against TCLP restrictions. This paper summarizes the results of these tests.

BACKGROUND

Microwave technology is not new to U.S. industry or the public. It has been used in the food and chemical industries since early 1970[1]. The majority of this work has been concentrated in the areas of food preparation and in the chemical industry. This familiarity promotes public acceptance and regulatory approval of the technology for production operations. In the area of radioactive materials processing, laboratory scale vitrification of calcined high-level nuclear wastes using microwave energy was done by the Idaho National Engineering Laboratory in 1979. Significant work with solidification of sludges has been performed at the

Rocky Flats Plant since 1986. Currently, a surrogate hydroxide coprecipitation sludge is successfully being processed using a full scale demonstration system. Other wastes that passed preliminary screening tests using a bench scale system include fluidized bed incinerator (FBI) ashes, nitrate salts, and soils. The FBI ashes contain chromium oxide catalyst and ash from shredded high efficiency particulate air filters. Nitrate salts were solidified by heating them to their melting points forming a salt cake[2]. The soils were collected from areas surrounding the RFP development laboratory.

The Japanese have actually implemented microwave technology into radioactive process operation. They have developed a high temperature technology for converting plutonium nitrate, recovered from spent fuel reprocessing, to plutonium oxide for nuclear fuel. Additionally, they are using the technology for solidifying ash from radioactive waste incinerators.

FIRST EXPERIMENTAL SERIES

Procedure

Surrogate wastes were produced to simulate the bulk physical and chemical properties of the hydroxide coprecipitation sludge from the RFP liquid waste treatment facilities and were processed through a bench scale microwave system. The sludge had a per batch composition of 967 g $CaSO_4x2H_2O$, 777 g $Fe(OH)_3$, 317 g $Mg(OH)_2$, 237 g $NaNO_3$, and 207 g diatomaceous earth (filter aid). The sludge was spiked with EPA regulated heavy metals at elevated levels (Table 1) to evaluate the impact of various operational parameters on the TCLP leach resistance of the final waste form. The metals selected for the spike were based on process knowledge and characterization of the sludge waste.

TABLE 1 -- Metal concentrations in surrogate and actual sludges, ppm

	Surrogate Sludge	Actual Sludge
Chromium	500	54 to 481
Nickel	500	no data
Lead	500	29 to 250
Cadmium	500	4.6 to 13.0
Silver	500	56 to 189

The following operating parameters were controlled during the experimental test runs:

- Frit Composition (B/D) -- weight percent ratio of borax (B) to diatomaceous earth (D) in the frit feed.
- Waste Loading (S/F) -- weight percent ratio of waste sludge (S) surrogate to the frit (F) fed to the melt chamber.
- Temperature (°C) -- measured with an infrared thermometer or a thermocouple.
- Quench rate -- the relative speed at which the temperature of the molten material is reduced after processing.

Minimum, nominal, and maximum values for each of the operating parameters were selected. A statistical design of experiment matrix was generated specifying the values of the various operational parameters the first series of test runs. An L_{16} orthogonal array was used, placing operating parameters in columns 1, 2, 4, and 8, while centering values were placed in the 4.5 and 12.5 row locations (Table 2).

TABLE 2 -- Test matrix for microwave solidification of surrogate hydroxide coprecipitation sludge

Run No.	Frit Comp B/D	Waste Load S/F	Temperature °C	Quench Rate
1	20/80	25/75	950	slow
2	20/80	25/75	950	fast
3	20/80	25/75	1200	slow
4	20/80	25/75	1200	fast
4.5	30/70	50/50	1075	medium
5	20/80	75/25	950	slow
6	20/80	75/25	950	fast
7	20/80	75/25	1200	slow
8	20/80	75/25	1200	fast
9	40/60	25/75	950	slow
10	40/60	25/75	950	fast
11	40/60	25/75	1200	slow
12	40/60	25/75	1200	fast
12.5	30/70	50/50	1075	medium
13	40/60	75/25	950	slow
14	40/60	75/25	950	fast
15	40/60	75/25	1200	slow
16	40/60	75/25	1200	fast

The final waste forms produced from these test runs were prepared for TCLP analyses according to EPA protocols. The solidified material was removed from the melting container and fractured using a hammer and chisel to collect a representative sample. The particle size of the samples was further reduced by placing the samples in a vice and applying pressure, thereby fracturing the samples. This preparation method was intended to reduce the amount of fine particles generated during the size reduction operation. The fines generated during the sampling and preparation operations were collected and measured to determine the weight percentage of fines.

