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Pacific Northwest National Laboratory
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Test Summary Report Vitrification Demonstration of an Optimized Hanford C-106/AY-102 Waste-Glass Formulation

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Abstract

In order to further the goal of optimizing Hanford's HLW borosilicate flowsheet, a glass-formulation effort was launched to develop an advanced high-capacity waste form exhibiting acceptable leach and crystal-formation characteristics. A simulated C-106/AY-102 waste envelope inclusive of LAW pretreatment products was chosen as the subject of these nonradioactive optimization efforts. To evaluate this optimized borosilicate waste formulation under continuous dynamic vitrification conditions, a research-scale Joule-heated ceramic melter was used to demonstrate the advanced waste form's flowsheet. The main objectives of this melter test was to evaluate 1) the processing characteristics of the newly formulated C-106/AY-102 surrogate melter-feed stream, 2) the effectiveness of sucrose as a glass-oxidation-state modifier, and 3) the impact of this reductant upon processing rates.

Summary

In Response to a U.S. Department of Energy (DOE) Headquarters directive to conduct a technical review of alternatives for solidification of high-level waste (HLW) that could achieve major cost reductions with reasonable long-term risks,[a] the Tanks Focus Area (TFA) chartered an independent Review Team to evaluate cost incentives associated with modifications to: waste-form product requirements, waste-stream processing constraints, product glass composition, and the reference waste-vitrification technology itself.

One of the conclusions drawn from the Review Team evaluation of alternative waste forms was that the borosilicate waste form has performed predictably and is firmly entrenched in the nuclear waste remediation program. However, it was felt that the vitrification process using this waste form had not been optimized (Perez et al. 2001). To further the goal of optimizing Hanford's HLW borosilicate flowsheet, a primary focus of the Review Team's effort, a TFA-sponsored glass-formulation effort was launched to develop an advanced high-capacity waste form exhibiting acceptable leach and crystal-formation characteristics (Peeler et al. 2002). Specifically, a simulated C-106/AY-102 waste envelope inclusive of low-activity waste (LAW) pretreatment products was chosen as the subject of these nonradioactive optimization efforts.

To evaluate the processing, off-gas emission, and product glass characteristics of this optimized borosilicate waste formulation under continuous dynamic vitrification conditions, a research-scale, Joule-heated, ceramic melter was used to demonstrate the advanced waste form's flowsheet. Specifically, the Pacific Northwest National Laboratory's (PNNL's) Research-Scale Melter (RSM) was used to conduct these initial melter-flowsheet evaluations. The RSM is a small (1/100-scale, DWPF basis) joule-heated melter that is capable of processing melter feed on a continuous basis. This capability is key for:

- developing/evaluating process flowsheets
- characterizing relationships between feed composition and the properties of the final glass produced
- establishing the fate and behavior of process effluent.

This melter system's capability to produce glass in a continuous manner is also essential for estimating the behavior of a full-scale system. Moreover, the size of the RSM allows the impacts of process variables upon melter performance or glass quality to be quickly and efficiently evaluated without undue expense or waste generation.

The experimental scope of this initial, 5-d, 120-h, C-106/AY-102 vitrification test was to:

- determine the feasibility of vitrifying surrogate C-106/AY-102, at 60 wt% waste loading, to produce a regulatory-acceptable borosilicate glass waste form
- evaluate the glass product with regard to composition, crystal growth and concentration, phase separation, chemical durability, and oxidation state

(a) TTP: Advanced High-Level Waste (HLW) Melter and Waste Products Review, 25 August 2000.

- characterize the composition and concentration of condensed-phase and selected gaseous melter-generated off-gas emissions and the composition of secondary off-gas system waste streams
- establish maximum process rates at a glass temperature of 1150°C and a 95% cold-cap coverage
- access whether the melt rate or processing conditions can be optimized by changing reductant and/or melter-operating conditions
- measure the volume-reduction factor for vitrified surrogate C-106/AY-102 waste stream
- quantify specific glass-production rates and waste-vitrification energy requirements.

