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MEMORANDUM

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TO: L. M. PAPOUCHADO

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CALCIA-ALUMINA-SILICATE GLASSES FOR THE IMMOBILIZATION OF SRP WASTE

INTRODUCTION

One criticism of proposed nuclear waste-glasses is that their silica content is too low and their boron and alkali contents too high. In particular, Penberthy Electromelt has repeatedly said that current waste-glass formulations are orders of magnitude less durable than calcia-alumina-silicate (CAS) formulations. The manufacture of such glasses has never been attractive from an operating standpoint because of the much higher melting temperatures (approximately 1380°C) required. Of particular concern are increased volatility of radionuclides and more rapid corrosion of melter materials.

A previous report[1] concluded that CAS formulations did not have the dramatic benefits claimed. Claims are now being made that new high-silica formulations are "far beyond" those tested previously. In this report, those glasses are considered as part of an entire melting system. We conclude that the problems presented by melter operation at the very high temperatures required are too severe, and the gain in durability too small, to justify investigating these compositions further.

SUMMARY

- The corrosion rates of molybdenum electrodes in these CAS glasses at 1380°C are 8-17 times that of Inconel 690 in borosilicate glass at 1150°C.

- Volatility during melting increases at least 3-6 times from current levels.

- Chemical durability is only slightly improved, at most approximately 4 times.

- Canister filling will be difficult, with significant loss of volatile radionuclides.

GLASSES - COMPOSITION AND PREPARATION

Four calcia-alumina-silicate (CAS) glasses were studied, two (P-19, PTG-1) based on immobilization of all waste (both salt and sludge), and two sludge-only glasses, one with aluminum removal (PTG/Stage 1) and one without (PTG-3). The composition of the all-waste glass P-19, the most recent formulation, has been previously published.[2] The composition of PTG-1, PTG-3 and PTG/Stage 1 are based on his P-7b composition[3], suggested for immobilization of fuel reprocessing waste at West Valley, New York. This composition was chosen because it requires the least amount of glass to immobilize SRP waste regardless of the waste processing option chosen (all waste - sludge and salt, sludge only, aluminum removal). The compositions of P-19, PTG-1, and PTG/Stage 1 are compared to 131/Stage 1 in Table 1.

These glasses as well as the reference 131/Stage 1 were doped with 0.5 wt % each of Cs_2O, SrO, and Dy_2O_3. Radioactive isotopes of cesium and strontium are present in the waste and are of particular interest in volatility and leaching studies for that reason. Dysprosium is chemically similar to the actinides and is especially well suited for trace analysis by neutron activation. For the CAS glasses, all chemicals were added as oxides, except for sodium, cesium and strontium which were added as carbonates. Cesium and strontium were also added to 131/Stage 1 as carbonates.

All samples were heated gradually from room temperature to the melting temperature - 1380°C for CAS glass and 1150°C for 131/Stage 1 and held there for 24 hours to ensure homogeneity. The glasses were cooled slowly. The all-waste formulations (P-19 and PTG-1) consistently made good glass, as did 131/Stage 1. However, both sludge-only CAS compositions (PTG-3 and PTG/Stage 1) showed signs of devitrification. For the latter composition, this was especially severe. The volume of glass produced was roughly equal to the volume of crystalline material.

LEACHING STUDIES

Leach tests were performed on P-19, PTG-1, PTG-3 and Frit 131/Stage 1 glasses. A sample of glass of unspecified composition (PGS) provided by Penberthy Electromelt was also leached. No leach tests were performed on PTG/Stage 1 glass because its severe devitrification precluded any possibility of a homogeneous sample.

All leach tests were performed at 90°C for 24 hours. The studies using buffers of pH 4, 7, and 10 involved 7.00g of -40+60 mesh powder and 30 ml of leachant. The equilibrium pH test, performed in deionized water, used 2.00g of -200 mesh powder and 100 ml of leachant. The results of this test are shown in Table 2. All glass powders and leaching solutions were analyzed for Cs by atomic absorption (AA), Si and Sr by ion-coupled plasma emission (ICP) and Dy by neutron activation analysis (NAA).

Leach rates were calculated using 70 cm^2/g for -40+60 mesh 131/Stage 1.[4] Taking the density of this glass to be 2.8 g cm^{-3} and that of CAS glasses to be 2.3 g cm^{-3}, the corresponding value for P-19, PTG-1, PTG-3 and PGS is 85 cm^2/g. For -200 mesh powder, an average diameter of 44μm was used. This gives surface areas for 131/Stage 1 and CAS glasses of 490 and 590 cm^2/g respectively. Calculated leach rates are listed in Table 3.

The most durable CAS glass is P-19. Its leach rate is in no case more than four times lower than that of 131/Stage 1, and the rate as averaged over all pH's and all analyses is only 1.5 times lower. This slight increase in durability is far from the "orders of magnitude" claimed. In fact, this difference is insignificant based on the recent MCC round robin tests which showed a factor of 2-3 variability in intra-laboratory leach results.

