# INITIAL DEMONSTRATION OF THE VITRIFICATION OF NUCLEAR WASTE SLUDGE CONTAINING AN ORGANIC Cs-LOADED ION EXCHANGE RESIN (U)

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# INITIAL DEMONSTRATION OF THE VITRIFICATION OF HIGH-LEVEL NUCLEAR WASTE SLUDGE CONTAINING AN ORGANIC Cs-LOADED ION EXCHANGE RESIN

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## ABSTRACT

When immobilizing into borosilicate glass the radio-nuclides in the caustic high-level radioactive wastes stored in the USA, the soluble fission product Cs-137 has to be removed from supernates of the wastes. In the current processes zeolites or an organic precipitant will be used to remove the Cs. These solids are then treated further and mixed with the radioactive sludges and vitrified into a borosilicate glass. This paper describes the vitrification of a mixture resulting from using a new process to remove Cs from the caustic supernate. An organic ion exchange resin is used. This resin was then mixed with sludge and frit and vitrified. Using an organic ion exchange resin rather than zeolite or the organic precipitant has certain advantages. Some of these are discussed in the paper. Results in the paper indicate that a mixture of the resin, sludge and frit can be successfully vitrified in a joule-heated, slurry fed melter. The redox state of the glass is lowered by the presence of the resin in the feed, but the glass is still suitable as a canistered wasteform for radioactive waste glass.

## INTRODUCTION

At the Hanford, West Valley, and the Savannah River Site (SRS), high-level radioactive nuclear wastes will be

immobilized into borosilicate glass for permanent disposal in a geologic repository. At all three sites, the wastes are stored as caustic slurries in million gallon underground tanks. Since the slurries are caustic, most of the fission products and the transuranic waste radionuclides are precipitated in a sludge as hydrous oxides; however, since Cs is soluble in caustic, most of the radioactive Cs-137 is in the supernate along with high concentrations of $Na^+$ ions (~4M) added as NaOH. Consequently, Cs-137 has to be removed from the supernate and consolidated with the sludge in order to immobilize all the radioactivity in the glass. At Hanford and West Valley, zeolite is used in the reference process to remove Cs. This zeolite will be mixed with sludge and an appropriate frit and then fed to a melter at 1150°C. The supernates at Savannah River Site (SRS) are too caustic to allow the use of zeolite. Cesium will be precipitated as cesium tetraphenylborate (CsTPB). Potassium is also precipitated from the supernate as KTPB. The tetraphenyl-borate precipitates will then be intentionally decomposed by hydrolysis. This produces benzene which is removed in order to reduce the amount of carbon going to the melter. The product of this hydrolysis will be mixed with the sludge and frit and then fed to a melter.

Recently, an organic ion exchange resin has been developed that can successfully compete with high concentrations of $Na^+$ ions in the caustic supernates and remove the Cs.[1] This resin has been tested on both actual and simulated radioactive supernates.[1] As a possible second generation process at SRS we are investigating the possibility of using this resin to remove Cs. The Cs-loaded resin would then be mixed with sludge and frit and then fed directly to a melter to make glass. The resin will be burned in the melter and the residual Cs immobilized in the borosilicate glass. This process may have advantages over both the zeolite and the

CsTPB precipitation processes. Since the resin is burned and the zeolites aren't, this process would produce less glass than the zeolite process. There are two apparent advantages over the CsTPB process. First, the resin process does not produce a secondary waste stream as does the CsTPB process. In the CsTPB process, benzene is produced by the hydrolysis step and has to be stored or destroyed in some manner. Second, with the resin process, the need for the complicated hydrolysis step is eliminated. However, as with any new process, integration of ion exchange streams and the burning of the spent resin in the melter must be piloted before the actual performance of the process can be assessed.

