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DISPERSION OF SIMULATED HIGH-LEVEL RADIOACTIVE WASTE POWDERS
IN A GLASS MATRIX

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ABSTRACT

High-level waste powders such as those from the Fluidized-Bed Volatility Process (FBVP) or those from spray calcination of waste solutions from aqueous fuel processing schemes may require some treatment beyond sealing the untreated powder in a disposal pot. These powders may be dispersed (not dissolved) in a glass matrix to yield a two-phase powder-glass system with improved chemical and physical properties. Representative materials from the spray calcination of Purex waste and from the Fluidized-Bed Volatility Process were changed from free-flowing dusty powders to hard, strong, void-free solids by dispersing them in lead-silicate glasses. The thermal conductivity of a FBVP powder in air was $0.25 \text{ Btu hr}^{-1} \text{ ft}^{-1} (\text{°F})^{-1}$ while the thermal conductivity of this powder dispersed in glass was $1.22 \text{ Btu hr}^{-1} \text{ ft}^{-1} (\text{°F})^{-1}$ — a fivefold increase in conductivity. The leach rate of ^{137}Cs from this powder was lowered by a factor of 1000 by dispersion in glass. The dispersion process was operated in both a batch and semicontinuous manner using a 2-in.-diam, 12-in.-high type 304 stainless steel pot in a 5-kw furnace.

The dispersion process appears intrinsically more flexible and versatile than a process that dissolves the waste solids. Also, dispersions gave volume reductions as good as, or better than, those of solid solutions incorporating the same quantity of waste.

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1. INTRODUCTION

Laboratory development work has indicated that some treatment of high-level radioactive waste powders may be required before they are sealed in a can. The powders may be too unstable, too poor thermal conductors at storage temperatures, or they may be too water soluble for safe interim storage and for safe transport to final storage. Dispersion of the waste powders in a glass matrix will improve the physical and chemical stability and the thermal conductivity, as well as decrease the solubility of the powders. Spray-calcined simulated Purex waste powder and simulated waste powders from the Fluidized-Bed Volatility Process (FBVP) were dispersed in lead-silicate glasses. This work indicated that zone heating and matching the particle sizes of the glass powder to those of the waste powder yielded the best product; that is, hard with few voids. No further work is planned immediately with this system, since responsibility for the study of the dispersion of FBVP waste powders in glass has been assigned to Brookhaven National Laboratory.

2. EQUIPMENT AND PROCEDURE

The experimental apparatus for the dispersion of waste powders in a glass matrix consisted basically of a stainless steel pot in a furnace with ancillary equipment such as a powder mixer-conveyor and temperature sensing and control devices. Figure 1 is a schematic diagram of the 2-in.-diam, 12-in.-high type 304 stainless steel pot in a 5-kw furnace with three independently controlled temperature zones. The temperature of the specimen was determined by means of a thermocouple which was movable within a thermocouple well (1/4-in. stainless steel tube) that extended the length of the pot (see Fig. 3). A photograph of the experimental apparatus is shown in Fig. 2.

Experiments were carried out in which spray-calcined simulated Purex waste (obtained from Pacific Northwest Laboratory, PNL) and simulated waste powders from the FBVP were dispersed in lead-silicate glasses. Physical and chemical properties of the powders and glasses used are given in Tables 1 and 2. The waste

Fig. 1. Schematic Diagram of Apparatus for the Dispersion of Waste Powders in a Glass Matrix.

Fig. 2. Experimental Apparatus for the Dispersion of Waste Powders in a Glass Matrix.

Fig. 3. Dispersion of $\text{Al}_2\text{O}_3\text{-AlF}_3$ Powder in Lead-Silicate Glass (Pemco 716B). Dispersion contains 35.4 wt % simulated waste powder and 64.6 wt % glass (see Table 1, experiment 13).

Table 1. Chemical Properties of Materials Used in Studies on Dispersion of Waste Powders in Glass.

