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REPORT

SOLIDIFICATION
OF HIGH LEVEL WASTES
PART IV

Phosphate Melts
for Fixation of Radioactive Residues
from Purex Type Wastes
Three to Fifty Per Cent
Fission Product Oxides

July, 1965

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PACIFIC NORTHWEST LABORATORY

RICHLAND, WASHINGTON

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SOLIDIFICATION OF HIGH LEVEL WASTES - PART IV

PHOSPHATE MELTS FOR FIXATION OF RADIOACTIVE RESIDUES FROM
PUREX TYPE WASTES - THREE TO FIFTY PER CENT FISSION PRODUCT OXIDES

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July, 1965

PACIFIC NORTHWEST LABORATORY
RICHLAND, WASHINGTON

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SOLIDIFICATION OF HIGH LEVEL WASTES - PART IV

PHOSPHATE MELTS FOR FIXATION OF RADIOACTIVE RESIDUES FROM
PUREX TYPE WASTES - THREE TO FIFTY PER CENT FISSION PRODUCT OXIDESINTRODUCTION

Various types of melts have been proposed to form glasses or ceramics to incorporate the radioactive waste products from the reprocessing of nuclear fuels. These have included primarily silicates, phosphates and borates, singly or in combination.

Considerable scouting work⁽¹⁾ at this laboratory led to the choice of the phosphate system as the first one to investigate on the basis of the following considerations: (1) Addition of phosphoric acid to the waste solution before final evaporation and drying would be the simplest process step. This would eliminate problems connected with metering and conveying solids or slurries. (2) Phosphates are generally lower melting and less viscous than silicates. (3) Borates have a tendency to form two liquid phases. This formation of two phases may result in undesirable segregation or concentration of certain fission products.

With the decision made that phosphates would be the choice for investigation first, it became necessary to then consider what simulated waste composition should be used to represent the actual plant product. Simulation is desirable because the activity associated with full-level waste makes direct experimentation with it slow and costly. In addition it has been found that the composition of the waste varies with operating conditions in the plant. Also, any power reactor fuels to be processed will contain large and variable quantities of fission products. Therefore, to provide knowledge on which to operate a process, one needs to know the composition range over which one can operate.

The experimental plan finally adopted provides for determining the properties of phosphate melts corresponding to a wide range of fuel exposure and process conditions.

Another choice which must be made concerns which of the many desirable properties of a solid are the most significant. Desirable properties for the ideal waste fixation form would include high thermal conductivity; low thermal expansion; low leachability; low melting or processing temperature; homogeneity; low melt viscosity; good mechanical strength; retention of sulfate; insensitivity of properties to variation in composition of the waste to be processed; no difficulties in the processing equipment such as dryer, filter, melter, storage vessel; and low corrosive properties either in final form or at any of the stages of production.

For this work it was decided that processing temperature and solubility would be the main screening criteria.

SUMMARY

The possible composition range for the high-level radioactive wastes generated from various power reactor fuels processed through a Purex-type process is very broad. This report covers a partial survey of this wide range in an effort to establish the composition limits that bound the operable range of the phosphate melt system. Two screening criteria have been used: (a) drip temperature, an empirical measure of flow temperature at which a container could be filled, and (b) solubility. Measurements have indicated the occurrence of two (or possibly more) optimum phosphate additions near M_2O/P_2O_5 ratios of 2.1 and 1.0.

It has been found that fission products equivalent to at least 50% of the weight of oxides in the plant waste can be successfully incorporated in

a phosphate melt that can be transferred as a fluid into containers at less than 900 C.

EXPERIMENTAL

Composition

A few representative compositions of wastes that might be turned out by a plant using the Purex process on fuels exposed to various levels are presented in Table I. Since considerable prior work^(1c) has been done on the effect of varying cation ratios for the orthophosphate system, some background was available. In view of this and the multiplicity of variables, it was decided to standardize on one process composition and one fission product composition, and to combine these in various ratios. The compositions used are presented in Table II. The two solutions were combined in proportions calculated to yield mixtures of oxides containing 3, 10 and 50 per cent fission products. This mixture in turn was combined with phosphoric acid to give the desired ratio of cations to phosphate.

The precious metal ions of ruthenium, rhodium and palladium are absent from the fission product simulation mixture. A series of experiments demonstrated that their absence would result in only a slightly higher drip temperature. It was decided this erroneous indication in the conservative direction could be tolerated for the survey experiments, and then defined when the compositions of greatest interest were known.

The phosphate addition was calculated to cover the range of M_2O/P_2O_5 ratios (where M_2O represents the total cation equivalents in the solution, this will hereafter be abbreviated as M/P) from that deficient to form the ortho ($M/P = 3.0$) salts to an excess of that to form the meta ($M/P = 1.0$) salts. The total range was 3.5 to 0.7, which represents a 5-fold change in the amount of phosphate added. Since some of the fission product elements

TABLE I

SOME COMPOSITIONS OF PUREX "PROCESS" WASTES

Element	Hanford ¹ Plant	FTW-65 ²	HIP ³	NFS ⁴		"Ultimate" ⁵
				1st Cycle	Combined	
Na	1.48 M	0.30	0.70	0.20	2.62	0.05
Fe	0.31	0.10	0.16	1.35	0.56	0.005
Al	0.18	0.05	0.08	----	----	0.01
Cr	0.017	0.02	0.032	0.005	0.001	0.0006
Ni	0.008	0.01	0.016	0.002	0.001	0.0006
Mo	----	----	----	0.089	0.025	----
U	0.004	----	0.001	?	?	0.001
Si	0.014	0.01	0.01	----	----	0.01
S	0.47	0.15	0.24	----	0.35	----
Volume	56 gal/MT	80	50	69	247	40

