

## IMMOBILIZATION OF ACID DIGESTION RESIDUE

W. O. Greenhalgh and C. R. Allen  
Westinghouse Hanford Company  
Richland, Washington

### ABSTRACT

Acid digestion treatment of nuclear waste is similar to incineration processes and results in the bulk of the waste being reduced in volume and weight to some residual solids termed "residue." The residue is composed of various dispersible solid materials and typically contains the resultant radioactivity from the waste. This report describes the immobilization of the residue in portland cement, borosilicate glass, and some other waste forms. Diagrams showing the cement and glass vitrification parameters are included in the report as well as process steps and candidate waste product forms. Cement immobilization is simplest and probably least expensive; glass vitrification exhibits the best overall volume reduction ratio.

### INTRODUCTION

Dry combustible waste is converted to carbon dioxide and water vapor when it is processed in an acid digestion unit. A by-product of the acid digestion process is a small fraction of inert solid residue. The carbon dioxide and water vapor products are filtered and exhausted to the air, while the residual by-product material (designated residue) remains behind in the digester. The resulting waste residue is a sulfated ash plus any chemically inert materials which may have been in or on the waste when processed. For nuclear waste, the residue will contain all nonvolatile radioactive contaminants such as the plutonium in TRU (transuranic) waste. The residue in an acid slurry form is typically removed from the digester, concentrated, and evaporated to dryness. The dry residue is handled in one of three ways: (1) direct disposal as a solid waste material; (2) immobilize and dispose of as a low-dispersible waste; or (3) transfer to a reclamation facility for recovery of radionuclides, such as plutonium, or chemically valuable elements. This study was undertaken to investigate immobilization of the residue as a radioactive waste material for disposal as described in option 2 above.

#### Residue Characteristics

The composition of the first process residue obtained was primarily that of iron sulfate. This was due in part to corrosion of the pot following bake-out of the residue in a carbon steel pot. The high iron content was mostly eliminated by switching from a carbon steel pot. The high iron content residue was found to be much easier to desulfate<sup>a</sup> as will be discussed in a later section, but it also increased the amount of residue generated.

The first pilot plant scale residue was generated using a nonradioactive standard waste mix designated HEDL "B" waste. The characteristics of HEDL "B" waste are listed in Tables I and II. The composition of the residue resulting from the processing of this standard waste is listed in Table III.

During the six-month period of Nov. 1987 through April 1979, the RADTU Facility successfully digested 2100 kg of potentially radioactive TRU waste. Six 210-liter drums containing 42 stainless steel canisters of residue averaging about 6 kg of dry residue per can were produced. The cans measured 15 cm (6.0 inches) in diameter by 79 cm (31.0 inches) high and had a maximum volume capacity of 13.8 liters. A standard drum holds nine canisters so the residue could have all been packaged in just 4 & 2/3's drums if all drums had been filled to capacity.

Three cans of residue from the drums were characterized. The physical characterization results are summarized in Table IV. Can No. 1 contained sludge from the cleanup of the digester tray and may not be as typical a residue as the other two cans. The chemical composition of Can No. 2 was determined in addition to the physical characterization, and is listed in Table V.

TABLE I  
COMPOSITION OF ASH CONTENT OF HEDL "B" WASTE

Waste	Waste (wt.%)	Ash Content (wt.%)	Percent Ash Contrib.
Paper	15	0.4	0.8
Cloth	15	0.9	1.7
Wood	10	5.7	7.2
Latex Rubber	5	1.2	0.8
Hypalon Rubber	10	31.0	39.3
Neoprene Rubber	10	39.0	49.5
PVC Plastic	20	0.2	0.5
Polyethylene	15	0.1	0.2
	100		100.0

<sup>a</sup>Residue desulfation (sulfate removal) is required prior to vitrifying the waste material into a glass product. Desulfation may be desirable for cementing also, but is optional.