This paper describes three kilogram scale melter runs designed to test whether a durable glass could be made by feeding a slurry of sludge, frit, and the organic resin to a joule-heated melter. Since it was known that the presence of the organic materials in the feed could reduce redox elements such as Fe, the redox of the final glass was measured by determining the Fe(II) content of the glass. The durability of the glass was measured by the Product Consistency Test (PCT). Another goal of this initial demonstration was to determine if the presence of resin significantly altered the performance of the melter and off-gas system. Each melter run used nominally 120 kg of slurry, lasted about three days and produced about 30 kg of glass. Prior to using the large melter, small scale crucible tests were performed to gain information on how the resin would affect the redox of the melt.

**EXPERIMENTAL**

The melter was a ceramic-lined, joule-heated melter that held about 18 kg of glass in its melt chamber. Feed for the melter was a slurry (nominally 58 weight percent water)

containing the sludge, frit and resin.  The melt was at
1150°C.  During the feeding process as the slurry fell on the
top surface of the melt, water was flashed off, any organic
material present was burned, sludge was dissolved in the
melt, and the frit was melted.  Molten glass was poured from
the bottom of the melt into one liter stainless steel
beakers.  The off-gas system collected the condensate from
the water fed to the melter as well as particulates entrained
in the off-gas.

Three melter runs were performed.  Each run contained the
same simulated sludge and frit.  Resin was added to the feed
for the second and third run.  For the first two runs the
melter was fed for two 16-hour intervals and one 8-hour
interval over three days.  The melter idled for 8 hours each
of the first two days and 16 hours the third day.  The first
run contained only frit and sludge and was performed to
determine the quality of the glass when resin was not in the
feed.  The second run was identical to the first except that
resin had been added to the feed.  In the third run, the
melter was fed continuously for 53 hours or 2.2 days.  Each
run produced 12 cans of glass with each can holding
approximately 2 kg.

The durability of the glass was determined by subjecting
samples of the glass from various cans to the PCT.[2]  This is
a crushed glass leach test at 90°C using deionized water.
The crushed glass (100-200 mesh) is leached for 7 days and
the amount of soluble elements (B, Na, Li, and Si) released
to the solution measured to determine the durability of the
glass.  The final pH of the leachate was also measured and is
an indication of the durability of the glass. Crushed glass
was obtained by grinding pieces of glass that were taken from
the liter stainless steel cans using a hammer and chisel.

The grinder contained a tungsten carbide blade to prevent iron contamination of the glass.

The redox property of the glass was measured by determining the Fe(II) content of the glass. A colorimetric technique was used after HF/HCl dissolution of crushed samples of the glass.[3]

## RESULTS AND DISCUSSION

### Preliminary Crucible Tests

To gain information about how the resin would affect the redox of the glass melt, small crucible tests were performed using varying amounts of resin and an oxidizing agent, nitrate ions. In these tests, the mixture of resin, sludge, and frit was dried and then melted for four hours at 1150°C. The glass was quenched and the Fe(II) content of the glass measured. The results of these tests indicated as expected that with increasing amounts of resin in the feed, more Fe(II) was present in the glass. The results also showed that both $NaNO_3$ and $HNO_3$ were effective in lowering the amount of Fe(II) formed. $HNO_3$ was more effective than $NaNO_3$. The crucible tests indicated that at a ratio of 5 grams of resin per 100 grams of glass, the Fe(II)/Fe(total) ratio should be ~0.3. This value has been proposed as an upper limit on the amount Fe(II) that should be present in the nuclear waste glasses that will be produced at SRS.[4] This upper limit is based on the standard state calculation of the stability of nickel sulfide in the melt.[5] If nickel sulfide forms, it is conductive and may create an electrical short and damage the melter electrodes. For the resin runs, it was decided to use enough resin to approach this upper limit, thus, 5 grams of resin were used for every 100 grams of glass expected in the run.

## Melter Feed Composition

Table 1 shows the major composition (on a dry basis) of the
simulated nuclear waste sludge used in this study. This
composition is typical for the sludges that will be processed
at SRS. When the sludge is present as melter feed, it will
be in a slurry that contains soluble formates, nitrates, and
nitrites. Formate is added to adjust the rheology of the
sludge and reduce Hg which is distilled from the sludge prior
to feeding it to the melter. Nitrates and nitrites are
present in the original sludge while it is stored in the
waste tanks. Nominal concentrations of these anions are 1.2M
for formate, 0.4M for nitrate, and 0.1M for nitrite. The
frit used was Frit 165. Its composition is given in
Table 2. On a dry basis, the final glass is 28 weight
percent sludge oxides and 72 weight percent frit oxides.