Weight Per Cent Fission Product Oxides for Various Exposure Level
Fuels Processed in Above Processes

Exposure MWD/MT						
1,000	5.4	12.5	11.2	2.9	0.82	69.5
5,000	22	42	39	13	4.0	91.9
10,000	36	59	56	23	7.6	95.8
20,000	53	74	72	38	14	
30,000	63	81	79	47	20	
40,000	69	85	83	55	25	
100,000	85	93	93	75	45	

- 1 Represents the analysis of one batch of waste used in the spray calciner work (HW 83896)
- 2 Projected waste to be produced after formaldehyde treatment is adopted in the plant.
- 3 (HW 78061) Hanford Isotopes Plant flowsheets
- 4 From ORNL-TM-1013
- 5 Possible waste from a process operated to contribute the least possible added material to the fission product waste.

TABLE IIComposition of Solutions Used in Preparing MixturesSimulated Purex Process Waste Stock

Na	1.4 M
Al	0.16
Fe	0.32
Cr	0.07
Ni	0.035
SO ₄ ⁼	0.52
SiO ₂	0.016
F ⁻	0.0016

Net cation equivalents ^{*}3.06/L, assuming the sulfate will volatilize out. All cations were added as nitrates, the sulfate as sulfuric acid, the silica as a colloidal sol (Ludox), and the fluoride as NaF.

Simulated Fission Product Waste Stock

<u>Element</u>	<u>Concentration x 10³</u>	<u>Form Added</u>
Se	1.69 M	Na ₂ SeO ₃
Rb	10.8	RbNO ₃
Sr	29.0	Sr(NO ₃) ₂
Zr	100	ZrO(NO ₃) ₂
Mo	77.8	Acidified Ammonium Molybdate
Te	9.0	TeO ₂
I	4.3	HIO ₃
Cs	45.4	CsNO ₃
Ba	21.7	Ba(NO ₃) ₂
Rare Earths	170.6	Mixed Rare Earth Nitrate Salt

Net Cation Equivalents 0.888/L

These are the fission product elements -- other than the noble gases, precious metals and technetium, that are present in excess of 1% of the amount of zirconium.

*Net cation equivalents are those available to combine with the added phosphate; i.e., they are those in excess of the quantity combined with the permanent anions of the solution. Such anions are silicate, tellurate, molybdate, etc.

normally form acidic oxides (Se, Mo, Te, I), these were allowed for in the calculation, and only the net cation equivalents indicated in Table II were used for computing the phosphate addition. It was assumed the sulfate would volatilize, but this was subject to verification by analysis of the melted products.

Prior to the present work it had been assumed that the fission products would constitute only a minor fraction ($< 3\%$) of the total oxides. When the calculations presented in Table I were made, it was apparent that this assumption was erroneous. Measurements of a simulated 10,000 MWD/T waste indicated that the drip temperature was raised 120 C by inclusion of the fission product elements. This, then, established the need to examine a wide range of fission product concentrations or fractions. A series of samples was prepared to investigate this, covering the range 3 to 100% fission products in the oxide fraction before phosphate addition. This was supposed to have been at a phosphate level 15% less than that forming the meta salt but, by now allowing for the sulfate and the acidic oxide constituents of the simulated fission product solution, the phosphate ratio actually varied from $M/P = 1.2$ to 1.5. A minimum drip temperature and maximum glassy character was observed for the sample containing 60% fission products.

The need for detailed examination of the effect of changing phosphate content was established by a sample left in a furnace at 700 C over a weekend. Initially the material just sintered at the temperature of the furnace (700 C), but on standing it melted. It was assumed that loss of phosphate could bring about this result. To determine whether there was a eutectic formed, a series of mixtures was prepared in which the M/P ratio was varied in 0.1 steps from 3.5 to 1.9 and the drip temperature of the powder was measured. This did

indeed show a minimum drip temperature. (The data are in Table III, page 15.) Accordingly, a pseudo ternary diagram was set up as a guide in planning the compositions to measure (Figure 1).

This is an interim report covering the measurements to date on the 3, 10 and 50% fission product oxide levels. The work will continue to extend the measurements to the 95% level to provide more complete knowledge of the behavior of very high burnup wastes.

Sample Preparation

Sample preparation consisted of three or four stages. As indicated above, a solution or slurry of a desired composition was first prepared and then reduced to a solid by evaporation of the water and nitric acid. For most of the compositions studied, this reduction was accomplished by drying in a laboratory spray drier⁽²⁾, which consisted of an Inconel tube 5 inches in diameter by 4 feet long, with 3 feet of this length heated to 800 to 850 C by resistance elements. The solution or slurry was sprayed from the top by means of a vibrating disc driven at approximately 580 c/s. The solid was collected in a pot at the bottom of the dryer. The solid was powdered and blended before testing or melting.

When the M/P ratio was 1.3 or less, the materials would not process satisfactorily in the short laboratory drying unit, so they were evaporated in stainless steel beakers until they formed a solid or a thick syrup that would solidify on cooling.

