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EFFECTS OF PROCESSING VARIABLES ON THE PRODUCT QUALITY OF LARGE-SCALE GLASS FORMS CONTAINING SIMULATED SRP WASTE

by

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ABSTRACT

The reference process for disposal of radioactive waste from the Savannah River Plant is immobilization in borosilicate glass. Full-scale canisters, containing simulated waste, have been made by two processes: in-can melting and continuous joule-heated melting. For each process, melter atmosphere and the degree of feed mixing have been varied. The effects of these variations on glass quality parameters such as leach rate, degree of fracture and porosity, and amount of crystalline material are discussed.

* The information contained in this article was developed during the course of work under Contract No. DE-AC09-76SR00001 with the U. S. Department of Energy.

INTRODUCTION

Radioactive wastes at the Savannah River Plant (SRP) are produced from the coprocessing of nuclear materials for defense programs. These alkaline wastes are made up of water-soluble salts and insoluble "sludges". Most of the waste actinides and fission products are contained in the insoluble sludges, which consist mainly of hydroxides and hydrous oxides of iron, aluminum, and manganese. The rest of the waste is either in the form of a soluble crystalline salt cake or a nearly saturated supernatant salt solution. This fraction contains about 95% of the fission product cesium and traces of other radionuclides.

Methods to immobilize SRP waste from long-term storage are currently being studied. In the present reference process (Slide 1), the supernatant liquid is pumped from the tanks and decontaminated by ion exchange. The sludge is slurried with water, and washed with hot caustic to remove about 75% of the aluminum. The sludge is then washed with water to remove soluble salts. The cesium-loaded zeolite from ion exchange is then mixed with the sludge. The radioactive sludge, cesium-loaded zeolite, and residual radionuclides from ion exchange are dried by spray calcination and melted, with glass frit, to form a borosilicate glass.

Two processes for immobilizing SRP waste in glass are currently under study. In the present reference process, frit and calcined waste are each fed continuously to a joule-heated ceramic melter (JM) where they are vitrified and poured into a storage canister. The other process, in-can melting (ICM), uses the canister as a crucible; frit and calcined waste are each fed to the heated canister where they form the final glass product.

In principle neither process is limited to low melting temperatures, but in practice materials of construction and off-gas considerations impose limits of 1050°C on ICM and 1200°C on JM.

Recently, both processes have been tested in full-scale equipment at Battelle-Pacific Northwest Laboratory and Savannah River Laboratory. An important part of this testing has been the qualitative evaluation of the vitrified products. Five glass-quality parameters were monitored (Slide 2):

(1) Leach rate in pH 4, 7, and 10 for 24 hours at 90°C

(2) Homogeneity, as determined by density and leach rate

(3) Presence of nonvitreous phase

(4) Porosity

(5) Degree of fracture

All the results discussed in this report are from canisters containing Frit 211 and a simulated average waste composition (Slide 3). Leaching, density, and phase behavior were compared to those of laboratory glass forms. The average waste was simulated either by a precipitated hydroxide slurry, or a mixture of oxides.

EFFECTS OF MIXING

As noted above in the reference process, calcine and frit are each fed to the melter. There is no attempt to insure good mixing of the two before vitrification. Thus, the burden of homogenizing the product falls on the melter, but melters are not able to overcome poor mixing of the feed (Slides 4, 5). Thus, in future process development studies, methods to better mix frit and waste will have to be investigated.

EFFECTS OF FINS ON ICM PRODUCT

The effects of heat transfer fins on the quality of ICM glass were examined for both mixed and unmixed feeds. In both cases, the product in canisters with fins was more highly fractured and contained more crystalline material (Slides 6 and 7). For unmixed feeds, the fins also catch calcine-rich material, and form refractory clinkers, which are difficult to dissolve in molten glass. However, the clinkers are very leachable in water, and thus must be avoided.

EFFECTS OF COAL IN THE FEED

In the reference process, the glass will be melted in a reducing atmosphere, due to the presence of coal in the feed. The coal had little effect on leach rate, porosity, or degree of fracture, but cut the amount of crystalline material in the product in half (Slide 8). Thus, it had a beneficial effect on product quality.