TABLE II

## ELEMENTAL ANALYSIS OF HEDL "B" WASTE ASH

Element Analyzed	Content (wt%)
Oxygen	41.0
Silicon	11.0
Titanium	11.0
Barium	8.0
Aluminum	7.0
Calcium	4.0
Sulfur	2.0
Potassium	0.9
Zinc	0.9
Cobalt	0.7
Magnesium	0.7
Iron	0.5
Lead	0.5
Halides	0.3
Sodium	0.2
Strontium	0.2
Manganese	0.1
Phosphorous	Trace
Unaccounted For	11.0

TABLE III

## ELEMENTAL ANALYSIS OF RADTU RESIDUE\*

Element	Content (wt.%)		
	Sample 1	Sample 2	Average
Oxygen	49	44	46.5
Sulfur	22	26	24
Iron	10	14	12
Silicon	5	4	4.5
Chromium	3	4	3.5
Nickel	2	1.5	1.8
Zinc	2	1.5	1.8
Aluminum	2	-0-	1.0
Titanium	0.8	0.8	0.8
Calcium	0.6	0.7	0.7
Sodium	0.5	-0-	0.3
Barium	0.5	0.9	0.7
Strontium	0.5	-0-	0.3
Molybdenum	0.5	0.5	0.5
Lead	0.3	0.3	0.3
Phosphorous	0.3	-0-	0.2
Manganese	0.2	-0-	0.1
Vanadium	0.1	-0-	0.1
TOTAL	99.3	98.2	99.1

\*Residue from processing HEDL "B" waste in RADTU.

TABLE IV

## CHARACTERIZATION OF CANISTER RESIDUE

Properties	Can No. 1	Can No. 2	Can No. 3	Average
Volume (l)	11.6	9.3	7.4	9.4
Weight (kg)	13.40	12.78	6.81	11.00
Wet Density (kg/l)	1.16	1.38	0.92	1.16
Dry Weight (kg)	8.96	8.59	5.22	0.81
Dry Density (kg/l)	0.77	0.92	0.70	0.81
Millable Solids (kg)	8.36	7.80	5.22	7.13
Hardware (kg)	0.60	0.69	0.00	0.36
Volatiles (g.)	4.44	4.19	1.59	3.41
Appearance	a)	b)	c)	

- a) Light green & glass fiber.  
 b) Light green & glass fiber.  
 c) Off-white, chalky, no fiber.

TABLE V

## CHEMICAL AND PARTICULATE CHARACTERISTICS OF RESIDUE FROM CAN NO. 2

Major Components		Minor Components	
Oxygen	46 wt.%	Chromium	0.7
Sulfur	24	Nickel	0.5
Silicon	15	Molybdenum	0.5
Iron	8	Sodium	0.3
Aluminum	2.7	Lead	0.3
Calcium	1.8	Barium	0.1
Zinc	1.7	Boron	0.1
Titanium	1.4	Copper	(<1%)
		Zirconium	(<1%)
		Cadium	Trace
		Tin	Trace

Mean particle size is 20 $\mu$ m

Only 5 wt.% of the particles are smaller than 7  $\mu$ m in diameter.

Initial ashing studies<sup>1</sup> had indicated that about 4 to 6 wt.% residue would be generated based upon studies using clean HEDL standard wastes. Early RADTU tests indicated an average residue content of about 11.5 wt.% in typical waste. More recent RADTU tests indicated an average residue content of 10.9 wt.%. About 55 kg of dry residue was generated after processing 502.6 kg of TRU and potentially TRU waste. The higher fractions found with actual waste processing runs can be attributed to the following:

- The presence of facility dust, dirt, and sand on the bulk waste.
- The presence of inert fillers from plastics, molds, gloves, etc., such as mineral talc, alumina, siliceous materials, and lead oxide from leaded glovebox gloves.
- Imperfect segregation of wastes introduced many non-combustibles such as fiber glass from filters and tapes; small glass and ceramic fragments; and small metal items such as staples, small clamps, tweezers, tools, nuts, and bolts.

Therefore, it appears the high ratio of residue content observed in the pilot plant work is realistic and it can be expected that general waste processing will generate 10 to 12 wt.% residue unless the waste is particularly clean and well segregated.