The third stage of sample preparation usually consisted of melting the solid. (Some powders were measured for drip temperature without prior melting.) Control and uniformity in this process was necessary. Data demonstrating this are presented in Table III, Column 3, for ratios 2.0 and 1.9. The parenthetical

FIGURE 1

Relationship of Fission Product, Process and Phosphorous Oxides in the Melts Studied

numbers are for material that had been melted for short periods, while the other data are for samples melted according to the following heating schedule: 1 hr. at 200, 1 hr. at 325, 1 hr. at 700, and 2 hrs. at 1,000 C. The platinum crucible was then removed from the furnace and the melt quickly poured onto a steel plate. The cast material was then crushed for property measurements.

The samples melted at 1200 C were heated to 1000 C on the above schedule, then transferred to another furnace and held at 1200 C for approximately one hour. (This was usually sufficient time for off-gassing to cease.)

The low-ratio materials (< 1.3) could not be heated by this schedule without bubbling out of the crucible, therefore, they were melted by putting the crucible in a furnace at 900 - 1000 C and then adding the material in small portions so that decomposition and melting could occur at such a rate that the gases released would not carry the material out of the crucible. This required approximately one half hour. The quiescent melt was then held at 1000 C for the same time (2 hrs.) as those prepared from powders.

The fourth stage, "devitrification" or recrystallization, was performed by heating the previously prepared 1000 or 1200 C material to the drip temperature and then slowly cooling ($< 2^\circ/\text{min}$). This material was then broken out of the crucible and crushed and screened as described below.

It is evident from the data that thermal history plays an important part in the final properties of these materials. More study is planned to determine how to control or minimize this effect.

Measurement of Properties

Two properties have been measured as the primary screening criteria: solubility and drip temperature. Solubility was measured by crushing the melted and cast or recrystallized material and screening it. The fraction passing a 45 mesh (350 micron) sieve and retained on a 60 mesh (250 micron)

sieve was used. It was freed of fines by suspending them with acetone and purging off. A weighed sample of approximately one gram was enclosed in a bag made from 200 mesh stainless steel wire cloth and suspended in 150 ml of distilled water. The water was heated to approximately 95° C and maintained there for 24 hours. Then the sample and bag was removed, dried, and weighed. The process was then repeated with fresh water.

Since this was a screening test, the results are expressed as per cent weight lost rather than in the more frequently used terms of loss per unit area. Several larger samples were prepared so that surface area measurements could be made by the BET method. Three samples gave areas of 135, 200 and 213 cm²/g. If an approximate area of 200 cm²/g is assumed, total dissolution of a 1 g sample in 24 hours corresponds to a rate of about 5×10^{-3} g/cm²/day, while a 1% loss is 5×10^{-5} g/cm²/day. Percentage loss is used as being a more easily grasped screening number.

The "drip temperature" measurement is an empirical measure, used because glasses have no true melting point, and what is desired is an indication of the temperature at which the material can be processed. In the test adopted, a platinum crucible of the cross section and dimensions shown in Figure 2 is loaded with 10 g of the powdered material under test (usually the fines from the material crushed for solubility measurement). The crucible is suspended in an alumina ring, just above the middle of the heated zone of a three by twelve inch tube furnace held in a vertical position. A thermocouple (chromel-alumel) in a platinum sheath or well is positioned so that the junction is about midway down the crucible outlet tube. The "drip temperature" is that temperature at which the first drop falls from the crucible. The system is calibrated with sodium chloride. A sharply melting salt such as NaCl flows freely at a constant temperature, but the mixtures of salts or glasses show

FIGURE 2

Platinum "Drip Temperature" Crucible

a temperature rise for each successive drop. By collecting the individual drops, determining their weight and volume, and the time between drops, it would also be possible to calculate viscosity and surface tension.

Approximate densities of the crushed particles were measured by a sink-float method, using heavy liquids adjusted to the nearest 0.1 density unit. These figures enable one to calculate an approximate volume reduction. The true volume reduction depends on the bulk density of the material as controlled by temperature and voids, and the values one assigns to freeboard in the final container.

Results and Discussion

The data on drip temperature and solubility are summarized in Tables III to V and Figures 3 to 8. The reproducibility of the drip temperature measurement is about ± 8 C for a given sample of powder that has not been previously melted. Measurements on the melted material are influenced by the melting history, as is demonstrated by the data for ratio 2.0 and 1.9 materials in Tables III and IV. The figures in parentheses are for samples melted and held for short times at 1000 C while the other numbers are for samples melted according to the schedule outlined above under sample preparation. Measurements on duplicate preparations have shown an average difference of 11° with one maximum case of 60° .

We can interpret the data on the assumption that the drip temperature represents the temperature to which a container would have to be heated to obtain complete filling, and that it is desirable to be able to do this at or below 900 C. There are three factors to consider; namely, thermal history, phosphate content, and fission product content.

