Vitrification of Simulated Radioactive Rocky Flats Plutonium Containing Ash Residue with a Stir Melter System

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OCT 04 1996

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A document prepared for TECHNICAL SOCIETY PUBLICATION - AMERICAN CERAMIC SOCIETY - CERAMIC TRANSACTIONS SERIES at , , from ? - ?.

DOE Contract No. DE-AC09-89SR18035

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VITRIFICATION OF SIMULATED RADIOACTIVE ROCKY FLATS PLUTONIUM CONTAINING ASH RESIDUE WITH A STIR-MELTER SYSTEM

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ABSTRACT

A demonstration trial has been completed in which a simulated Rocky Flats ash consisting of an industrial fly-ash material doped with cerium oxide was vitrified in an alloy tank Stir-Melter™ System. The cerium oxide served as a substitute for plutonium oxide present in the actual Rocky Flats residue stream. The glass developed falls within the $\text{SiO}_2 + \text{Al}_2\text{O}_3 / \Sigma\text{Alkali} / \text{B}_2\text{O}_3$ system. The glass batch contained approximately 40 wt % of ash, the ash was modified to contain ~ 5 wt % CeO_2 to simulate plutonium chemistry in the glass. The ash simulant was mixed with water and fed to the Stir-Melter as a slurry with a 60 wt % water to 40 wt % solids ratio. Glass melting temperature was maintained at approximately 1050°C during the melting trials. Melting rates as functions of impeller speed and slurry feed rate were determined. An optimal melting rate was established through a series of evolutionary variations of the control variables' settings. The optimal melting rate condition was used for a continuous six hour steady state run of the vitrification system. Glass mass flow rates out of the melter were measured and correlated with the slurry feed mass flow. Melter off-gas was sampled for particulate and volatile species over a period of four hours during the steady state run. Glass composition and durability studies were run on samples collected during the steady state run.

INTRODUCTION

A significant need exists to develop viable methods of immobilizing radioactive residues which contain quantities of plutonium oxide. Vitrification of the residues into a stable leach resistant glass provides a very durable method of immobilization. A team effort incorporating the expertise of three groups has successfully demonstrated the manner in which a vitrification program can be established through surrogate waste glass development, vitrification system operation, and technical analyses of the demonstrated process output streams.

VITRIFICATION DEMONSTRATION TEAM

Three independent groups teamed together to complete the vitrification demonstration. The team members were Stir-Melter, Inc., Westinghouse Savannah River Co., and Clemson Environmental

Systems Engineering. Stir-Melter, Inc. provided the operating prototype vitrification system and project coordination, Westinghouse Savannah River Co. identified the simulated "waste stream" and developed the waste glass composition, and Clemson Environmental Systems Engineering supplied the blended dry "waste stream" demonstration batch materials and directed the demonstration vitrification process off-gas analysis.

SIMULATED "WASTE STREAM"

An industrial fly-ash material was identified as being chemically and physically similar to the ash held at DOE-Rocky Flats less the radioactive plutonium oxide component. The oxide components of the industrial fly-ash are shown in Table I as the WASTE OXIDE combined with the addition of the required CeO_2 content to form the simulated "waste oxide" composition. A total of ~5 wt% CeO_2 was added to the industrial fly-ash to serve as the plutonium oxide surrogate.

Table I. Oxide Compositions, Components of "Fly-Ash 6" Glass

GLASS ID =	FLY ASH - 6		
FRIT WT%	60		
WASTE WT%	40		
ELEMENT	FRIT	WASTE	GLASS
OXIDE	OXIDE wt%	OXIDE wt%	OXIDE wt%
Al/ Al_2O_3		25.72	10.28
B/ B_2O_3	25.00		15.00
Ca/ CaO		1.84	0.74
Cr/ Cr_2O_3			
Cs/ Cs_2O			
Fe/ Fe_2O_3		12.28	4.91
K/ K_2O		1.71	0.68
Li/ Li_2O			
Mg/ MgO		0.76	0.30
Mn/ MnO_2			
Ti/ TiO_2		1.45	0.58
Na/ NaCl			
Ce/ CeO_2		4.50	1.80
Na/ NaI			
Na/ Na_2O	33.00	0.33	19.39
P/ P_2O_5		0.44	0.18
S/ SO_3		1.44	0.58
Si/ SiO_2	42.00	49.36	44.94
Sr/ SrO		0.18	0.07
Zr/ ZrO_2			
SUMS	100.00	100.01	100.00