Immobilization of Residue with Cement

A typical acid digestion operation will generate about 10 to 12 wt.% residue solids as indicated in the previous Section. If one assumes the amount of residue generated on the average is about 11.5 wt.%, consistent with the largest RADTU test run, then the processing of 100 drums containing 45.35 kg (100 lbs.) waste per drum would generate 521.5 kg of dry residue. If the residue was not immobilized, but packaged directly in the 15 cm diameter by 79 cm canisters to about 90% full with nine canisters per drum, then six full drums of residue waste would result. Direct disposal of the dry residue might not be a problem if it is a non-TRU, low level waste; otherwise some immobilization might be required. If it is determined that immobilization of the residue is required, then direct cementation of the dry residue is an option to consider.

Direct cementation of dry acid digestion residue can be carried out quite simply. The residue if dried in the 15 cm canisters will be in solid cake form. To make a good cement product, the residue cake will need to be milled directly with portland cement powder, and either water and/or aqueous wastes can be added to make a suitable cement paste. A cement-residue-water three phase diagram has been completed for the system and is shown in Fig. 1. The amount of dry residue selected would probably be limited to about 15 to 20 wt.%.

If it is assumed that the residue-cement composition has at least 15 wt.% residue, then 13 or less drums of waste will be generated based on the formation of a 1.5 kg/l cement density. This is shown in Fig. 2 as one of the immobilization options. It is readily apparent that the direct cementation of residue powder significantly decreases the volume reduction advantage of the acid digestion system.

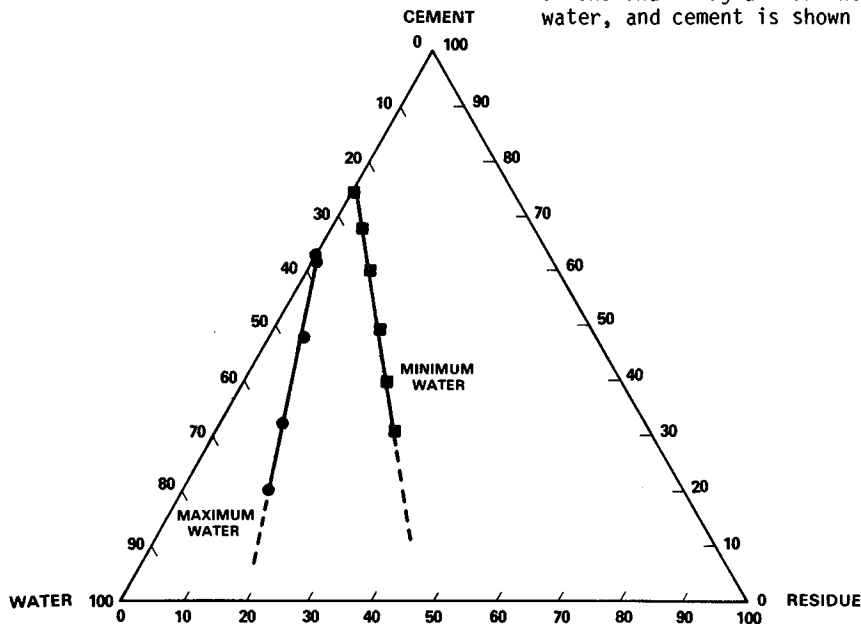


Fig. 1. Cement Immobilization of Acid Digestion Residue.