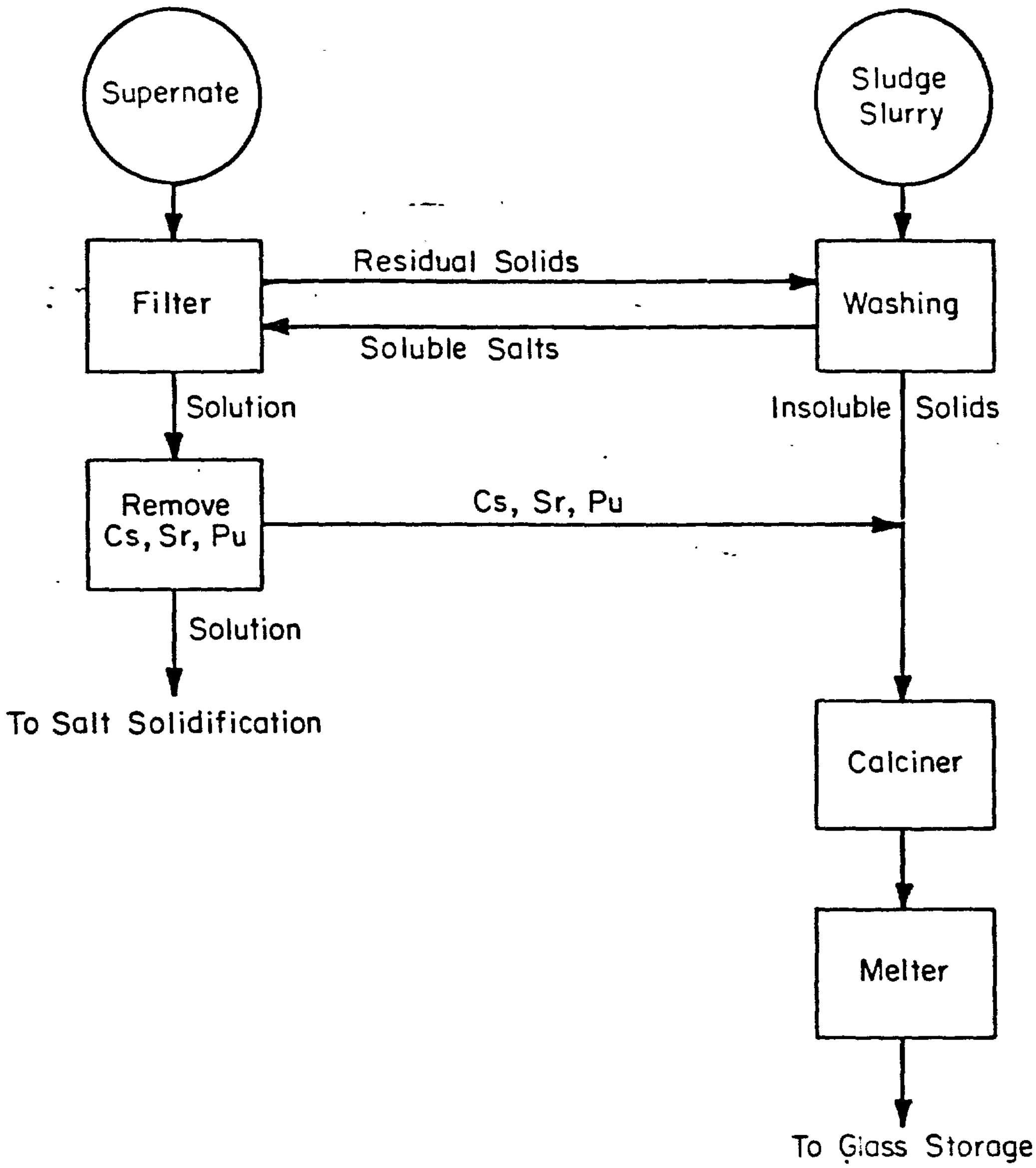
JM vs ICM

In general, there is virtually no difference between the two, for premixed feeds. For unmixed feeds, the JM product is better than the ICM product, which is probably due to the greater convection currents in the JM (Slides 9, 10). However, the degree of difference is not enough to disqualify ICM from further study.

CONCLUSIONS

Based on the results here (Slide 11):

- Premixing waste and frit is necessary to achieve optimum product quality.
- ICM glass is roughly equivalent to joule-melted glass.
- Heat transfer fins increase glass fracture, increase the crystalline content of the glass, and act as catch points for clinkers.


Supernate
Sludge Slurry
Filter
Residual Solids
Soluble Salts
Washing
Solution
Insoluble Solids
Remove Cs, Sr, Pu
Cs, Sr, Pu
Solution
To Salt Solidification
Calciner
Melter
To Glass Storage

Slide 1

SLIDE 2

GLASS QUALITY FACTORS

LEACH RATE:	Static tests - glass cores - 24 hours at 90°C pH 4, 7, 10
HOMOGENEITY:	Density, other measures under development.
PRESENCE OF NONVITROUS MATERIAL:	Devitrification, unreacted batch, Na_2SO_4.
POROSITY:	Fraction of samples with significant porosity.
DEGREE OF FRACTURE:	Distance between cracks along core.