A number of samples were measured as the raw powder before the decomposition - melting cycle. The results on the 3% fission product materials (Table III

TABLE III

"Drip Temperature" for Mixtures of 3 Parts Synthetic Fission Product Oxides:
97 Parts Process Oxides, with Various Quantities of Phosphoric Acid

Ratio M/P	Drip Temperature for Product		
	Powder	1000 C Melt	1200 C Melt
3.5	934	914	850
3.4	941	904	851
3.3	928	931	846
3.2	934	954	856
3.1	938	891	844
3.0	941	894	849
2.9	936	888	867
2.8	928	869	878
2.7	926	866	904
2.6	944	854	914
2.5	924	849	918
2.4	916	842	894
2.3	928	810 827	859 864
2.2		810	853
2.1	951	756	
2.1		829	843
2.0	928	(916 948)*	842
2.0	954	(802)	869
2.0		876	876
1.9	966	(911)*	884
1.9	961	(854 823)*	891
1.9		881	909
1.8		849	931
1.7		871	950
1.6		874	972
1.5		916	972
1.4		854 914	922
1.3		834 829	880
1.2		824	890
1.1		856	863
1.0		866	833
0.9		758	802 After recrystallization
0.8		725	800 749
0.7		1023	802 700

*See text for discussion of these results.

TABLE III (cont.)

Solubility of Mixtures of Synthetic Fission Product Oxides,
Process Oxides (Wt. Ratio 3:97) with Phosphoric Acid.
Melted at 1000 C.

Ratio M/P	As Cast			Recrystallized		
	Periods of 24 hrs			Periods of 24 hrs		
	1st	2nd	3rd	1st	2nd	3rd
3.5	22.2%	2.21%	0.80 %			
3.4	14.3	1.84	0.93			
3.3	25.0	2.04	0.83			
3.2	24.7	1.96	0.62			
3.1	13.9	2.49	1.92			
3.0	14.7	2.27	1.50			
2.9	2.03	0.44	0.55			
2.8	0.89	1.14	----	14.2 %	0.86 %	1.01 %
2.7	0.94	0.47	----	11.4	2.88	1.99
2.6	0.98	0.57	----	22.2	6.20	3.99
2.5	0.90	0.40	----	5.42	6.51	5.36
2.4	0.72	0.36	----	35.8	4.68	2.52
2.3	2.56	1.43	----	32.3	7.97	3.38
	15.7					
2.2	44.9					
2.1	46.7 (43.4) *					
	42.4					
2.0	91.4					
	48.7					
	51.2 (45.4) *					
1.9	69.3					
	58.8					
	86.8 (45.2) *					
1.8	98.2 (45.4) *					
1.7	97.2 (43.8) *					
1.6	99.6 (43.2) *					
1.5	99.4 (42.0) *					
1.4	96.9 (44.5) *					
1.3	53.6					
1.2	14.4	15.0				
1.1	5.9	6.85				
1.0	2.8	3.31				
0.9	74.6					
0.8	78.6					
0.7	78.3					

*Solubility calculated from weight of fine solids that sifted through bag and were collected with fritted glass filter.

TABLE III (cont.)

Solubility of Mixtures of Synthetic Fission Product Oxides,
Process Oxides (Wt. Ratio 3:97) with Phosphoric Acid.
Melted at 1200 C.

Ratio M /P	As Cast			Rescrystallized		
	Periods of 24 hrs.			Periods of 24 hrs		
	1st	2nd	3rd	1st	2nd	3rd
3.5	22.6%	2.90%	1.96%			
3.4	17.9	3.95	2.49			
3.3	19.2	5.45	2.90			
3.2	15.1	5.67	5.59			
3.1	7.49	3.02	2.58			
3.0	10.9	2.76	2.64			
2.9	1.84	1.07	< .01			
2.8	0.40	1.80	0.62			
2.7	0.86	0.46	0.39			
2.6	0.75	0.44	0.51			
2.5	0.80	0.60	0.45			
2.4	0.65	0.32	0.36			
2.3	0.51	0.37	0.32			
	0.32	0.18	0.08			
2.2	0.20	0.14	0.06			
2.1	0.29	0.26	0.12			
2.0	0.25	0.23	0.05			
1.9	0.22	0.19	0.06			
1.8	0.29	0.19	0.07			
1.7	0.28	0.21	0.08			
1.6	0.20	0.22	0.02			
1.5	0.52	0.13	0.19			
1.4	0.47	0.29	0.40			
1.3	1.42	2.44	3.15			
1.2	1.09	3.87	4.54	6.17%	3.00%	1.80%
1.1	1.10	2.24	5.55	1.14	1.54	1.43
1.0	1.43	1.77	3.03	1.80	3.28	2.38
0.9	3.21	2.56	2.68	8.64	6.09	2.75
0.8	7.03	5.85	6.13	61.4	2.08	0.79
0.7	18.5	18.3	11.8	71.3	7.44	7.51

TABLE IV

Drip Temperatures for Mixtures of Synthetic Fission Product
Oxides, Process Oxides (Wt. Ratio 1:9) and Phosphoric Acid

Ratio M/P	Drip Temperature for Product		
	Powder	1000 C Melt	1200 C Melt
3.5	929	918	789
3.4	935	887	800
3.3		887	833
3.25		854	
3.2		866	875
3.1		878	864
3.0		824	908
2.9		839	896
2.8		827	901
2.75		827	901
2.7		859	918
2.6		836	928
2.5		860	947
2.4		861	954
2.3		871	915
2.2		827	873
2.1		842	839
2.0	951	854 (904)*	
	944	866 (891)	
		856	874
1.9	979	876 (916)	
	964	874 (856)	
		881	881
1.8		901	917
1.75		908	926
1.7		903	944
1.6		896	977
1.5		874 866	974 972
1.4		888	942 912
1.3		897	892 886 (944) held at 1200 C
1.2		885	885 over a weekend
1.1		868 879	865
1.0		871	864
0.9		805	853
0.82		871	865
0.75		817	901

*See text for discussion of results in parentheses.