Chemical Composition	Material ^a (wt %)						
	Alcoa T-61	FBVE 11	Norton RR	Purex Calcine	Pemco PB-41	Pemco PB-716	Pemco PB-716B
Na ₂ O	0.02	--	0.50	4.43	--	--	--
Al ₂ O ₃	99.5+	83.73	99.28	--	--	--	--
SiO ₂	0.06	--	0.05	--	13.4	26.8	26.8
Fe ₂ O ₃	0.06	2.73	0.15	28.3	--	--	--
U ₃ O ₈	--	0.24	--	--	--	--	--
Cr ₂ O ₃	--	0.45	--	--	--	--	--
NiO	--	0.37	--	--	--	--	--
AlF ₃	--	10.22	--	--	--	--	--
Na ₂ SO ₄	--	--	--	23.73	--	--	--
NaNO ₃	--	--	--	16.75	--	--	--
PbO	--	--	--	--	72.2	67.6	67.6
B ₂ O ₃	--	--	--	--	9.0	--	--
CaO	--	--	--	--	--	5.6	5.6
ZnO	--	--	--	--	5.4	--	--

^aComposition of Corning 8463 is proprietary information of the Corning Glass Company.

Table 2. Physical Properties of Materials Used in Studies on Dispersion of Waste Powders in Glass.

Material	Screen Size (U.S. Standard Mesh)	Mass Mean Particle Size (μ)	Standard Deviation (μ)	Pore Free Density (g/cc)	Bulk Density (g/cc)
Waste powders					
Alcoa T-61	-14 +14C	419	156	3.72	1.56
FBVE 11	-100 +400	108	22.5	3.84	1.65
Norton RR	-30 +400	96	27	3.95	1.67
Purex calcine	-20 +400	138	162	3.50	0.79
Glass powders					
Corning 8463	<230	39.7	18	6.30	3.46
Pemco PB-41	<200	48	25	5.97	2.76
Pemco 716	<200	29	15.5	5.35	2.68
Pemco 716B	-80 +200	131	32	5.57	2.33

powder and glass frit were mixed in the approximate ratio of 1-to-2 by weight in all experiments. Glass frit with particle sizes less than those of the waste powders and glass frit with particle sizes about the same as those of waste powders were used. The thirteen experiments are summarized in Table 3. A rising-level technique for filling the storage pot was used in the first seven experiments. In this technique, the mixed waste and glass powders were added continuously at a rate approximately equal to the rate at which the glass melted, until the pot was full. The feed rates varied from about 1 to 5 g/min with mixed powders. (The small scale of the equipment precluded meaningful process rate studies.) In the remaining six experiments, the pot was filled with the mixed powders while being tapped. The filled pot was placed in the furnace and heated to temperature.

Three modes of heating were used. In the three initial experiments (Table 3, experiments 1, 2, and 3), the pot was heated to temperature and the feed to it was started. In the next eight experiments, the feed to the pot was started (Table 3, experiments 4, 5, 6, and 7) or the filled pot was placed in the furnace (Table 3, experiments 8, 9, 10, and 11), and the heating of the furnace was then begun. In all the above experiments the three zones of the furnace were heated simultaneously and to the same final temperature. Zone heating was utilized in two experiments (Table 3, experiments 12 and 13). In experiment 12 the bottom zone was heated to 900°C. After 4 hr the middle zone was turned on and heated to 900°C, and after 4 more hours the top zone was turned on and heated to 900°C. In experiment 13, power was turned on to all zones at the same time; however, the temperature rise of each zone was manually programmed so that the temperature of the bottom zone rose fastest, about 14°C/min, and the top rose the slowest, about 10°C/min, to the final temperature of 790°C.

3. RESULTS

Spray-calcined Purex waste powder (from PNL) and simulated FBVP waste powders were successfully dispersed in lead-silicate glass matrices. The stainless steel pots were sawed lengthwise to evaluate the products and the corrosion of

Table 3. Summary of Laboratory Tests for Dispersion of Waste Powders in Glass.