During the 120 h of experimental testing, a validated C-106/AY-102, Envelope-D surrogate[(a)] was prepared, combined, at 60 wt% waste loading, with an optimized suite of glass formers, composed of B, Li and Si, and successfully vitrified in a Joule-heated melter. Beyond the processing characteristics of the optimized, baseline glass formulation, the impacts of a sugar-reductant additive at varying concentrations (2.5, 5, 7.5, and 9 g/L-waste) upon processing rates, gaseous emission characteristics, and glass oxidation state [Fe(II):Fe(III)] were also evaluated. The effects of a ~10% increase in melter-feed-water concentration upon melter performance was also assessed during melter testing.

The melting kinetics of the optimized CY-106/AY-102 feed formulation was found to be influenced by sugar-additive concentration. Although initial short-term processing of the baseline feed formulation, without the use of sugar additive, was quite successful, the glass formed was highly oxidized, and because of its relatively high Mn content, was quite susceptible to foaming. Without physical methods to mitigate the impact of foam-layer development, long-term processing of feeds without a supplemental reductant does not appear to be a viable option.

Less dynamic foaming occurred when a waste sugar concentration of 2.5 g/L was employed, but unstable processing conditions nevertheless resulted from a glass that remained too highly oxidized. Stable long-term melter processing conditions were achieved at all other sugar concentrations evaluated. At a sugar waste loading of 5 g/L, the product glass' Fe(II):Fe(total) ratio was <5% while at 9 g/L, a value slightly less than the limiting condition of 30% was measured

Although stable melting conditions resulted for waste sugar loadings ≥5 g/L, cold-cap characteristics appeared to be deleteriously affected by the sugar additive. The addition of sugar at all levels seemed to exacerbate feed coning beneath melter's feed nozzle. The collapse of dried feed matter that accumulated within the cone produced temporary processing instabilities by creating 100% cold-cap coverage conditions at all sugar loadings used. Water dilution of the incoming feed stream was used somewhat successfully to spread the incoming feed material over the entire glass pool; however, reduced glass production rates resulted from the power losses required to dry the diluted feed.

Melter-glass production rates varied from 8.3 to 4.3 $lbs/h/ft^2$ for the various feed batches processed. These values comfortably exceed the reference (cold-lid) Liquid Fed Ceramic Melter (LFCM) design production rate of 4 $lbs/h/ft^2$ that is often quoted and used for flowsheet and equipment sizing estimates

(a) WK Kot, H Gan, and IL Pegg. 2000. *Physical and Rheological Properties of Waste Simulants and Melter Feeds for RPP-WTP HLW Vitrification*, Vitreous State Laboratory, The Catholic State University, Washington, D.C.

(Perez et al. 2001). Indeed, this reference-normalized production rate is exceeded even when projections are based upon the overall average rate data (5.5 $lbs/h/ft^2$) that are inclusive of all idle-batching periods.

Average measured Joule heating power was used with corresponding batch feeding rates, reductant loadings, and heat of combustion information to derive specific process energy requirements for the surrogate C-106/AY-102 feeds. The average value derived for all batches processed, 3.9 kW•h/kg, agrees well with typical energy requirements for slurry-fed, Joule-heated ceramic melters: 2 to 4 kW•h/kg of glass produced (Perez et al. 2001).

Representative glass samples generated throughout the duration of RSM testing were subjected to standard durability tests. Specifically, glass samples were subjected to both product consistency test (PCT) (ASTM 1997) and toxicity characteristic leach procedure (TCLP 1992) leach-testing protocols. The PCT results suggest that all C-106/AY-102 glasses were more durable than the standard environmental assessment glass to which they were compared. Although marginal Ag results were obtained, corresponding TCLP tests indicate that all glasses produced, even the more highly reduced ones, conform to all existing Resource Conservation and Recovery Act (RCRA) land-disposal limits (40 CFR 268).