TABLE IV (cont.)

Solubility of Mixtures of Synthetic Fission Product Oxides,
Process Oxides (Wt. Ratio 1:9) with Phosphoric Acid.
Melted at 1000 C and Cast on a Steel Plate.

Ratio M ⁺ /P	Loss in 24 hr Periods		
	1st	2nd	3rd
3.5	23.7%	1.36%	0.99%
3.4	19.2	1.35	1.16
3.3	18.2	2.34	1.29
3.25	21.3	2.55	1.47
3.2	18.3	5.15	2.86
3.1	18.7	2.69	2.22
3.0	16.0	4.47	2.30
2.9	14.6	1.06	1.09
2.8	12.6	1.81	1.52
2.75	27.6	3.15	2.29
2.7	19.7	1.63	1.46
2.6	17.2	9.64	3.86
2.5	8.69	7.60	6.48
2.4	2.77	1.97	11.8
2.3	0.93	0.69	0.53
2.2	11.5	5.21	3.45
2.1	26.7	3.43	2.87
2.0	33.4	5.64	3.19
	58.3		
	58.7		
1.9	40.7		
	48.8		
	31.9	10.1	1.64
1.8	44.0		
1.75	66.8 (45.1)*	10.3 (3.35)*	2.32
1.7	39.0	2.40	3.05
1.6	44.5 (40.4)*	7.71 (2.93)*	9.43
1.5	7.88	4.78	2.26
1.4	29.5	3.05	3.10
1.3	2.12	0.90	0.63
1.2	1.73	1.52	0.61
1.1	2.97	1.42	0.66
1.0	0.82	0.67	1.10
	2.15	2.40	3.31
0.9	28.4	17.6	10.7
0.82	80.5 (37.5)*		
0.75	45.8	12.1	11.2

*Solubility calculated from weight of fine solids that sifted through bag and were collected with fritted glass filter.

TABLE IV (cont.)

Solubility of Mixtures of Synthetic Fission Product Oxides,
Process Oxides (Wt. Ratio 1:9) with Phosphoric Acid.
Melted at 1200 C

Ratio M /P	Loss in Periods of 24 Hrs.					
	As Cast			Recrystallized		
	1st	2nd	3rd	1st	2nd	3rd
3.5	9.98	7.24	4.39	28.8	2.62	0.82
3.4	16.9	4.84	2.82	16.0	4.11	2.50
3.3	13.3	4.77	2.89	24.0	3.11	1.23
3.2	2.79	1.64	1.28	12.8	5.54	3.43
3.1	13.1	4.88	2.69	11.2	4.48	1.89
3.0	2.01	1.24	4.56	18.9	3.63	1.35
2.9	2.14	1.14	0.97	17.3	4.23	3.02
2.8	1.02	0.33	0.28	23.6	1.62	0.97
2.75	1.15	0.73	0.58	25.6	2.27	1.82
2.7	1.18	0.53	0.34	26.4	1.44	0.49
2.6	1.06	0.52	0.38	30.4 (25.8)*	42.0 (3.84)*	5.12
2.5	0.92	0.64	0.32	31.4	2.27	0.90
2.4	0.46	0.25	0.19	5.03	2.68	2.01
2.3	0.33	0.23	0.26	2.76	2.32	0.18
2.2	0.15	0.20	0.11	10.6	5.33	5.47
2.1	0.24	0.14	0.09	21.8	14.8	6.51
2.0	0.26	0.28	0.11	12.8	13.2	11.0
1.9	0.23	0.23	0.09	26.9	14.4	4.95
1.8	0.25	0.16	0.13	44.5	1.84	1.82
1.75	0.18	0.05	0.07	49.3 (43.8)*	4.73	6.22
1.7	1.25	0.18	0.14	48.0 (44.1)*	3.24	3.54
1.6	0.39	0.17	0.03	56.8 (44.1)*	2.82	4.71
1.5	0.66	0.24	0.14	45.7	0.93	0.76
1.4	0.48	0.61	0.20	49.5	14.9	6.20
1.3	0.62	0.55	0.30	50.8	0.52	0.16
1.2	1.28	2.09	1.52	56.9	10.4	4.04
1.1	1.73	2.30	2.23	12.1	10.5	8.95
1.0	1.29	0.78	0.48	3.03	3.79	3.80
0.9	2.24	1.44	1.37	58.8	10.8	4.77
0.82	2.34	2.00	1.54	60.2	5.40	9.18
0.75	0.16	2.00	0.79	63.3	4.93	4.10
1.3	0.34	0.28	0.18	(Held at temperature of 1200 over a weekend)		

*Solubility calculated from weight of fine solids that sifted through bag and were collected with fritted glass filter.

TABLE V

Drip Temperature for Mixtures of Synthetic Fission Product
Oxides, Process Oxides (Wt. Ratio 1:1) and Phosphoric Acid

Drip Temperature for Product

<u>Ratio</u> <u>Mt/P</u>	<u>1000 Melt</u>	<u>1200 Melt</u>
3.5	915	954
3.3	918	899
3.1	897	888
3.0	905	899
2.9	909	920
2.7	906	908
2.5	977	905
2.4	895	909
2.3	866	922
2.2	859	893
2.1	858	896
2.0	904	856
1.9	937	903
1.8	911	861
1.7	936	925
1.6	948	948
1.5	931	930
1.4	953	946
1.3	949	906
1.2	896	933
1.1	886	898
1.0	777	840
0.9	748	855
0.8	859	926
0.7	853	929

TABLE V (cont.)