The elemental composition of the Cs-loaded resin is given in
Table 3. Prior to putting the resin into the melter feed
tank, the resin was saturated with Cs by removing Cs from a
simulated radioactive caustic supernate. The composition of
this supernate was 4.0 M $NaNO_3$, 1.5 M NaOH, and 2.5 X $10^{-4}$ M
$CsNO_3$. The Na form of the resin was used. To have enough
resin for both runs, approximately 3 kg of dry resin were
needed. This amount of resin was used to remove the Cs from
1700 liters of simulated supernate. The only pretreatment of
the resin prior to adding it to the melter feed tank was to
filter it from the supernate and air dry it. (Air drying
would probably not be necessary during large scale
processing.) The correct amount dried resin was then mixed
with the sludge and frit slurry in the melter feed tank.

Addition of the resin adds negligible amounts of alkali
metals to the glass. For example, from Table 3 it can be

seen that the presence of the resin adds only ~0.4 weight
percent Na and 0.004 weight percent K to the glass. The
amount of Cs added is even lower.

## Effect of Resin on Melter Operation

When resin was present in the feed, no differences in melter
operation were evident. There was no effect of resin on the
amount of current necessary to pass through the electrodes in
order to maintain the melt at 1150°C. This suggests that the
resin did not produce any conductive species in the melt
which would short out the electrodes. The presence of the
resin also did not introduce any adverse effects such as
pluggage of the melter feed tube or off-gas system. Finally
there was no apparent affect on the pourability (viscosity)
of the glass melt.

## Final Glass Compositions

The composition of a sample of glass from each of the three
runs is given in Table 4. For the sludge only run (Run 1)
and the intermittent sludge-resin run (Run 2) the samples
were taken from the seventh can collected. For the
continuous resin run, the sample was from the third can
collected. Except for the Fe(II) and Fe(III) contents, the
compositions are very similar. This is expected since the
only difference in the feed was whether resin was present or
not. When resin was present, the amount of Fe(II) increased
which indicates that the glass is in a more reduced state.
Further, in the melter run where the melter had been fed
continuously for 2.2 days, the amount of Fe(II) was the
highest.

## Effect of Resin on Glass Redox and Durability

Table 5 summarizes the results for the redox ratios
(Fe(II)/Fe(total)) and the durabilities for samples of glass
from five of the twelve cans collected in each of the three
melter runs. The cans were collected in the numerical
sequence given by the sample numbers in the first column of
Table 5. For example, Sample 2-07 was from the 7th can
collected in the second run (the intermittent resin run). As
each run progressed (run times given in column 2), the glass
became more reduced (the iron redox ratio increased) and less
durable as measured by the PCT. Lower durabilities are
indicated by the increased pH values (Column 4) and B
concentrations (Column 5) in the PCT tests. Similar trends
were indicated by the Na, Li, and Si leached from the glass
in the PCT tests. The pH increases are due to hydronium ions
in the leach water exchanging with alkali ions in the glass.
The B, Na, and other ions in the leachates result from
dissolution and alteration of the glass. An increase in the
Fe(II) concentration in the glass decreases its durability
because Fe(II) acts as a network modifier in the glass while
Fe(III) can be a network former. In the sludge only run,
reduction in the melt was caused by formic acid. When resin
was present, increased reduction was caused by the organic
resin.