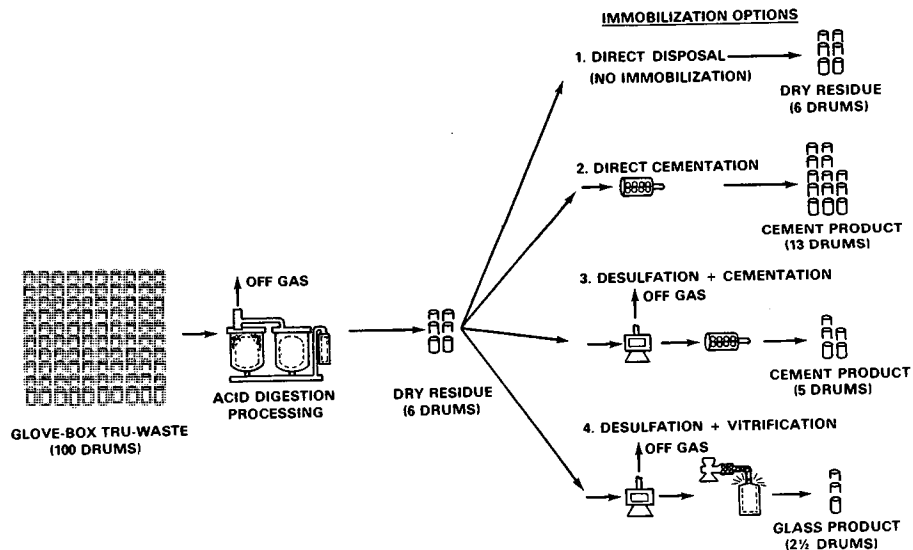


Fig. 2. Optional Methods of Immobilizing Acid Digestion Residue.

The residue content could be increased to as much as 20% in some cases and still produce a product exhibiting good physical characteristics. This would decrease the number of waste drums generated to 10 or less.

Desulfation and Immobilization of Residue in Cement

The sulfate fraction accounts for at least 50% of the weight of the residue. Sulfate materials also tend to limit the fraction of residue that can be immobilized in concrete and still exhibit good waste product characteristics. If one removes the sulfate by heat and a reducing agent, the residue from 100 drums of waste could be incorporated into only 5 drums. The generation of only 5 drums of waste product is a substantial volume reduction from direct cementation as shown in Fig. 2. It is slightly less volume than direct disposal (without immobilization) of the residue which requires 6 drums. A three dimensional diagram for the desulfated residue, water, and cement is shown in Fig. 3.

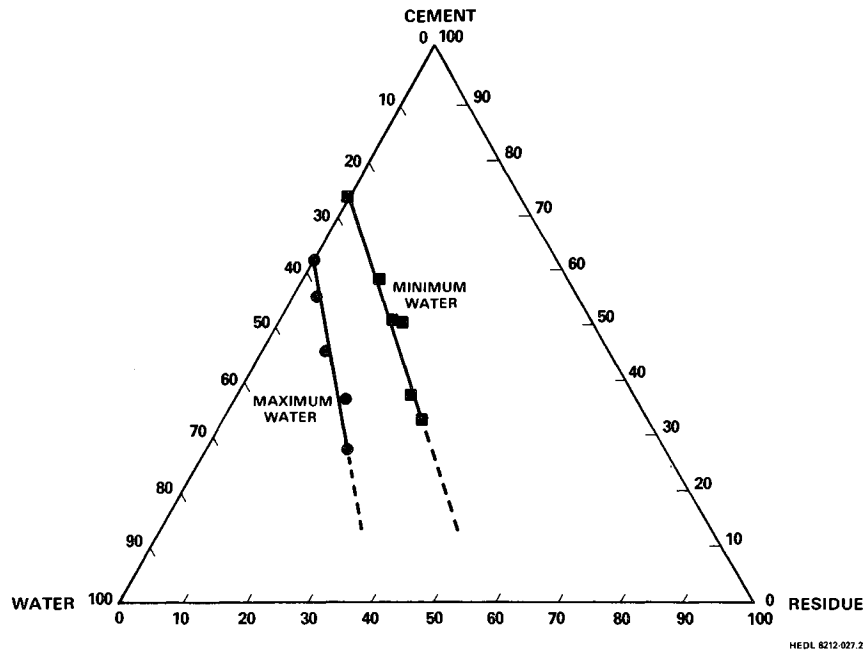


Fig. 3. Cement Immobilization of Desulfated Residue.