Solubility of Mixtures of Synthetic Fission Product Oxides,
 Process Oxides (Wt. Ratio 1:1) with Phosphoric Acid.
 Melted at 1000 C and Cast on a Steel Plate

Ratio M ⁺ /P	Loss in Periods of 24 Hrs.		
	1st	2nd	3rd
3.5	21.4	1.13	1.09
3.3	23.0	1.47	1.19
3.1	22.5	1.40	1.50
3.0	22.4	2.11	1.24
2.9	23.0	1.29	0.82
2.7	21.4	1.76	1.62
2.5	18.9	6.02	1.81
2.4	21.8	3.84	0.71
2.3	14.7	9.45	3.21
2.2	2.21	1.20	1.46
2.1	4.23	2.74	3.15
2.0	0.33	0.40	0.30
1.9	3.34	2.41	2.66
1.8	0.25	0.28	0.24
1.7	3.85	2.83	4.32
1.6	28.3	4.11	1.92
1.5	33.3	4.54	2.28
1.4	0.05	0.15	0.17
1.3	0.20	0.23	0.45
1.2	1.40	0.44	0.31
1.1	0.64	0.70	0.65
1.0	0.42	0.43	0.43
0.9	0.73	0.42	0.55
0.8	1.39	1.43	1.43
0.7	9.19	12.9	11.6

TABLE V (Cont.)

Solubility of Mixtures of Synthetic Fission Product Oxides,
Process Oxides (Wt. Ratio 1:1) with Phosphoric Acid.
Melted at 1200 C

Ratio M/P	Loss per 24 Hr. Period					
	As Cast			Recrystallized		
	1st	2nd	3rd	1st	2nd	3rd
3.5	23.3	1.85	0.40	19.9	1.75	0.44
3.3	23.5	1.99	0.88	20.6	2.48	0.53
3.1	23.9	2.03	0.85	20.4	2.65	0.54
3.0	23.3	2.67	1.19	15.3	2.21	0.84
2.9	22.1	2.57	0.99	17.1	2.29	0.81
2.7	12.2	12.0	0.87	19.8	2.61	0.94
2.5	22.6	2.50	0.69	21.0	2.71	0.71
2.4	21.1	4.94	1.50	23.7	1.51	0.71
2.3	8.05	9.06	5.99	24.0	1.62	0.69
2.2	2.92	1.55	1.33	4.36 3.97	3.63 3.21	17.9 5.93
2.1	3.14	1.81	2.00	6.07 6.39	11.1 10.2	9.41 8.89
2.0	1.56	0.73	0.73	26.2 28.4	2.77 2.53	1.32 0.85
1.9	0.53	0.38	0.30	4.70 7.64	3.20 8.91	3.98 4.40
1.8	0.79	0.49	0.50	3.49	1.98	1.83
1.7	0.25	0.23	0.27	7.25	8.81	6.17
1.6	0.44	0.28	0.11	33.1	1.40	0.84
1.5	0.25	0.15	0.06	43.8	1.92	2.64
1.4	0.14	0.10	0.03	47.8	2.90	5.17
1.3	0.69	0.75	0.83	0.56 7.37	0.52 6.68	0.37 8.15
1.2	0.14	0.20	0.12	52.7	3.28	3.04
1.1	0.42	0.37	0.44	0.36	0.24	0.16
1.0	1.17	1.13	1.23	0.23	0.31	0.18
0.9	1.77	1.96	1.80	0.49	0.29	0.30
0.8	3.63	3.83	3.54	27.4	20.1	10.8
0.7	6.58	5.83	5.35	33.4	22.4	11.3

FIGURE 3

Drip Temperature
3% Fission Product Oxides, 97% Process Oxides

FIGURE 4

Drip Temperature
10% Fission Product Oxides, 90% Process Oxides

FIGURE 5

Drip Temperature
50% Fission Product Oxides, 50% Process Oxides

FIGURE 6

Solubility
3% Fission Product Oxides, 97% Process Oxides and Phosphoric Acid
for Indicated Ratio

FIGURE 7

Solubility
10% Fission Product Oxide, 90% Process Oxides and Phosphoric Acid
for Indicated Ratio

FIGURE 8

Solubility
50% Fission Product Oxides, 50% Process Oxides and Phosphoric Acid
for Indicated Ratio

and Fig. 3) suggest that the processes involved in converting the solid to a melt of the fluidity and surface tension that result in drop formation are so balanced that a similar temperature is required over a wide range of phosphate addition. The fact that the drip temperature is higher for these new powders than for the pre-melted powder may be the result of two effects. First, there are possible solid state reactions to produce the equilibrium chemical assemblages in which higher melting compounds decompose and recombine to form lower melting ones. Second, the gases that are being evolved from decomposition reactions have a buoyant effect that reduces the effective weight of a given drop and thus delays its detachment. This effect can be observed in the formation and decay of pendant drops as bubbles form and burst while the material is being heated. From these results one would conclude that it is preferable, if not necessary, to carry out the melting operation separate from the final container filling; i.e., it would be better if a melt were fed to the container, rather than a powder or an aqueous solution.