This data is in line with the results of MCC-1 tests performed at Battelle-Pacific Northwest Laboratory.[5] In those tests, the CAS glass was only about 4 times more durable than PNL's 76-68 based on Si, about 10X more durable based on Cs, and about 10X less durable based on Sr.

The claimed higher durability of the CAS glasses was based on their higher silica content and on assumed congruent glass dissolution. However, a recently published study[6] indicates that waste glass is not leached congruently. Formation of surface films rich in minor constituents not only takes place but also inhibits further leaching. This was observed indirectly when leach rates were found to drop two orders of magnitude as waste loading in the glass was increased.[7]

VOLATILITY STUDIES

Claims have also been made that the volatility of CAS glass will be much lower than that of borosilicate glasses due to higher viscosity and the absence of boron.[2] The data clearly show that the higher melting temperatures required for CAS glasses more than offset any advantages in composition or viscosity.

One hundred grams of chemical for each of five glass compositions were placed into separate 200 ml alumina crucibles. All were slowly raised to the proposed melting temperature - 1380°C for the high-silica glass and 1150° for the borosilicate glass - and held there for 65 hours. The amount of material lost for each composition were corrected for loss of components such as CO_2, NO_x, and O_2, and normalized. These values represent the amount of semivolatiles lost and are reported in Table 4.

During glass melting material may be lost either by volatilization or by entrainment. As has been shown by Gray,[8] volatility at a given temperature decreases as the viscosity of the melt increases. However, it is not correct to draw any conclusions from this about two different glasses at two different melting temperatures. In fact, the data indicate that the higher melting temperatures of the CAS glasses dominate any other factors affecting volatility.

Ryder, Taylor and Tanner[9] found that a plot of the logarithm of particulate emission rate vs. inverse melting temperature gave a straight line of negative slope:

$$\log\left(\frac{R_1}{R_2}\right) = -1.75 \times 10^4 \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where R_1 and R_2 are the total particulate emission rates at temperatures T_1 and T_2 (in Kelvin) respectively. This relationship predicts the amount of entrained material to increase by a factor of 50 if the melting temperature is increased from 1150 to 1380°C.

Besides increased volatility and entrainment during melting, one other burden on the off-gas system deserves mention: volatility from the pouring glass stream. Tests at SRL and PNL have shown that a viscosity of 500 poise is necessary to ensure proper filling of a canister of glass. For low temperature borosilicate glasses, this means pouring temperatures of 900-950°C. However, the CAS glasses would have to be poured at approximately 1350°C. Using previously published data for borosilicate glass at 900°C, 450-900X more material would be volatilized from the CAS glasses during pouring.[10]

CORROSION STUDIES

The refractory material Monofrax K-3 and Penberthy Electromelt's proposed electrode material, molybdenum, were tested for corrosion by each of the four CAS glasses. The glasses used in this study had previously been melted for twenty-four hours at 1380°C. As noted above, PTG/Stage 1 underwent severe devitrification. These corrosion tests used only the glassy part of this sample and may not be representative of the behavior of the formulation as a whole.

Glass made of Frit 131 with TDS waste simulation has already been tested for corrosion of Monofrax K-3 and of Inconel 690[11], the proposed DWPF electrode material. Since Inconel 690 melts below 1380°C, it cannot be used with CAS glasses. This alloy is preferred over molybdenum as an electrode material for operation at 1150°C because it shows superior corrosion resistance, is less sensitive to the oxidation-reduction state of the glass, and can be exposed to air.

Corrosion rates of melter components in CAS glasses and 131/TDS are compared in Table 5. Corrosion of electrode material is 8-17 times more severe for CAS glasses than for 131/TDS. Rates of corrosion of K-3 refractory by the CAS glasses range from 0.8 to 9 times those by 131/TDS.

These data on molybdenum electrodes are consistent with a recent study[12] which identifies oxidation as the primary corrosion mechanism. Corrosion was found to be enhanced not only by increased temperature but also by Na_2SO_4 and NiO, both of which are present in SRP waste.

PROCESSABILITY

Vitrification of all waste - both salt and sludge - would require a dramatic increase in the amount of glass produced. In the current reference process, 15000 tons of glass will be produced during vitrification of sludge and radioactive components of the salts.[13] After decontamination, the nonradioactive salts, which constitute 88% of the waste, can then be disposed of as low-level waste. One CAS composition, P-19, (whose waste loading is determined not by the radionuclides in the sludge but by sodium in the salts) requires 233,000 tons of glass to vitrify the same waste, a factor of 15.5 more. The concentration of radionuclides in P-19 is lower than in 131/Stage 1 by this same factor, of course, but is still high enough to require shielded facilities, and isolation in a geologic repository.

Not only will some 15 times more glass be required, but it is also said that all of the waste can be immobilized in only three years, as opposed to the 15-20 years presently estimated for the DWPF. The overall glass production rate would have to increase by a factor of 75 (17700 lb/hr). Large furnaces in the glass industry often produce glass at a rate of 20-25 lb of glass/hr ft^2. If one assumes that a slurry-fed melter can produce glass at this same rate, the melting area required is 770 ft^2, or 25-30 melters the size of that currently being designed for the DWPF.