When preparing the final 50 g subsample for extraction, the proper percentage of fines was included. According to the pH testing procedure, TCLP Fluid #1 was determined to be the proper extraction fluid for all of the samples. The 50 g subsamples were extracted and filtered as required by the TCLP protocol. The resulting leachates were digested and analyzed for the spiked metals using a Leeman Labs Plasma Spec inductively coupled plasma atomic emission spectrophotometer.

Results and Discussion

The results of the TCLP analyses for the first experimental series are given below (Table 3). Averages of the results for high and low values for each of the operating parameters are also given below (Table 4). By comparing the averages in Table 4, an assessment can be made as to which operating parameters have the greatest impact on the TCLP leachability of the final waste form.

Evaluating the data indicates that waste loading was the most critical operating parameter impacting the TCLP results. In every case, the leach results increased as the waste loading increased. Also, the magnitude of the impact for this operating parameter was greater than for any other. This result is not surprising since greater waste loading results in higher metal concentration in the final waste form and greater metal availability for dissolution. However, high waste loading is a very desirable characteristic for the final waste form due to its favorable impact on process economics. Obviously, this operating parameter is critical and must be fully optimized.

TABLE 3 -- TCLP results from microwave solidified surrogate hydroxide coprecipitation sludge, ppm

Run No.	Chromium	Nickel	Lead	Cadmium	Silver
1	0.070	0.046	0.030	0.150	ND
2	0.059	0.045	0.047	0.109	0.003
3	0.053	0.043	ND	0.092	ND
4	0.055	0.049	0.105	0.147	ND
4.5	0.072	0.039	0.219	0.339	ND
5	0.034	0.075	1.23	2.18	0.011
6	0.036	0.146	1.30	2.74	0.309
7	0.055	0.063	1.02	2.15	0.003
8	0.021	0.144	1.39	3.52	0.062
9	0.072	0.132	0.122	1.64	ND
10	0.049	0.105	0.058	0.470	0.022
11	0.044	0.106	0.070	0.295	0.015
12	0.054	0.100	0.007	0.228	0.037
12.5	0.044	0.105	0.284	1.06	0.205
13	0.380	0.173	0.059	1.63	0.135
14	0.273	0.376	1.63	3.92	0.150
15	0.054	0.277	1.61	4.52	0.202
16	ND	0.127	0.182	3.81	0.112

ND -- Not Detected.

A slight response was observed for frit composition. Higher borax concentration in the frit composition resulted in higher TCLP leachability. Borax is a constituent in the glass forming frit added to the sludge before microwave processing. It modifies the melt during the process, thereby lowering the melting temperature of the waste mixture. This is an important operating consideration. Since the process is being conducted in-drum (ie., the waste container), high temperatures could result in failure of the drum. However, as these results show, increasing the borax concentration to lower the melting temperature can lead to undesirable leachability of the final waste form. Again, this operating parameter must be fully optimized for microwave processing.

TABLE 4 -- Impact of operating parameter on TCLP results for microwave solidified surrogate sludge, ppm

Operating Parameter	Chromium	Nickel	Lead	Cadmium	Silver
Frit Comp, B/D					
20/80	0.048	0.076	0.640	1.39	0.049
30/70	0.058	0.072	0.251	0.700	0.103
40/60	0.116	0.175	0.467	2.06	0.084
Waste Load, S/F					
25/75	0.057	0.078	0.055	0.391	0.009
50/50	0.058	0.072	0.251	0.700	0.103
75/25	0.107	0.173	1.05	3.06	0.123
Temperature, °C					
950	0.123	0.137	0.560	1.60	0.079
1075	0.058	0.072	0.251	0.700	0.103
1200	0.042	0.114	0.548	1.85	0.054
Quench Rate					
slow	0.095	0.114	0.518	1.58	0.046
medium	0.058	0.072	0.251	0.700	0.103
fast	0.068	0.137	0.590	1.87	0.087

Temperature and quench rate did not appear to impact significantly the TCLP leachability of the final waste form. Therefore, it is not critical to optimize these operating parameters.

SECOND EXPERIMENTAL TEST SERIES

A second series of experimental tests was conducted. Using the information obtained from the first series, these tests were constructed with a two-fold purpose; (1) to provide a preliminary estimate of the optimum levels for the critical operating parameters, and (2) to confirm TCLP performance of the microwave product using surrogates spiked with heavy metals at levels anticipated in the actual waste stream.

