WSRC-TR-97-0004

Glass Formulation Requirements for DWPF Coupled Operations Using Crystalline Silicotitanates(U)

by

J. R. Harbour

Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808

M. K. Andrews

DOE Contract No. DE-AC09-96SR18500

DISCLAIMER

WESTINGHOUSE SAVANNAH RIVER COMPANY
SAVANNAH RIVER TECHNOLOGY CENTER

WSRC-TR-97-0004
Revision 0

Keywords: TFA, CST, Cesium, DWPF, ORNL, Coupled

January 9, 1997

GLASS FORMULATION REQUIREMENTS FOR DWPF COUPLED OPERATIONS USING CRYSTALLINE SILICOTITANATES (U)

Mary K. Andrews and John R. Harbour
Westinghouse Savannah River Company
Savannah River Technology Center
Aiken, South Carolina

INTRODUCTION

The design basis DWPF flowsheet couples the vitrification of two waste streams: (1) a washed sludge and (2) a hydrolyzed sodium tetraphenylborate precipitate product, PHA. The PHA contains cesium-137 which had been preciptitated from the tank supernate with sodium tetraphenylborate. Smaller amounts of strontium and plutonium adsorbed on sodium titanate are also present with the PHA feed. Currently, DWPF is running a sludge-only flowsheet while working towards solutions to the problems encountered with In Tank Precipitation (ITP). The sludge loading for the sludge-only flowsheet and for the anticipated coupled operations is 28 wt% on an oxide basis[1]. For the coupled operation, it is essential to balance the treatment of the two waste streams such that no supernate remains after immobilization of all the sludge. (Under the current plans, this will involve filling over 5,000 canisters in ~ 20 years[1]).

An alternative to ITP and sodium titanate is the removal of Cs-137, Sr-90, and plutonium from the tank supernate by ion exchange using crystalline silicotitanate (CST)[2]. This material has been shown to effectively sorb these elements from the supernate[2]. It is also known that CST sorbs plutonium[2]. The loaded CST could then be immobilized with the sludge during vitrification. It has recently been demonstrated that CST loadings approaching 70 wt% for a CST-only glass can be achieved using a borosilicate glass formulation which can be processed by the DWPF melter[3]. Initial efforts on coupled waste streams with simulated DWPF sludge show promise that a borosilicate glass formulation can incorporate both sludge and CST. This paper presents the bases for research efforts to develop a glass formulation which will incorporate sludge and CST at loadings appropriate for DWPF operation.

DWPF BACKGROUND

During the anticipated coupled operation at DWPF, glass will be produced that contains 28 wt% sludge oxides and 8 wt% oxides from precipitate processing. The remaining 64 wt% will be the borosilicate frit. The 28 wt% sludge will be the minimum acceptable loading for the CST- coupled formulation work.

The design basis glass for the DWPF coupled operation contains 4.33E+04 Curies of Cs-137 per canister[1] (based on 3,700 pounds of glass/canister). Since there are 1.153E-02 grams of Cs-137/Ci, each DWPF canister will contain 499 grams of Cs-137. For a canister containing 1678 kg (3,700 lbs), this is equivalent to a 0.03 wt% loading of Cs-137 in the glass. This 0.03 wt% Cs-137 loading must be achieved or exceeded in order for CST to be a viable alternative for the DWPF. Since the Cs-137 accounts for approximately 38 atom% of the cesium present in the supernate, the total cesium concentration in the glass must be at least 0.08 wt% .

CST CAPACITY

Capacity measurements for Cs-137 loading on CST have been performed using a DWPF simulated salt solution. McCabe has demonstrated a range of 1.2 to 4.6 wt% cesium sorption on powdered CST depending upon the cesium concentration in solution (for fixed sodium and potassium levels). For the DWPF supernate, which contains 38 atom% Cs-137, these values translate to 0.5 to 1.8 wt% Cs-137 sorption on the CST. The measured capacities of CST for Cs at various concentrations of Cs in solution are provided in Table 1.