The glass collected in the first can from each run is more
oxidized and more durable than the glass collected later in
the runs. This is because the melter idled at 1050°C for
several days between runs. During this idling period, $O_2$
diffused into the melt and reoxidized the Fe(II). Thus, the
glass collected in the first can in the next run would be
from this oxidized melt. The most reduced glass had a redox
ratio of 0.44 and resulted from the continuous resin run (Run
3). In the two resin runs, the redox ratio of the glass in

many cans exceeded the upper limit of 0.3 proposed[4] for this
ratio. However, during these runs, there was no indication
of a decrease in the electrical resistance of the melt. We
are now examining the glass by scanning electron microscopy
to see if any reduced metals are present. The final redox
ratios in the intermittent resin run were not as high as the
continuous resin run. During the intermittent run, $O_2$
diffused into the melt during the 8 hours per day when the
melter was idling. Consequently, the melt did not become as
reduced as in the continuous run.

The acceptability of the glass from this process as a waste
form for SRS radioactive waste can be assessed by comparing
its durability with that of the glass which has been
qualified in the DWPF Environmental Assessment (EA glass).
Preliminary PCT results[6] with the EA glass indicate a B
concentration nominally 10X higher than the highest B
concentration in Table 5. On this basis, it can be concluded
that glass prepared by vitrification of waste containing an
organic ion exchange resin would be acceptable as a
canistered waste material.

## CONCLUSIONS

The data obtained in this initial demonstration support the
following conclusions.

1. An organic ion exchange resin can be mixed with simulated
high-level radioactive waste sludge and frit and then
successfully vitrified in a  slurry fed, joule-heated
melter.

2. Presence of the resin is not expected to significantly affect the operation of the melter and off-gas system. However, this will have to be tested with longer runs and with a larger melter.

3. Presence of the resin causes the glass to become more reduced which decreases its durability.  However when compared to preliminary results with the DWPF EA glass, this glass is an acceptable waste form for immobilization of radioactive waste.

## FUTURE WORK

The advantages of using an organic ion exchange resin for removing Cs from caustic supernates justify further tests to refine the vitrification process.  Efforts will be made to adjust the melter feed to produce a more oxidized and durable glass.  For example, based on the crucible tests, if nitric rather than formic acid is used to adjust the rheology of the sludge, the glass will be more oxidized.  Further, it may be possible to reduce the amount of resin in the feed and still have enough resin to remove Cs-137 from the supernates. Lastly methods of eluting the Cs off the resin need to be investigated.

## ACKNOWLEDGMENT

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TABLE 1. MAJOR COMPONENTS IN SRS SIMULATED SLUDGE ON A DRY BASIS

| Element | Weight Percent | Element | Weight Percent |
|---------|---------------|---------|---------------|
| Fe | 12.1 | Na | 7.1 |
| Si | 5.1 | Al | 3.5 |
| Mn | 2.8 | Ca | 1.7 |
| B | 0.64 | Li | 0.53 |
| Mg | 0.30 | Zn | 0.20 |

TABLE 2: OXIDE COMPOSITION OF FRIT 165 ON A DRY BASIS

| Oxide | Weight Percent | Oxide | Weight Percent |
|-------|---------------|-------|---------------|
| $SiO_2$ | 65.0 | $Na_2O$ | 11.0 |
| $B_2O_3$ | 10.5 | $Li_2O$ | 6.9 |
| $ZrO_2$ | 2.4 | $TiO_2$ | 2.0 |
| $K_2O$ | 1.0 | MgO | 0.64 |
| $PbO_2$ | 0.2 | CaO | 0.23 |
| $Al_2O_3$ | 0.3 | $Fe_2O_3$ | 0.04 |

TABLE 3: ELEMENTAL COMPOSITION OF Cs SPECIFIC ION EXCHANGE RESIN
AFTER REMOVING Cs FROM A SIMULATED HLW SUPERNATE
(Weight Percent on a Dry Basis)

| Element | Weight Percent | Element | Weight Percent |
|---------|---------------|---------|---------------|
| C | 35.5 | O | 45.5 |
| Na | 7.0 | H | 5.8 |
| Cs | 0.95 | K | 0.07 |