#### Desulfation and Vitrification of Residue

Simulated waste residue was first used for the desulfation and vitrification studies until substantial quantities were available from digester operations. The first residue which could be closely simulated by using ferric sulfate was found to decompose completely to the oxide by heating in a ventilated furnace above 650°C. Sulfates in general are incompatible with glass and if present in any appreciable concentration will cause second phase formation. The vitrification diagram shown in Fig. 4 consisted of three major components; namely, sodium borate glass, silica, and ferric oxide (the desulfated ferric sulfate residue stand-in). The phase characteristics were determined on powder compositions heated for one hour at 1200°C. A glass composition was selected which incorporated at least 30 wt.% residue, but held to a minimum the amount of borax glass to limit water leaching effects. The glass mix selected was composed of 33-1/3% borax glass, 33-1/3% silica, and 33-1/3% residue. Later two percent alumina was substituted for part of the silica to improve the thermal stability of the glass product. Lime (CaO) could also have been used for a stabilizer additive. The alumina stabilized composition was found to exhibit more favorable characteristics for the glass waste product required.

The vitrification steps for converting the residue to glass are listed in Table VI and illustrated in Fig. 5. The process steps have been modified to handle low ferric sulfate residue more consistent with the latest residue characteristics. Dry, granular (and/or milled) residue is blended with graphite, a reducing agent, and heated at 800° or above to decompose the sulfates. After the residue is completely desulfated, characterized by cessation of SO<sub>x</sub> gas emission, the residue is cooled down and blended with the borax glass, silica, and alumina glass formers. The blended mix is then heated in a stainless steel pot at 1100°C until a uniform melt is achieved (2 hours). The molten glass is then allowed to cool slowly to room temperature. The canister of glass is capped, bagged-out of the glovebox, and loaded into a drum in preparation for disposal. Nine glass canisters can typically be loaded into one drum for a total package weight of about 700 lbs.

The various forms of the residue as it is converted to a glass are shown in Fig. 6 namely residue, desulfated residue, and glass. Fig. 7 shows a 6-inch diameter, 30-inch long canister of actual RADTU glass. The digester glass shown in Fig. 7 is essentially black with a 2.6 g/cc density.

Other vitrification facilities and processes have been considered other than the one described above. Various types of glass melters and/or button or marble machines could undoubtedly be used with the above general glass composition without much modification. The above hardware was chosen for simplicity, economy, and adaptability to manual operation in a glovebox. Other glass systems such as the acidic borosilicate system with components boric acid anhydride (B<sub>2</sub>O<sub>3</sub>), silica, and ferric oxide (residue stand-in) were also tested, but the system when diagrammed did not appear to be very useful because of the small area of glass formation. A sodium silicate, boric acid anhydride, and ferric oxide system was considered, but it was found to be very similar to the original with the sodium oxide being associated with the silica rather than the boric acid. The lime silicate glass system was not considered because of the higher melting temperatures required.

TABLE VI

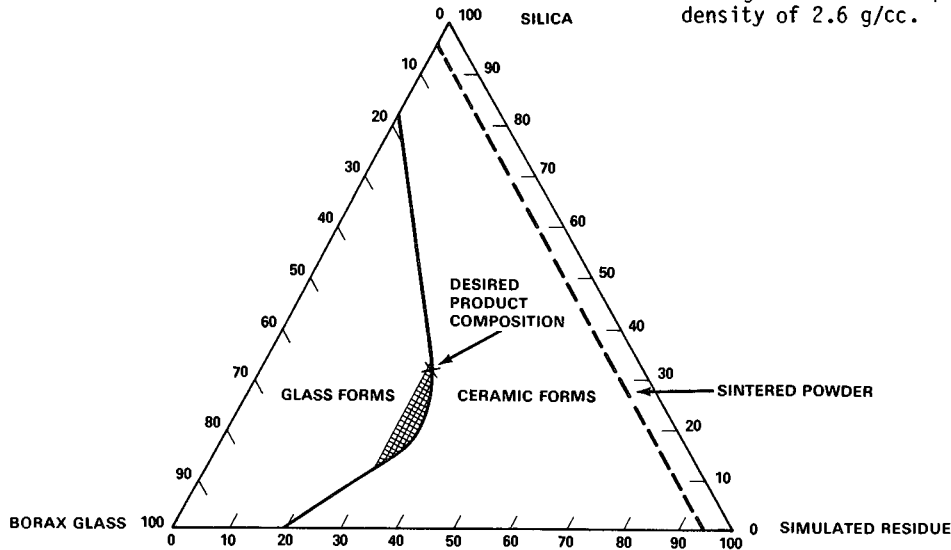
#### RESIDUE DRYING, DESULFATION, AND VITRIFICATION PROCESS