Procedure

The surrogate for the second series was produced in the same manner as that used in the first series. However, the spike formulation was selected to correlate with levels obtained from actual waste characterization data (Table 5).

TABLE 5 -- Metal concentrations for surrogate sludge in the second experimental series, ppm

Chromium	500
Nickel	100
Lead	250
Cadmium	15
Silver	200

Based on the results of the first experimental series, only frit composition (B/D) and waste loading (S/F) was considered in this experimental series. Bounding levels for these parameters were selected as indicated by the results from first series and an experimental test matrix was generated for two variables at three levels. In this case, an L_9 orthogonal array was used, placing the variables in columns 1 and 2. This type of design provides information on curvature of the response surface for the parameters (Table 6).

TABLE 6 -- Test matrix for second experimental series

Run No.	Frit Comp B/D	Waste Load S/F
1	5/95	25/75
2	5/95	40/60
3	5/95	55/45
4	15/85	25/75
5	15/85	40/60
6	15/85	55/45
7	25/75	25/75
8	25/75	40/60
9	25/75	55/45

Since operating temperature was identified as being non-critical, a target of 1200°C was selected for this series of tests. Similarly, the slow quench rate method was used for cooling the products. Surrogates wastes were mixed with glass formers and processed in the bench-scale microwave system according to the matrix in Table 6. After processing, the samples were recovered from the melting container and subjected to TCLP analyses as previously discussed.

Results and Discussion

The results from the second experimental test series are contained in the table below (Table 7). The EPA Constituent Concentrations in Waste Extract limits for land disposal are listed at the bottom of the table. Examining Table 7 it is apparent that all samples produced TCLP results that were below the limits for land disposal.

TABLE 7 -- TCLP results from second experimental series, ppm

Run No.	Chromium	Nickel	Lead	Cadmium	Silver
1	0.030	0.015	0	0.015	0
2	0.051	0.043	0.05	0.015	0
3	0.045	0.032	0.05	0.015	0
4	0.035	0.015	0	0.015	0
5	0.015	0.015	0.13	0.038	0.05
6	0.030	0.015	0.05	0.042	0.05
7	0.043	0.030	0.05	0.015	0
8	0.054	0.061	0.14	0.038	0.05
9	0.015	0.015	0.05	0.060	0.05
Limits EPA, F006	5.2	0.32	0.51	0.066	0.072

The results from corresponding operating conditions were averaged and tabulated (Table 8). The curvature of the response surfaces indicate that for chromium and nickel 15% borax in the glass former formulation yields lower leachability in the product. However, for lead, cadmium, and silver, the 5% borax content produced a better product.

TABLE 8 -- Impact of operating parameter on TCLP results for second experimental series, ppm

Operating Parameter	Chromium	Nickel	Lead	Cadmium	Silver
Frit Comp, B/D					
5/95	0.042	0.030	0.03	0.015	0.00
15/85	0.027	0.015	0.06	0.032	0.03
25/75	0.037	0.035	0.08	0.038	0.03
Waste Load, S/F					
25/75	0.036	0.020	0.02	0.015	0.00
40/60	0.040	0.040	0.11	0.030	0.03
55/45	0.030	0.021	0.05	0.039	0.03

In terms of waste loading, the results indicate that chromium, nickel, and lead are leached at lower levels at either <u>low or high</u> waste load percentages. These results appear to contradict the results from the first test series which indicated that high waste loading produces high leachability. These results are most likely due to the low spike levels in the surrogate materials. This in turn produced low concentrations in the TCLP extract solutions which were very near the instrument detection limits. This situation can introduce large uncertainties in the results. However, this is not entirely detrimental to the study. Low concentration in the TCLP extract is the objective of the treatment process. It appears that waste loading as high as 55% will produce a product that meets the limitations of the RCRA land disposal restrictions.

CONCLUSIONS

The results from the first experimental series indicate that the critical operating parameters for the microwave solidification process are waste loading and borax concentration in the glass forming frit. Temperature and quench rate do not effect the leach resistance of the product. This simplifies optimization of process and development of control algorithms for production operations.

The second experimental series confirmed the robust nature of the microwave solidified product. Eventhough the operating parameters and feed compositions were varied significantly over a wide range of values, the product from the microwave treatment process was not significantly impacted. It satisfied the EPA's restrictions for land disposal under all circumstances.

These results are very encouraging and support the view that the microwave solidified waste form is highly desirable for the hydroxide precipitation sludge.

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