Vitrification of both salt and sludge also poses other problems. Since the waste is mostly neutralized nitric acid, it is very high in nitrates. If these are fed to the melter directly, copious amounts of NO_x will be produced. Furthermore, since nitrate is a strong oxidizing agent, the molybdenum electrodes would be in jeopardy. Treatment of the waste before it enters the melter is a possible solution to these problems. Treatment of the wastes with a reductant, such as charcoal, to run the melter under reducing conditions, the preferred operating mode, can present potentially severe explosion problems from reaction of nitrates with organics.

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13. Calculated by assuming that 500 canisters containing 1-1/2 tons of glass each will be produced per year for about 20 years.

TABLE 1

Glass Compositions (Wt %)*

Component	Calcia-Alumina-Silicate Glasses P-19	PTG-1	PTG-3	PTG/Stage 1	131/Stage 1
SiO_2	67.7	54.6	50.5	49.0	43.7
Na_2O	14.0	16.9	15.5	15.0	13.3
Li_2O	-	-	-	-	3.9
Cs_2O	0.5	0.5	0.5	0.5	0.5
CaO	9.9	10.2	10.1	9.8	1.5
SrO	0.5	0.5	0.5	0.5	0.5
NiO	0.1	0.1	0.4	1.0	1.1
MgO	-	2.4	4.6	4.4	1.4
Al_2O_3	6.0	12.9	12.2	4.2	4.7
Fe_2O_3	0.4	0.5	1.6	5.7	6.4
FeO	0.4	0.4	1.4	5.1	5.8
Dy_2O_3	0.5	0.5	0.5	0.5	0.5
B_2O_3	-	-	-	-	10.3
MnO	-	0.2	1.2	2.5	2.9
Zeolite	-	0.2	1.0	1.8	2.0
TiO_2	-	-	-	-	0.7
ZrO_2	-	-	-	-	0.4
La_2O_3	-	-	-	-	0.4
NaCl	-	0.1	-	-	-

*Assuming one-half of Fe_2O_3 is converted to FeO, and that MnO_2 is completely converted to MnO.

TABLE 2

Results of Equilibrium pH Test

Glass	pH After 24 Hrs. at 90°C
P-19	10.48
PGS	10.43
PTG-1	10.43
PTG-3	10.44
131/Stage 1	10.05

TABLE 3

Leach Rates of CAS and 131/Stage 1 Glasses

pH	Leach Rates Based on Cs Analysis ($gm^{-2}d^{-1}$) P-19	PGS	PTG-1	PTG-3	131/Stage 1
4	0.64	0.21	0.16	0.51	1.06
7	0.28	0.12	0.08	0.13	0.29
10	0.11	0.08	0.10	0.13	0.14
Equil.	0.06	0.08	0.06	0.05	0.09

pH	Leach Rates Based on Sr Analysis ($gm^{-2}d^{-1}$) P-19	PGS	PTG-1	PTG-3	131k/Stage 1
4	0.30	0.08	0.09	0.48	0.42
7	0.01	0.01	0.01	0.01	0.01
10	0.01	0.01	0.01	0.01	0.02
Equil.	0.08	0.06	0.03	0.02	0.02

pH	Leach Rates Based on Dy Analysis ($gm^{-2}d^{-1}$) P-19	PGS*	PTG-1	PTG-3	131/Stage
4	0.14	-	0.04	0.29	0.27
7	0.01	-	<0.01	<0.01	0.01
10	<0.01	-	<0.01	<0.01	0.01
Equil.	0.02	-	0.02	0.01	0.05

*This glass, provided by Penberthy Electromelt, contained no detectable Dy.

pH	Leach Rates Based on Si Analysis of Leaching Solutions and Calculated Si Content of Glass ($gm^{-2}d^{-1}$) P-19	PGS*	PTG-1	PTG-3	131/Stage 1
4	0.09	0.01	0.04	0.15	0.14
7	0.04	0.03	0.03	0.07	0.06
10	0.11	0.06	0.06	0.06	0.09
Equil.	0.13	0.17	0.09	0.09	0.30

*Based on Si content of glass assumed equal to that of P-19.

TABLE 4

Semivolatile Loss After 65 Hours

Glass	Semivolatiles Lost (Wt % of Glass)
PTG-1	6.22
PTG-3	4.96
PTG/Stage 1	3.76
P-19	3.09
131/Stage 1	1.14

TABLE 5

Corrosion Rates (Mil/Day)

Material		PTG-1[a]	PTG-3[a]	PTG/ST1[a]	P-19[a]	131/TDS[b]
Molybdenum		3.9	4.3	5.6	2.7	-
Inconel 690		-	-	-	-	0.33
Monofrax K-3	(Melt Line)	3.1	2.0	0.98	2.5	1.2
Monofrax K-3	(Half-down)	0.38	0.30	0.52	0.63	0.07

a) at 1380°C
b) at 1150°C