Step	Operation
1.	Remove volatiles and liquids (sulfuric acid and water) from the acid digestion slurry by drying it at 450°C.
2.	Remove the residue from the drier and mill any lumps into fine powder.
3.	Blend powdered carbon or graphite with the residue and heat the mixture to 900°C in a ventilated oven to decompose the sulfates to oxides and gaseous sulfur dioxide.
4.	Blend the glass formers (silica, borax glass, and alumina) in dry powder form with the sulfate-free residue.

TABLE VI (Cont'd)

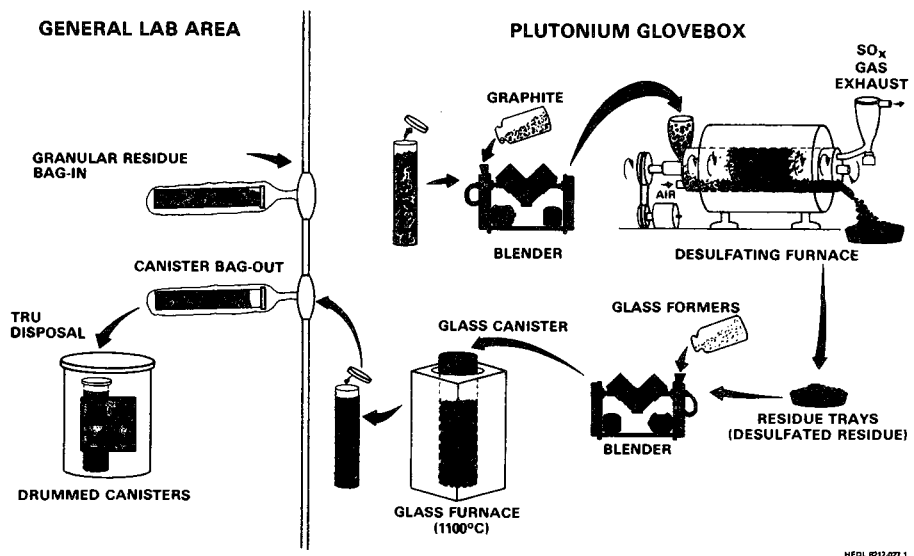
Step	Operation
5.	Add the blended powders to a stainless steel melting pot and melt the mixture at 1100°C for a minimum of two hours.
6.	Cool the glass slowly to room temperature to anneal the product, seal the canister, bag it out of the glovebox, and place it into a waste drum for disposal or storage.

In addition to glass specimens, high-density hard-ceramic specimens containing 60% acid digestion residue were also prepared. Two examples of ceramic specimens are shown in Figs. 8 and 9. The specimens shown contained 60 wt.% residue, 20% sodium borate glass, and 20% silica. The ceramic specimens shown were pressed into a pellet under 1000 psi pressure and then fired at 800°C and 1000°C, respectively. The best quality ceramic specimens were made by pressing the powder, firing the specimen, regrinding the specimen, repressing it, and firing again. Fig. 10 shows the comparative volume and characteristic product of each step as one proceeds from left to right. The final product is a firm solid with a density of 2.6 g/cc.



HEDL 8212-137

Fig. 4. Phase Diagram for the Silica-Borax Glass-Residue System at 1200°C.



HEDL 8212 427 1

Fig. 5. The Glass Vitrification Process for Immobilization of Residue.



Fig. 6. Processing Forms of Residue.



Fig. 7. Glass Canister.

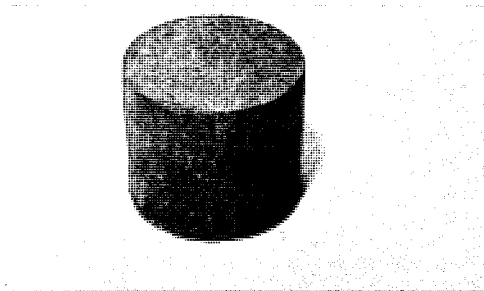


Fig. 8. A Residue-Borosilicate Ceramic Pellet Fired at 800°C.