TABLE 4: COMPOSITIONS OF THREE GLASSES FROM THREE MELTER RUNS
TESTING THE EFFECT OF ORGANIC RESIN ON SLUDGE VITRIFICATION

| | Composition (weight percent) | | |
|---|---|---|---|
| Oxide | Glass-1-07[a] | Glass-2-07[b] | Glass-3-03[c] |
| $K_2O$ | 1.21 | 0.96 | 1.0 |
| $Al_2O_3$ | 4.04 | 3.62 | 3.77 |
| $B_2O_3$ | 7.32 | 7.16 | 6.62 |
| CaO | .92 | .81 | .87 |
| Cr | .37 | .38 | .33 |
| CuO | .05 | .06 | .03 |
| $Fe_2O_3$ | 8.53 | 6.09 | 6.64 |
| FeO | 1.05 | 2.82 | 3.15 |
| $Li_2O$ | 4.51 | 4.65 | 4.45 |
| MgO | 0.77 | 0.74 | 0.73 |
| MnO | 1.48 | 1.43 | 1.56 |
| $Na_2O$ | 11.69 | 12.13 | 11.91 |
| NiO | 0.69 | 0.58 | 0.55 |
| PbO | 0.11 | 0.10 | 0.10 |
| $SiO_2$ | 50.2 | 50.1 | 49.6 |
| $TiO_2$ | 1.06 | 1.06 | 1.01 |
| ZnO | 0.17 | 0.18 | 0.22 |
| $ZrO_2$ | 1.26 | 1.36 | 1.31 |

[a]Glass from Can 7 of the intermittent sludge only run.
[b]Glass from Can 7 of the intermittent sludge-resin run.
[c]Glass from Can 3 of the continuous sludge-resin run.

## TABLE 5: IRON REDOX RATIO AND PCT RESPONSE FOR GLASS SAMPLES FROM VITRIFICATION OF A SLURRY OF FRIT, SIMULATED HLW SLUDGE AND AN ORGANIC ION EXCHANGE RESIN

| Sample Number | Time from Start of Run (hr.)[a] | Iron Redox Ratio[b] | PCT Response pH[c] | PCT Response B Conc.[d] |
|---|---|---|---|---|
| Intermittent Sludge Only Run[e] | | | | |
| 1-01 | 5.0 | 0.02 | 10.3 | 16.0 |
| 1-03 | 11.7 | 0.09 | 10.2 | 15.7 |
| 1-07 | 44.9 | 0.12 | 10.3 | 18.7 |
| 1-10 | 58.9 | 0.13 | 10.4 | 20.6 |
| 1-12 | 76.7 | 0.12 | 10.4 | 19.3 |
| Intermittent Sludge-Resin Run[e] | | | | |
| 2-01 | 3.2 | 0.07 | 10.5 | 15.6 |
| 2-03 | 12.2 | 0.28 | 10.6 | 22.7 |
| 2-07 | 45.8 | 0.34 | 10.7 | 38.3 |
| 2-10 | 59.9 | 0.35 | 10.8 | 36.4 |
| 2-12 | 77.2 | 0.33 | 10.8 | 36.2 |
| Continuous Sludge-Resin Run[f] | | | | |
| 3-01 | 4.8 | 0.14 | 10.3 | 16.1 |
| 3-03 | 13.3 | 0.34 | 10.7 | 22.0 |
| 3-06 | 31.0 | 0.42 | 10.7 | 30.5 |
| 3-09 | 45.5 | 0.40 | 10.9 | 38.6 |
| 3-12 | 53.7 | 0.44 | 10.9 | 42.6 |

[a]Time that the can was removed from the melter pour chamber. Nominally 4-5 hours were required to fill a can.
[b]Measured $Fe(II)/Fe(total)$ ratio in the glass.
[c]Final pH in the PCT leach test. Initial pH = 6.5.
[d]Final boron concentration (ppm) in the PCT leach test. Initial = 0.0. Similar trends were observed for Na, Si, and Li.
[e]Melter was fed and glass poured for three 16 hour and one 8 hour intervals with 8 hour intervals in between. Total time = 3.2 days.
[f]Melter was fed and glass poured continuously for 2.2 days.

# END

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