Pour-stream glass samples taken throughout the melter testing campaign were examined for the presence of secondary phases. The results obtained indicated that spinel crystals were present at an average concentration of 0.5 wt% (~0.25 vol%), which was significantly lower than a comparable, pre-test, qualifying crucible test result (1.8 wt%) obtained at 1150°C. In addition, post-test core drilling of the solidified melter glass pool allowed spinel crystal uniformity throughout the melt volume to be accessed. No significant stratification of spinel could be discerned from the somewhat noisy and scattered data obtained.

For the surrogate C-106/AY-102 melter feed used during RSM testing, CO_2 and NO_x (specifically NO) were the major non-condensable (~ 25°C) gases produced by the vitrification process. Feed nitrates were found to be efficiently reduced to N_2 under all waste sugar loadings as evidenced by significantly reduced NO emission rates. Of the process-generated combustible gases of concern, CO was undetectable (<250 ppm) at all reductant concentrations, and the maximum concentration of H_2 recorded was 0.02%. These concentrations are well below the lower flammability limits of these combustible gases, 4.65% for H_2 and 15.5% for CO and, consequently pose no reasonable off-gas system hazard under any conceivable processing conditions..

Condensed-phase effluents were also monitored during C-106/AY-102 melter testing. The melter's aerosol mass decontamination factors (DFs), as measured by isokinetic filter catches, were determined while processing feed containing a waste-sugar concentration of 7.5 g/L. These melter aerosol mass DFs ranged from 500 to 1200. Cold-cap accumulation (coning) during off-gas sampling is likely responsible for the range of the observed values. The overall mass DF as determined from secondary waste stream compositions is 240.

Melter partitioning for individual feed components was also derived from the off-gas sampling and secondary waste-stream data. With the exception of boron, sulfur, and the halogens, essentially all feed constituents (excluding C, N, H_2O, etc.) were found to be primarily in a condensed state downstream of the film cooler. Overall, the element-specific DFs recorded during the current test are reasonably close to general expectations and are generally consistent with previous melter-testing results. Furthermore, both off-gas sampling and secondary waste-stream-derived DF values exhibited the same relative trends for related groups of elements and were of comparable magnitudes for corresponding waste constituents. Indeed, the very reasonable mass closure demonstrated for most of the feed constituents for which complete analytical data exist suggests that the current melter test has successfully characterized the vitrification flowsheet of the optimized, 60 wt% C-106/AY-102 glass formulation.

During the July 2002 melter-flowsheet evaluation studies, 100 L (26 gal) of 60 wt% C-106/AY-102 simulated melter feed (~90 L-waste), having a total mass of 142 kg, was processed by the RSM, producing 20 L (5.3 gal) of glass having a total mass of 51 kg. These results suggest that an overall waste-volume-reduction factor of 4.6 was achieved during the RSM processing of the optimized C-106/AY-102 melter-feed formulation.

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Acronyms / Symbols

APEL	Applied Process Engineering Laboratory
DF	decontamination factor
DOE	U.S. Department of Energy
EA	environmental assessment
EPA	U.S. Environmental Protection Agency
EVS	ejector venturi scrubber
HEME	high-efficiency mist eliminator
HEPA	high-efficiency particulate air (filter)
HLW	high-level waste
LAW	low-activity waste
LFCM	Liquid Fed Ceramic Melter
LOD	loss on drying
LOI	loss on ignition
MOG	melter off-gas
PCT	Product Consistency Test
PLC	Programmable Logic Controller
PNNL	Pacific Northwest National Laboratory
POG	process off-gas
RCRA	Resource Conservation and Recovery Act
RSM	Research-Scale Melter
SCR	silicon-controlled rectifier
SRS	Savannah River Site
TCLP	toxicity characteristic leach procedure
TFA	Tanks Focus Area
UDS	undissolved solids
UTS	Universal Test Standard
----	not measured / not detected / not available / not applicable

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