TABLE 1
CESIUM CAPACITY MEASUREMENTS ON CST FROM McCABE, WSRC-RP-94-1123 (@5.6 M NaOH AND 0.015 M KNO_3)

Initial [Cs]	Kd	Cs/g CST	
mg/L	mL/g	mg	(wt%)
28.25	1948	11.59	(1.2%)
48.67	1971	19.73	(2.0%)
63.17	1980	24.7	(2.5%)
74.41	1796	28.76	(2.9%)
117.2	1094	40.31	(4.0%)
139	988	45.61	(4.6%)

CST GLASS LOADING REQUIREMENTS

A 0.03 wt% loading of Cs-137 in the final glass waste form must be achieved for a balanced coupled operation. Table 2 provides the required Cs-137 loading on CST (for various loadings of CST in glass) that will meet the overall 0.03 wt% Cs-137. These results are plotted in Figure 1. (Figure 1 presents data up to 20 wt% CST in glass. Table 2 provides CST loadings in glass up to 40 wt%.)

At 5 wt% CST in glass, a loading of 0.6 wt% Cs-137 must be achieved. However at 20 wt% CST, the amount of Cs-137 sorbed must reach only 0.15 wt% Cs-137. This corresponds to 0.127 Ci/g CST. At 40 wt% CST, the amount of Cs-137 sorbed on CST must reach 0.07 wt%. The path forward (see below) will use these data to provide some flexibility, if possible, for the use of CST as a replacement for ITP for the DWPF.

TABLE 2

CST GLASS LOADING REQUIRED AS A FUNCTION OF SORBED Cs-137 FOR 0.025 Ci/g GLASS

GLASS CST Loading (wt%)	CST Ci Cs137/g CST	CST Wt% Cs-137
1	2.547	2.94
2	1.274	1.47
3	0.849	0.98
4	0.637	0.73
5	0.509	0.59
6	0.425	0.49
7	0.364	0.42
8	0.318	0.37
9	0.283	0.33
10	0.255	0.29
11	0.232	0.27
12	0.212	0.25
13	0.196	0.23
14	0.182	0.21
15	0.17	0.2
16	0.159	0.18
17	0.15	0.17
18	0.142	0.16
19	0.134	0.15
20	0.127	0.15
25	0.102	0.12
30	0.085	0.1
35	0.073	0.08
40	0.064	0.07