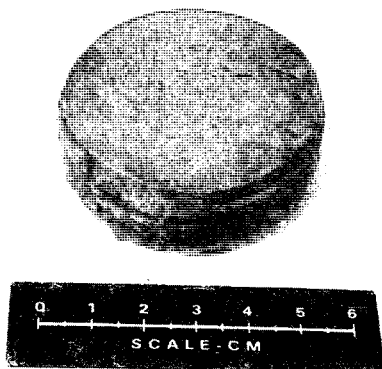


Fig. 9. A Residue-Borosilicate Ceramic Pellet Fired at 1000°C.

Fixation of dry acid digestion residue in urea-formaldehyde was also tested. Figure 11 shows a product of two volumes of dry residue powder to one volume of urea-formaldehyde polymer materials plus 2 volume % catalyst. The resulting product was a hard plastic material with initially good mechanical characteristics. Hairline cracks were apparent after several days exposure to the dry room atmosphere; however, no further degradation occurred after about two weeks time. Other specimens showed more degradation probably due to compositions of a higher moisture content which appeared to degrade with exposure to dry air. Some compositions exhibited no visible degradation, but appeared to yield a good product form. Product reproducibility on a consistent basis was a problem however.

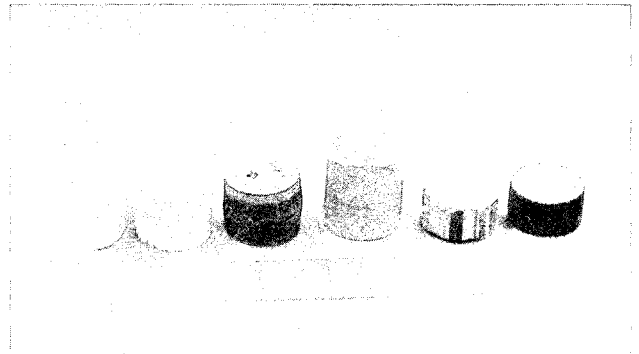


Fig. 10. Characteristic Forms Obtained Stepwise in the Pelletized Process.



Fig. 11. A Urea-Formaldehyde Immobilization Product from Dry Residue.

In other organic polymer work, acid digestion residue was tested for immobilization in polyesters. This work was carried out by contract to Washington State University. The study was based on work reported by Subramanian and Raff.<sup>(1)</sup> Results of the work showed that it was possible to successfully incorporate acidic acid digestion residue<sup>a</sup> into polyester polymer products in concentrations up to 65 wt.% dry residue. Figure 12 shows a WEP (Water Extended Polyester) product containing about 45 wt.% residue. The polyester products were similar to a piece of hard rubber and exhibited compression strengths of about 5 kg/cm<sup>2</sup> varying slightly with composition. Leach rate measurements with doped

<sup>a</sup>Residue at the time this work was performed was not completely dry generally, but contained some residual sulfuric acid; later drying improvements allowed 100% sulfuric acid removal.

sodium and cobalt showed the higher content residue solids to be moderately leachable, whereas a 30 wt.% product incorporated into Hetron 197-P (Ashland Chemical) polymer was excellent. Only 3% of the waste material would be expected to leach out the first 1000 years if placed in a 210 liter drum.

One problem with using polyesters has to do with controlling the heat generated during the peroxide initiated polymerization; the inner temperature of large volumes such as a drum of polyester has to be carefully controlled. Incorporation of acid digestion residues into polyester waste products should be investigated further.