SLIDE 3

COMPOSITION OF SIMULATED WASTE GLASS

Component	Amount (wt%)	Source*
SiO_2	42.0	F
B_2O_3	8.0	F
Li_2O	3.2	F
Na_2O	15.2	F & W
CaO	5.1	F & W
Fe_2O_3	14.5	W
MnO_2	3.8	W
Al_2O_3	3.2	W
Zeolite**	2.8	W
NiO	1.7	W
Na_2SO_4	0.4	W

SLIDE 4

EFFECTS OF MIXING ON QUALITY OF IN-CAN MELTER GLASS

	Mixed Feed	Unmixed Feed
Leach Rate, 90°C, 24 h*		
pH=4	2.0	3.2
pH=7	1.2	2.3
pH=10	1.8	2.0
Homogeneity-density	2.78 ± 0.07	2.72 ± 0.50
Amount of nonvitreous material (Vol%)	0-2	40
Fraction of porous samples(%)	0	15
Relative degree of fracture	1	1
Major second phase(s)	$NiFe_2O_4$	Acmite, Na_2SO_4

* *Relative to laboratory melt of same composition.*

SLIDE 5

EFFECTS OF MIXING ON QUALITY OF JOULE-MELTED GLASS

	Mixed Feed	Unmixed Feed
Leach Rate, 90°C, 24 h*		
pH=4	2.1	3.5
pH=7	1.0	1.6
pH=10	1.5	1.7
Homogeneity-density	2.75 ± 0.10	2.82 ± 0.35
Amount of nonvitreous Material (Vol%)	<1	30
Fraction of porous samples(%)	5	20
Relative degree of fracture	1	5
Major second phase	$NiFe_2O_4$	Acmite

* *Relative to laboratory melt of same composition.*

SLIDE 6

EFFECT OF FINS ON ICM GLASS - MIXED FEED

	No fins	8 or 16 fins
Leach Rate, 90°C, 24 h*		
pH=4	1.6	1.8
pH=7	1.2	1.2
pH=10	1.8	1.4
Homogeneity-density	2.78 ± 0.07	2.81 ± 0.10
Amount of nonvitreous Material (Vol%)	0-2	0-2
Fraction of porous samples(%)	0	10
Relative degree of fracture	1	3-6
Major second phase(s)	$NiFe_2O_4$	$NiFe_2O_4$, Na_2SO_4

* *Relative to laboratory melt of same composition.*

SLIDE 7

EFFECT OF FINS ON ICM GLASS - UNMIXED FEED

	No fins	8 or 16 fins**
Leach Rate, 90°C, 24 h*		
pH=4	3.2	6.9(71.7)
pH=7	2.3	11.4(102)
pH=10	2.0	3.8(14.6)
Homogeneity-density	2.72 ± 0.50	2.79 ± 0.44
Amount of nonvitreous material (Vol%)	40	60
Fraction of porous samples (%)	15	20
Relative degree of fracture	1	3-6
Major second phase	Acmite	Acmite, Na_2SO_4

Relative to laboratory melt of same composition.

***Results for material caught on top of fins listed in parentheses, but not used to calculate average leach rates.*

SLIDE 8

EFFECT OF COAL ON QUALITY OF JM GLASS

	Without Coal	With Coal
Leach rate, 90°C, 24 h*		
pH=4	3.5	3.3
pH=7	1.6	1.6
pH=10	1.7	1.8
Homogeneity-density	2.82 $\pm$ 0.35	2.71 $\pm$ 0.22
Amount of nonvitreous material (Vol%)	30	15
Fraction or porous samples(%)	20	20
Relative degree of fracture	5	2
Major second phase	Acmite	Acmite

**Relative to laboratory melt of same composition.*

SLIDE 9

COMPARISON OF JM AND ICM GLASS - MIXED FEEDS

	JM	ICM
Leach rate, 90°C, 24 h*		
pH=4	2.1	1.6
pH=7	1.0	1.2
pH=10	1.5	1.8
Homogeneity-density	2.75 ± 0.10	2.78 ± 0.07
Amount of nonvitreous material (Vol%)	<1	0-2
Fraction of porous samples(%)	5	0
Relative degree of fracture	1	3
Major second phase(s)	$NiFe_2O_4$	$NiFe_2O_4$

* *Relative to laboratory melt of same composition.*

SLIDE 10

COMPARISON OF JM AND ICM GLASS - UNMIXED FEEDS

	JM	ICM
Leach Rate, 90°C, 24 h*		
pH=4	3.5	3.2
pH=7	1.6	2.3
pH=10	1.7	2.0
Homogeneity-density	2.82 ± 0.35	2.72 ± 0.50
Amount of nonvitreous material (Vol%)	30	40
Fraction of porous samples(%)	20	15
Relative degree of fracture	1	1
Major second phase(s)	Acmite	Acmite, Na_2SO_4

* *Relative to laboratory melt of same composition.*

SLIDE 11

CONCLUSIONS

Premixing frit and waste necessary for good product.

ICM glass ≈ JM glass, if no fins.

Heat Transfer fins -

- Increase glass fracture
- Increase crystalline content
- Act as catch point for clinkers