Expt. No.	Composition (wt %)		Maximum Temperature (°C)	Time at Maximum Temperature (hr)	Product Quality (% Voids)
	Waste Powder	Glass			
1	35.4% Alcoa T-61	64.6% Corning 8463	770	1.5	40 - 50
2	36.6% Alcoa T-61	63.4% Corning 8463	925	3.5	40 - 50
3	38.5% Alcoa T-61	61.5% Pemco PB-41	935	3	40 - 50
4	34.5% Norton RR	65.5% Pemco 716	940	4	4 - 5
5 ^a	33.0% FBVE 11 3.7% CaO	63.3% Pemco 716	920	10	40 - 50
6	33.3% Purex calcine	66.7% Pemco 716	905	5.5	2 - 3
7	33.3% Purex calcine	66.7% Pemco 716	930	15	2 - 3
8 ^b	32.9% Norton RR 5.1% $\text{Al}_2\text{F}_6 \cdot x\text{H}_2\text{O}$	62.0% Pemco 716	950	13	20 - 25
9 ^b	32.9% Norton RR 5.1% $\text{Al}_2\text{F}_6 \cdot x\text{H}_2\text{O}$	62.0% Pemco 716	940	18	20 - 25
10 ^b	32.9% Norton RR 5.1% $\text{Al}_2\text{F}_6 \cdot x\text{H}_2\text{O}$	62.0% Pemco 716	930	18	20 - 25
11 ^b	32.9% Norton RR 5.1% $\text{Al}_2\text{F}_6 \cdot x\text{H}_2\text{O}$	62.0% Pemco 716	950	20	10 - 15
12 ^b	32.9% Norton RR 5.1% $\text{Al}_2\text{F}_6 \cdot x\text{H}_2\text{O}$	62.0% Pemco 716	900	24	10 - 15
13	34.2% Norton RR 1.2% Al_2F_6	64.6% Pemco 716B	790	1.5	2 - 3

^aFBVE 11 contained 1.7 wt % H_2O , and the CaO contained 1.1 wt % H_2O .

^b $\text{Al}_2\text{F}_6 \cdot x\text{H}_2\text{O}$ contained 62 wt % Al_2F_6 and 33 wt % H_2O .

the pots. All experiments (Table 3) produced hard products, but some products contained too many voids (10 to 50%). Too many voids were undesirable, since they will lower the thermal conductivity and volume reduction (volume of waste per volume of product) of the system significantly. Good products were those that were hard, strong, and had only a few percent voids. Experiments 6 and 7 produced good products with spray-calcined Purex waste. These products represented volume reductions the same (about a factor of 10) as those obtained in processes forming ceramics or single-phase glasses with this waste. Experiment 13 produced the best product with FBVP powders (Fig. 3). This experiment also showed that a temperature less than 800°C was sufficient for operation with Pemco 716 glass and that the earlier use of temperatures greater than 900°C with this glass was not necessary to produce a good product in this arrangement of equipment. This dense, hard, almost void-free product seemed to be a result of both zone heating and matching of the particle sizes of the glass to those of the waste. Since the glass merely fills the interstices of the FBVP powder, the volume of waste to be stored would be the same for the untreated powder and for the dispersion. Products with a very high percentage of voids (40 to 50%) were made with glass powders that contained B_2O_3 (Table 3, experiments 1, 2, and 3). The very high percentage of voids in experiment 5 (Table 3) is probably explained by the fact that FBVE 11 contains an appreciable quantity of volatile fluorides. Products with moderately high percentages of voids (10 to 25%) were made with powders that contained about two percent moisture (Table 3, experiments 8, 9, 10, 11, and 12). In passing, it is worthy of note that in earlier small-batch experiments with FBVP and glass powders, all mixtures (40 out of 130) with glasses containing B_2O_3 had a very high percentage of voids. Thus B_2O_3 seems to cause excessive bubbling in this system. Moisture seems to cause voids, since the steam formed is trapped in the matrix. No apparent corrosion of the stainless steel pots was observed in any of the 13 experiments.