The thermal history of the material influences the drip temperature because of changes brought about by: (a) decomposition and elimination of volatile compounds and (b) the dissolution of solid compounds in a fluid matrix raising its melting point. Both effects are illustrated in Fig. 3, where (a) the decrease in "drip temperature" brought about by heating the low-phosphate mixtures to 1200 (M/P range 3.5 - 2.9) is probably related to sulfate elimination (discussed in detail below) while (b) the maximum "drip temperature" developed at M/P 1.5 - 1.6 is attributed to the dissolution of crystalline compounds in a fluid matrix with consequent increase of its melting point. The lowered "drip temperatures" for the 0.8 and 0.7 materials (Table III) after recrystallization lent further support to this explanation.

Varying the phosphate content of these mixtures leads to at least two minima, one in the vicinity of $M/P = 2.3$ and the other near 0.9. The fission product levels tested have a drip temperature less than 900 C when the M/P ratio is either between 2.0 and 2.4 or between 1.1 and 0.9. Increasing the fission product fraction raises the drip temperature. One of the major remaining questions concerning the relationship of drip temperature and usable phosphate addition range is concerned with the upper limit of fission product fraction that can be incorporated at a usable temperature. This work will be extended to the 95% fission product level to provide the answer to this question.

One other observation is pertinent to the phosphate system as a whole. The low phosphate compositions deposit a crystalline mass that appears to be iron and related oxides to a M/P ratio of 2.6; i.e., from 3.5 to 2.6. It would be undesirable to have a layer of this oxide build up in a melter. Some other experiments have indicated this is a less severe problem in a sulfate-free system, in that the oxides are suspended rather than deposited; but they still form over the same composition range. So, even though a melt of adequately low drip temperature can be formed with less phosphate than required for $M/P = 2.6$, it would be undesirable to risk depositing material in the melter.

When the data for initial (first 24 hours) solubility are examined, there are three influences readily observed: initial melting temperature, composition, and recrystallization. The influence of initial melting temperature quite possibly should not be segregated from recrystallization, since it is largely the same phenomenon; i.e., the separation of phases of different compositions at a given temperature results whether the temperature is approached from above as long as it is slow enough for phase formation and separation. This

is well illustrated by the data for the 3% fission product mixture in Table III and Fig. 6. The materials in the as-cast condition were very similar in appearance for the range 3.5 to 2.4, those from 3.5 to 2.9 being microcrystalline solids, and from 2.9 to 2.4 mixtures of glass and crystal, increasing in proportion of glass from 2.9 to 2.4, but all being largely glass. Starting at 2.3 there was a marked difference in the samples that had been heated only to 1000 C. These crystallized rapidly after being poured, whereas those heated to 1200 C were glasses. The glasses were uniformly low in solubility; but after recrystallizing (by reheating to 1000 and slow cooling) they were markedly more soluble. This phenomenon of increased glassiness and decreased solubility has been observed over the whole work so far. There are some anomalies, though, in the behavior of the materials at ratio 2.3 and 2.2. The 10 and 50 per cent fission product materials at these ratios (2.3 at 10% and 2.2 at 50%) when recrystallized, showed comparatively small increases in solubility. This is an area that needs further examination. One observation of some significance is that the 1000 C melt samples of 3% fission product material at ratios 2.0 to 1.6 all disintegrated to a fine powder when exposed to water. This effect was not as marked with the higher fission product levels, but was still observed. Apparently there are many small crystals that form in a soluble matrix. For an understanding of what is going on, one would need to make a detailed investigation of the crystals formed and the phosphorus bonding (i.e., is it ring, chain, discrete molecule, etc?), as well as the matrix rejected from the crystals.

The region of low solubility at $M/P = 1.0$ is related more directly to the resistance of this composition to recrystallization. The samples that were subjected to the slow cooling cycle that readily recrystallized materials richer and poorer in phosphate were only slightly crystallized. So the data

presented are more a measure of this resistance to devitrification than a true compositional effect as is found near ratio 2.3.

The low-phosphate solubility minima decrease in M/P ratio as fission product content increases in the order 3% - 2.5; 10% - 2.3, and 50% - 2.2.

The effects of radiation on devitrification and solubility are being examined in separate studies to be reported later. Preliminary results indicate cracking in crystalline solids,⁽³⁾ but only slight increase in solubility. A change in BNL hot glass may or may not be radiation induced.⁽⁴⁾

If drip temperature and solubility are the only criteria by which one decides the composition to be used, one must still make certain compromises, i.e., the least solubility does not coincide with the lowest drip temperature, although there is a tendency in this direction. The minima near M/P 2.3 also vary with changing fission product and thermal history. Therefore, if one elects to form a phosphate melt with minimum solubility of its devitrified form, he has two (or four) choices of phosphate ratio. He must know the analysis of the waste within about $\pm 4\%$. It is also necessary to know the fission product fraction in order to select the proper phosphate ratio.

Volume Reduction

The density of particles of the crushed melts also was measured. These measurements were made by a "sink-float" method, with heavy organic liquids adjusted to the nearest 0.1 density unit. From these approximate density measurements an approximate volume reduction was calculated. The results are given in Table VI.