WASTE GLASS DEVELOPMENT

A group of glasses was developed to incorporate the "waste stream" into their compositions. The several compositions developed fell in the $\text{SiO}_2 + \text{Al}_2\text{O}_3 / \Sigma \text{Alkali} / \text{B}_2\text{O}_3$ system as shown in Figure I. Variations in the level of fly-ash surrogate were made over a 35%-50% wt% range. PCT tests were run on the glasses of the crucible studies with acceptable results compared to the HLW benchmark environmental assessment glass (EA-glass).

Figure I. Ternary Plot Showing the Developed Waste Glasses

Figure I. Ternary Plot Showing the Developed Waste Glasses

A single glass composition from the crucible study was selected to serve as the material to be evaluated in the vitrification process study; it had an ash loading of 40 wt% in its batch composition. The selected glass is shown in Table I as "FLY ASH - 6," with its oxide composition listed along with the frit oxide and waste oxide components blended to obtain the glass. The PCT test results for "FLY ASH - 6" crucible samples are shown in Table II. Toxicity Characteristic Leaching Procedure (TCLP) tests have shown that leaching of hazardous metals in the glasses developed are below regulatory limits.

Table II. Comparative PCT Test Results for Crucible Samples

PCT Releases, Surrogate Rocky Flats Ash Glasses			
Glass	Normalized Release (g/L)		
	Na	Si	B
Comp. 2	2.07	0.23	2.89
Comp. 1	1.06	0.28	1.06
EA Glass	13.35	3.92	16.70

Approximately 200 kg (~440 lb_m) dry batch material was prepared for the demonstration vitrification run. The industrial fly-ash was blended with cerium carbonate to provide the equivalent of ~5 wt% cerium oxide which served as the surrogate for plutonium oxide in the Rocky Flats ash. The fly-ash blend provided 40 wt% of the total waste glass composition. The

remaining components of the batch, borax, soda ash, and silica were blended with the fly-ash to develop the glass described in Table I as the GLASS OXIDE.

STIR-MELTER VITRIFICATION SYSTEM

Stir-Melter, Inc. lab facility's alloy A-0.5 joule-heated, double wall, melter system¹ was used for the vitrification demonstration. The melter was connected to an operating off-gas collection system which consisted of a water spray packed cooling column, 65% ASHRAE filter, 95% ASHRAE bag filter, and 99.9% HEPA filter. A 190 liter (50 gallon) slurry maintenance and pumping system was used to mix and deliver the demonstration feed material.

The Stir-Melter System had a 0.05 m^2 (0.5 ft^2) melter area Inconel 601 melting vessel which had an approximate constant working volume of 0.01 m^3 (0.36 ft^3) with a bottom fed overflow U-tube delivery spout for the glass product. An Inconel 690 impeller served as the AC electrode with the vessel maintained at ground potential. Impeller speed was controllable from 0-500 rpm and the impeller height could be controlled within the working volume of the vessel. Joule-heating power available to the unit was 10 KVA, auxiliary resistance heating power was 3 KVA, and impeller drive power was 1 KVA. The melter system operated at a temperature of 1050°C . The melter had a slurry feed port, a dry material feed port, an off-gas port, and a video/photo port available for process operation and monitoring.

VITRIFICATION DEMONSTRATION PREPARATION

Dry batch material received from Clemson Environmental Systems Engineering was charged into the drained, hot, Stir-Melter system to provide the initial glass volume required for the start of the joule-heating process. Sufficient dry batch was introduced to the melter to achieve its fixed constant working volume of glass. The initial batch charge was melted with heat supplied by the auxiliary heaters.

A water based slurry of the supplied batch was prepared. The slurry was mixed to provide a 60 wt% water to 40 wt% solids ratio for feeding directly into the operating Stir-Melter system. A water cooled slurry feed tube served to introduce the slurry into the melter. A calibrated peristaltic pump controlled the slurry mass flow feed rate to the melter.

The details of the off-gas sampling requirements were specified by Clemson Environmental Systems Engineering. An outside vendor was contracted to provide the off-gas sampling and analysis service during the continuous run portion of the demonstration.