Thermal conductivities of a FBVP waste powder in glass dispersion and a waste powder in air were measured. The conductivity of the dispersion was $1.22 \text{ Btu hr}^{-1} \text{ ft}^{-1} (\text{°F})^{-1}$ at 140°F, while that of the powder in air was 0.25 at this temperature.

Thus the dispersion represents about a fivefold improvement in thermal conductivity over the untreated waste powder.

Leach tests were made to compare the solubility of the waste powders and the glass dispersions in water. Waste powder was spiked with ^{137}Cs . A 50-g charge of the powder was dispersed in glass to give a 2.25-in.-diam, 0.5-in.-high right circular cylinder with a surface area of 11.49 in.². This glass sample and a 50-g powder sample were placed in separate 1-liter polyethylene bottles. A volume of 500 ml of distilled water was added to each bottle, and the bottles were placed on a mechanical shaker which shook them continuously. The leachate was completely removed daily from the powder sample and weekly from the glass sample and was replaced by fresh water. The entire leachate sample was submitted for chemical analysis. The solubility of the powder as compared with the relatively insoluble glass dispersion is shown in Fig. 4. For example, after 11 days of leaching, the leach rate of ^{137}Cs from the glass dispersion was about one-thousandth that of the waste powder, namely, 9.5×10^{-7} vs 1.1×10^{-3} fraction of original amount leached per day.

4. CONCLUSIONS AND RECOMMENDATIONS

The experiments showed that the dispersion-in-glass process works equally well for Purex waste calcine (basically Fe_2O_3 and Na_2SO_4) and a fluidized-bed waste (basically Al_2O_3 and AlF_3). Further, they showed that raising the temperature of the material by zones and that matching of the particle sizes of the glass frit to those of the waste powder yielded the superior product. The thermal conductivity of the waste product to be stored is increased if waste powders are dispersed in glass. This makes it possible to store the waste sooner, or in larger pots, without exceeding some predetermined safe temperature for the system. Leach studies indicate that dispersion of the powder in glass significantly reduces solubility and, therefore, provides a safer material for transport and storage.

Fig. 4. Comparison of Leaching of Waste Powder and Powder Dispersed in Glass.

Dispersion of waste solids in glass matrices (two-phase systems) has several apparent advantages over dissolving the solids to form solid solutions (single-phase systems). These apparent advantages over single-phase glasses and ceramics need to be evaluated further. For example, the softening point of the two-phase dispersions is set by that of the continuous phase. Thus a large number of low-melting (800°C or below), fairly noncorrosive, readily available commercial glasses can be used as matrices on an as-received basis. This means that the dispersion process can be carried out in containers made of stainless steel or other nonnoble metals. For a given quantity of waste solids contained in the mass to be stored, dispersions give as good volume reductions and as low leach rates as solid solutions, and higher thermal conductivities than single-phase glasses. In fact, for FBVP powders the volume to be stored would be 2 to 3 times greater if the powder were dissolved to give a good single-phase glass. This is true because of the solubility limits of the constituents making up the powder. As mentioned previously, the FBVP powder and the powder dispersed (not dissolved) in a matrix occupy the same volume. The dispersion process is intrinsically more flexible and versatile than a process that dissolves the waste solids. This is so since dispersion is basically a problem involving physical properties (mixing and melting) and not both physical and chemical properties (mixing, melting, network or compound formation, solubility limits, eutectics, etc.). A good commercial glass can accommodate a wide range and amount of inert powders, independent of their origin, as a second phase at a fixed temperature. However, if any of these powders must be dissolved, the kind and amount of chemical additives become more important and restricted. In addition, the temperature of the operation is no longer an independent variable but is fixed by the chemical system. Thus the dispersion process seems to offer the possibility of producing stable, nonleachable solids for long-term storage using fixed equipment, at a fixed reasonable temperature, with a fixed mode of operation for a wide variety of wastes. All these conditions lend themselves to smooth, trouble-free plant operation — especially remote operation.

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