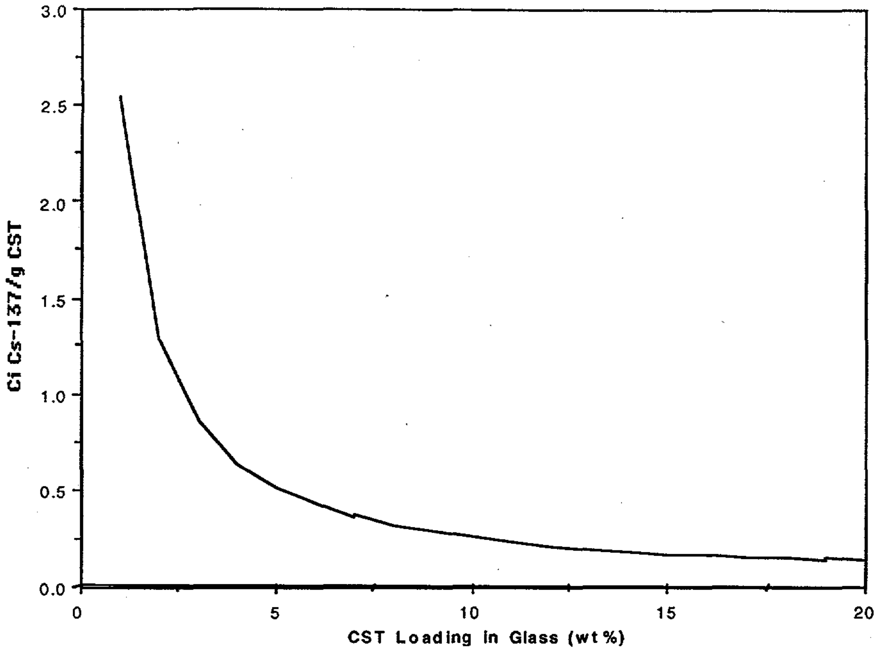

Figure 1. Curie Loading on CST a a function of CST Loading in the Glass

DWPF TANK CHEMISTRY

It is clear that the capacity of the CST for cesium will depend on the chemistry of the supernate. For example, an increase in potassium concentration at a constant sodium concentration will reduce the capacity of the CST for cesium.[2] The DWPF tank supernate has significant, variable quantities of dissolved potassium[4] (see Table 3). Another variable affecting the amount of cesium sorbed is the concentration of Cs in the supernate at constant sodium and potassium levels (see Table 1). For DWPF, the Cs concentrations in the supernate are variable[4] (Table 3). Therefore, any glass formulation developed for the coupled operation may have to accomodate the Cs-137, Na, and K variations. (Pretreatment of the supernate to optimize Cs, Na, or K concentrations may be possible.) Table 3 provides the sodium and potassium concentrations along with the Cs-137 levels for various tank supernates. These particular tank supernates are expected to be the first supernates which will be treated in ITP. Although saltcake will eventually be redissolved and treated, its effect is not included in this report.

An Operational Safety Requirement (OSR) limits the total sodium concentration in the supernate to 5 M with the added requirement that hydroxyl ion concentration can not exceed half of the sodium level (2.5 M). Thus, dilution of these tank supernates may be necessary. The concentrations of cesium at 5M sodium are therefore included in Table 3.

TABLE 3
DWPF TANK CHEMISTRY

	Na (Molar)	K (Molar)	TOTAL OH (Molar)	Cs-137 (mg/L)	Cs-137 @ 5M Na
TANK 25	13.6	0.17	10.6	13	4.8
TANK 26	16.7	0.18	15.2	16.7	5
TANK 27	12.1	0.14	9.9	11.4	4.7
TANK 28	13.2	0.13	8.5	13.5	5.1
TANK 29	14	0.086	6.5	33.8	12.1
TANK 30	9.1	0.039	3.9	24.9	13.7
TANK 32	5.3	0.019	2.1	11.4	10.8
TANK 38	19.1	0.083	9.6	11.4	3
TANK 43	14.4	0.085	10.4	7.8	2.7

For the supernates listed in Table 3, the concentrations of Cs-137 range from 7.8 to 33.8 mg/L . Dilution to 5 M Na^+ reduces the Cs levels and leads to a Cs-137 range of 2.7 to 13.7 mg/L. Assuming a linear extrapolation of McCabe's data to zero, one can calculate capacities for those cesium concentrations below that actually measured by McCabe. From the data in Table 2, one can then obtain the amount of CST which must be incorporated into the glass to achieve the required 0.03 wt% Cs-137. These results (some of which were taken from within McCabe's data range and some from extrapolation) are summarized in Tables 4 and 5.

TABLE 4
RANGE OF Cs-137 AND TOTAL Cs CONCENTRATIONS IN DWPF TANK SUPERNATES

	CONCENTRATED RANGE	DILUTED RANGE
Cs-137 (mg/L)	7.8 - 33.8	2.7 - 13.7
Total Cs (mg/L)	20.53 - 88.95	7.11 - 36.05

TABLE 5
RANGE OF Cs-137 AND TOTAL Cs SORBED ON CST AND CORRESPONDING CST LOADINGS IN GLASS

	CONCENTRATED RANGE	DILUTED RANGE
Cs/CST (wt%)	0.86 - 3.51	0.3 - 1.5
Cs-137/CST (wt%)	0.33 - 1.41	0.12 - 0.57
CST/Glass (wt%)	9 - 2	27 - 5

ORNL DEMONSTRATION

ORNL is in the middle of a demonstration[5] in which supernate from the Melton Valley Storage Tanks (MVST) is being treated with CST. ORNL was only able to sorb Cs-137 at 0.007 Ci/g CST. This is much less sorption than measured by McCabe with the DWPF surrogate supernate.