It is seen that the added phosphate required to go from the first region of minimum solubility near ratio M/P of 2.3 to the second minimum at 1.0 increases the volume by a factor of almost two. Since storage costs are largely a direct function of volume, it would appear undesirable to add the larger quantity of phosphate except for stability against devitrification,

TABLE VI

Calculated Volume Reduction From a Waste
Solution of 50 gal/T Uranium (Table I HIP Composition)

<u>M/P</u>	<u>3% Fission Products</u>	<u>10% Fission Products</u>	<u>50% Fission Products</u>
3.5	36	35	28
3.0	33	34	26
2.5	32	32	22
2.0	30	28	20
1.5	24	24	17
1.0	17	17	12

or unless there are improvements in other properties not yet apparent.

Sulfate Volatilization

Data also were obtained on loss of sulfate from some of the samples. These are presented in Table VII. It can be seen that a large fraction was volatilized from all the melts. This is in keeping with what one would predict from the relative amounts of phosphate, sulfate, and cations. The phosphate must not all be present as the "ortho" ion in the low-ratio materials. If it were, there would not be free oxides separating out at ratios less than 3.0. This occurs to a ratio of 2.6. Of course, it is possible that phosphorus is being volatilized out of the powder or melt and so could not combine with the oxide formers. Most of the sulfate is expelled when the materials are heated to 1200 C, but sufficient is retained to somewhat modify the properties of the product. It is planned to make a series of parallel measurements on a sulfate-free system to determine how much value there would be in operating the separation process to produce a sulfate-free waste.

Some analyses have been performed on the products to determine the phosphate loss. The results are not consistent with the other data that have been obtained so they are being investigated further.

Conclusions

Melts having a wide range of phosphate content can be formed that have drip temperatures below 900 C. If the ratio of cations to phosphate (M/P) is kept below 2.6, a homogenous system is produced. There are minima in the drip temperatures of these melts near ratios of 2.1 and 0.9.

There also are minima in the solubility vs. phosphate curves near these same compositions, but not coinciding exactly. These compositions having the minimum solubility are rather sharply defined. To produce them consistently would require precise analytical control or experimental verification

TABLE VII

SULFUR CONTENT, AS A FUNCTION OF
MELT COMPOSITION AND TEMPERATURE

$\frac{M_2O}{P_2O_5}$	3% Fission Products*		10% Fission Products		
	Theoretical S	1000° C Melt Analyzed S	Theoretical S	1000° C Melt Analyzed S	1200° C Melt Analyzed S
3.5	8.59%	3.8 %	8.24%	2.5%	0.41 %
3.4	8.50	3.9	8.17	4.5	0.56
3.3	8.42	3.3	8.09	3.9	0.35
3.2		2.9	8.00	3.4	0.23
3.1	8.24	3.1	7.92	2.4	0.16
3.0		2.6	7.83	2.1	0.46
2.9	8.04	2.2	7.73	4.8	0.074
2.8		2.3	7.63	3.4	0.038
2.7	7.82	2.4	7.53	4.4	0.027
2.6		2.1	7.43	2.8	0.019
2.5	7.59	1.3	7.30	1.6	0.014
2.4		0.80			
2.3	7.33	0.73			
2.2					
2.1	7.05	0.35			
2.0		0.43			
1.9	6.73	0.20			
1.0			4.57	0.09	0.007

*Mixture of synthetic fission products and process oxides given in Table II to give the indicated percentage of fission product oxides in the mixed oxides before phosphate addition.

of the optimum phosphate addition to each batch of waste. However, the solubility of even these materials is too high to ever permit them to be exposed to ground water that would be reused, so minimum solubility should not be the controlling factor in deciding the composition to be used.

By rapid chilling from 1200 C, glasses are formed from a wide range of phosphate compositions. However, it is only near the M/P ratio of 1.0 that the glass is resistant to devitrification. Under the self-heating conditions of high level waste storage it is presumed that this composition also would eventually devitrify.

Generally, devitrification greatly increased the solubility of the products, but those having minimum solubility near ratio M_2O/P_2O_5 of 2.3 increased much less.

References

1. G. B. Barton

- (a) G. B. Barton. Solidification of High Level Wastes Part I. Evaporation and Calcination of Purex 1WW-Volatility and Leachability of Fission Products. HW-57686 Aug. 4, 1959. (Secret)
- (b) G. B. Barton. Solidification of High Level Wastes Part II. Some Readily Melted Systems Incorporating Redox Wastes. HW-63307. Dec. 31, 1959. (Conf.)
- (c) G. B. Barton. Solidification of High Level Wastes Part III. Solubility, Melting Point, Flow Temperature and Thermal Conductivity of Some Calcined Synthetic Purex-Type Wastes. HW-66091. July 15, 1960. (Declass.)
- (d) G. B. Barton in continuing series of Quarterly Progress Reports, Research and Development Activities. Fixation of Radioactive Residues. Edited by D. W. Pearce, E. R. Irish, A. M. Platt.

- 2. G. B. Barton, Report of Invention, Generation of Droplets by a Vibrating Element. HW-82827. June 12, 1964.
- 3. G. B. Barton in Quarterly Progress Report, Research and Development Activities. Fixation of Radioactive Residues. April-June 1964. HW-83320, p. 8.
- 4. U. L. Upson, private communication. Terminal report on Hot Cell Preparation of Battelle Northwest Glass in which details are given, is in process.

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