VITRIFICATION RATE OPTIMIZATION

A designed experimental matrix of slurry feed rate and impeller speed provided the basis for investigation of the optimal slurry feed rate to the Stir-Melter system. Each set of operating conditions was maintained for 30 minutes, which was sufficient time for the verification of process mass flow equilibrium based upon slurry input, solids content, ignition loss, and glass output. Following the completion of the experimental matrix design, a series of evolutionary feed rate and impeller settings were investigated to determine the optimal settings to yield the

maximum glass output rate for the steady state vitrification demonstration. The results of the study showed optimal vitrification of the "waste stream" for the following conditions.

- Slurry feed rate of 6.25 kg/hr
- Melter temperature of 1050°C
- Impeller speed of 350 rpm
- Glass output rate of 2.5 kg/hr

CONTINUOUS VITRIFICATION DEMONSTRATION

A six (6) hour continuous vitrification demonstration run was completed. The Stir-Melter system was set to control its operational set points at a melting temperature of 1050°C and an impeller speed of 350 rpm. The slurry feed system was set for an input rate of 6.25 kg/hr. The off-gas system was set to maintain a -0.025 kiloPascal (-0.1 in.wc.) head space pressure above the melt surface within the alloy tank to assure extraction of the generated steam and off-gas species from the process. The slurry feed composition for the demonstration is shown in Table III as SL-FEED CA-1, -2. The dry batch materials used to form the slurry are shown in Table III as DR-FEED CA-1, -2. The solids content of the slurry were analyzed and are shown in Table IV.

Table III. Feed Material Analyses

Feed Composition (wt %)					
Oxide	Target	SL-FEED CA-1	SL-FEED CA-2	DR-FEED CA-1	DR-FEED CA-2
SiO ₂	44.94	41.18	40.95	39.03	40.19
Na ₂ O	19.93	19.43	17.14	16.48	17.03
Al ₂ O ₃	10.29	8.11	8.17	8.40	8.42
B ₂ O ₃	15.00	10.46	9.44	9.02	7.62
CeO ₂	1.80	1.11	0.98	0.80	0.68
CaO	0.74	0.69	0.73	0.60	0.63
Fe ₂ O ₃	4.91	3.66	7.69	4.01	4.17
K ₂ O	0.68	0.59	0.65	0.61	0.57
TiO ₂	0.58	0.49	0.50	0.51	0.54
P ₂ O ₅	0.18	0.20	0.24	0.23	0.26
SrO ₂	0.07	0.06	0.06	0.06	0.06
Cr ₂ O ₃	0.00	0.12	0.05	0.02	0.20
Li ₂ O	0.00	0.03	0.04	0.02	0.03
MgO	0.30	0.25	0.26	0.26	0.26
SO ₃	0.58	n/a	n/a	n/a	n/a
TOTAL	100.00	86.38	86.90	80.05	80.66

n/a = not analyzed

Low silica, alumina and ceria numbers may be attributable to difficulties in dissolving the ash feed (i.e. silica, cerium carbonate, etc) when analyzing.

Table IV. Solids Loading in Slurry Feed Samples

<u>Microwave Drying Results</u>			
Wt % Solids			
<u>Sample</u>	<u>Test 1</u>	<u>Test 2</u>	<u>Test 3</u>
SOL-1	40.68	41.48	41.72
SOL-2	39.58	40.06	39.87

Glass output mass flow samples were taken at 15 minute intervals throughout the demonstration period. The glass samples collected also served as analysis specimens for chemical analysis, PCT, crystallinity and homogeneity tests. One hour into the run after assured steady state operation had been established, a four hour period of operation for off-gas sampling was maintained. The samples were collected from the off-gas line approximately 1.5 meters from the melt surface. Additionally, stack samples were taken from the off-gas system at a location downstream of the HEPA filter at the building exhaust stack. The vitrification process continued an additional hour following the off-gas sampling period to complete the six hour demonstration. The dynamics of the melt surface, slurry introduction, impeller draw-down of the slurry, and off-gas generation from within the melt were documented with video recordings and still photos during the demonstration.