The reason for this low sorption appears to be related to the very low amount of cesium in solution. The MVST supernate contains only 0.58 ppm total cesium and 0.14 ppm of Cs-137. This can be compared to McCabe's lowest value of 28.8 mg/L or ~28.8 ppm total cesium. The difference is ~50 times less Cs-137 in the MVST than in the DWPF supernate surrogate. The sodium concentration in the MVST supernate is 4.1 Molar (95400 ppm) and is relatively close to that used by McCabe for the DWPF study. However, the potassium concentration in the MVST supernate is 14700 ppm or 0.4 molar. This is almost an order of magnitude higher than the concentration of potassium in the DWPF supernate. Since potassium competes with cesium for sorption, the higher levels of potassium could also account for lower cesium sorption.

If one extrapolates McCabe's data to 0.14 ppm Cs-137, then the expected sorption of Cs on CST would be 0.006 wt%. ORNL measured a value of 0.008 wt%. This good agreement suggests that that the level of cesium in solution may be the major reason why ORNL has lower sorption of cesium.

PATH FORWARD

Two separate cases for glass formulation development are proposed in order to account for the uncertainties in the amount of Cs-137 which will load on CST and to provide limits for processing options.

Case 1. CONCENTRATED In the first case it is assumed that the amount of Cs sorbed is roughly equivalent to that demonstrated by McCabe using a surrogate DWPF supernate. A glass which incorporates 6% CST (with a loading of ~0.5 wt% Cs-137 on the CST) would yield a glass with 0.03 wt% Cs-137, the value which is needed by DWPF to equalize the sludge and supernate. Therefore, a value near 5 wt% CST in the glass was chosen as a goal for Case 1. The sludge loading may be varied but will maintain at least a 28 wt% loading in the glass.

Case 2. DILUTED In this case, it is assumed that the amount of cesium sorbed on the CST may vary considerably. For tanks with supernates having low concentrations of cesium or high concentrations of competing ions, the amount of cesium sorbed on the CST may be less than reported by McCabe. Options for processing may also lead to a reduction in the amount of cesium sorbed by the CST. Therefore, an attempt will be made to maximize the amount of CST which can be incorporated in the glass along with the sludge. This will provide an upper limit for the amount of CST and consequently, a range for the amount of cesium which can be successfully loaded into a borosilicate waste glass containing DWPF sludge.

REFERENCES

1. M. J. Plodinec and S. L. Marra, **Projected Radionuclide Inventories and Radiogenic Properties of the DWPF Product (U),** WSRC-IM-91-116-3, Rev. 0, October, 1994.

2. R. Braun, T. J. Dangieri, D. J. Fennelly, J. D. Sherman, W. C. Schwerin, R. R. Willis et al, **Crystalline Silicotitanates-Novel Commercial Cesium Ion Exchangers**, Spectrum '96, Seattle, Washington, August 1996.

3. M. K. Andrews and J. R. Harbour**, Effect of CST Ion Exchange Loading on the Volume of Glass Produced During the Vitrification Demonstration at SRTC (U),** WSRC-TR-96-0372, Rev. 0, November, 1996.

4. R. S. Ondrejcin, **Chemical Compositions of Supernates Stored in SRP High Level Waste Tanks**, DP-1347, UC-70, Rev. 0, August, 1974.

5. J. F. Walker Jr., **LMER Pretreatment TPP**, OR1-6-WT-41, October, 1996.