ANALYSES RESULTS OF COLLECTED DEMONSTRATION GLASSES

The glass samples collected during the course of the demonstration were submitted for analyses by WSRC laboratories. A complete set of analyses was requested to verify the glass chemical composition, crystallinity, homogeneity and PCT qualities.

PCT ANALYSES OF DEMONSTRATION GLASSES

Seven day PCT tests were completed on the demonstration glasses collected during the test run. Results of the tests are shown in Table V. for two sampling periods RF-2, -4 and are compared to the "EA Glass."

Table V. Comparative PCT Test Results for Demonstration Samples

<u>PCT Releases Surrogate Rocky Flats Ash</u>			
<u>Demonstration Glasses</u>			
Normalized Release (g/L)			
<u>Glass</u>	<u>Na</u>	<u>Si</u>	<u>B</u>
RF-2	3.48	0.48	2.75
RF-4	3.73	0.48	2.96
EA Glass	13.35	3.92	16.70

XRD ANALYSES

X-Ray Diffraction analyses of the samples collected during the demonstration run show that the output of the melter was all amorphous material. The action of the impeller in combination with

the melting temperature of 1050°C provided a well melted and blended output glass from a slurry feed of the batch blend. The results are shown in Figure II.

Figure II. Typical X-Ray Diffraction Analyses of Sampled Demonstration Glass

GLASS CHEMICAL ANALYSES

Chemical analyses of the samples collected during the demonstration run were completed. Five (5) samples of glass output taken during the demonstration yielded a set of results which show close correspondence with the target glass composition. The variation of composition generated during the run was quite small as seen by the several sets of analyses results. The results are shown in Table VI, as CA-1, -2, ..., -5.

Table VI. Chemical Analyses of Collected Demonstration Process Glass Samples

Oxide	Target	AVG. CA-1 to CA-5	STDEV	CA-1	CA-2	CA-3	CA-4	CA-5
SiO ₂	44.94	47.43	0.23	47.57	47.19	47.17	47.57	47.63
Na ₂ O	19.93	19.48	1.59	22.04	19.98	18.30	18.75	18.31
Al ₂ O ₃	10.29	8.52	0.51	9.03	8.21	9.10	8.00	8.28
B ₂ O ₃	15.00	12.56	0.06	12.66	12.49	12.55	12.56	12.54
CeO ₂	1.80	1.35	0.18	1.47	1.30	1.61	1.22	1.17
CaO	0.74	0.76	0.05	0.72	0.72	0.76	0.78	0.83
Fe ₂ O ₃	4.91	4.61	0.22	4.93	4.60	4.70	4.39	4.44
K ₂ O	0.68	0.80	0.02	0.78	0.84	0.79	0.81	0.79
TiO ₂	0.58	0.57	0.01	0.58	0.56	0.57	0.56	0.57
P ₂ O ₅	0.18	0.09	0.01	0.10	0.10	0.09	0.09	0.08
SnO	0.07	0.06	0.00	0.06	0.06	0.06	0.06	0.06
Cr ₂ O ₃	0.00	0.21	0.02	0.24	0.22	0.21	0.20	0.19
Li ₂ O	0.00	0.22	0.03	0.26	0.23	0.22	0.20	0.18
MgO	0.30	0.40	0.01	0.42	0.39	0.39	0.39	0.39
SO ₃	0.58			n/a	n/a	n/a	n/a	n/a
Total	100.00	97.06	2.21	100.86	96.89	96.52	95.58	95.46

n/a = not analyzed

OFF-GAS ANALYSES RESULTS OF DEMONSTRATION RUN

The analyses of the off-gas constituents are still in progress at the outside vendor as the paper is being prepared for publication.

CONCLUSION

A cooperative multidisciplinary team approach to the development of waste stream vitrification processes has been shown to be effective in terms of waste glass definition, prototypical vitrification process demonstration, and analysis of the results of the vitrification process. Rapid generation of successful surrogate technology demonstrations is possible. Direct application of the demonstrated technology package to the actual radioactive waste stream provides a sound base for the establishment of working vitrification facilities.

REFERENCES

¹Kormanyos, Kenneth R. and Cox, Stephen F., "A Double Wall Alloy Construction Vitrification System for Application to Hazardous and Radioactive Wastes," Proceedings of the 1995 International Incineration Conference, pp. 517-519.