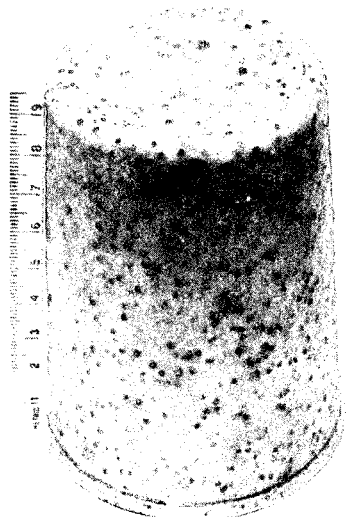


Fig. 12. A Water Extended Polyester Polymer--Residue Product.

#### Physical Properties of Immobilization Products

A key aspect of immobilization work is product quality. All waste products were tested in some manner to obtain an indication of product integrity, particularly from the standpoint of retention of radioactive contamination. Compression strength testing was used primarily with cements to obtain an indication of mechanical integrity. A 30 foot canister drop test was used to indicate the impact resistance of vitrified waste. A few water leach tests were conducted with cement, glass, and ceramic specimens to determine radionuclide retention under wet climatic conditions.

Compression strength for typical concrete used in buildings is about 175 to 210 kg/cm<sup>2</sup> after a 28 day cure. The cement products tested here were all air cured and compression strength tested at the 7 day mark. The strength after 7 days is typically about 50 to 70% that of the 28 day cure material. In this study a couple of control samples without residue were made to make comparisons with. The control samples at 28 days should test at least 210 kg/cm<sup>2</sup> (1470 psi) for a composition with the maximum possible water. Cement incorporated with waste or waste residues will generally exhibit compression strengths considerably less than the control values. For cement-waste products, non-dispersibility rather than structural strength is probably the characteristic that is most important. Earlier work with a different cemented waste showed that products exhibiting a compression strength of greater than 10 kg/cm<sup>2</sup> for a 7-day cure sample were

reasonably non-dispersive, while below 10 kg/cm<sup>2</sup> samples were dispersive under abrasive conditions.(2) Therefore, if one uses this value as an indication of acceptable products then usable cement compositions can be selected. Tables VII and VIII show the cement-residue compositions and their correspondingly measured product compression strengths. The tabulated results indicate that about 15% residue is all that should be immobilized in cement if the residue has a high sulfate content. However, 20 to 25% can be immobilized if the residue has been desulfated.

TABLE VII

#### CHARACTERISTICS OF CEMENT-RESIDUE IMMOBILIZATION PRODUCTS

Sam. No.	Water Bound. (a)	Comp. (wt.%)			Proc. Dens. (g/cc)	Comp. Strength (kg/cm <sup>2</sup> )
		Cem.	Water	Res.		
1	Max.	63.8	36.2	0.0	1.57	10
2	----	52.7	42.0	5.3	1.44	25
3	----	44.0	47.0	9.0	1.33	15
4	Max.	46.5	48.2	5.3	1.26	5
5	Max.	31.7	59.2	9.1	1.08	5
6	Max.	19.3	66.3	14.4	didn't set	0
7	Min.	74.5	25.5	0.0	1.89	290
8	Min.	68.3	26.8	4.9	1.82	150
9	Min.	60.2	30.5	9.3	1.62	70
10	Min.	49.4	34.3	16.3	1.53	20
11	Min.	38.4	39.2	22.4	1.24	7
12	Min.	30.7	41.2	28.1	0.98	5
13	----	37.2	44.1	18.7	1.31	10

TABLE VIII

#### CHARACTERISTICS OF CEMENT-DESULFATED RESIDUE IMMOBILIZATION PRODUCTS

Sam. No.	Water Bound. (a)	Comp. (wt.%)			Proc. Dens. (g/cc)	Comp. Strength (kg/cm <sup>2</sup> )
		Cem.	Water	Res.		
1	Max.	62.5	37.5	0.0	1.48	75
2	Max.	53.9	40.7	5.4	1.36	45
3	Max.	46.1	42.4	11.5	1.32	30
4	Max.	37.3	44.0	18.7	1.41	40
5	Max.	28.2	45.6	26.2	1.47	7
6	Min.	72.9	27.1	0.0	1.21	215
7	----	65.6	28.7	5.7	1.87	265
8	----	56.2	32.9	10.9	1.72	149
9	----	48.3	35.1	16.6	1.68	125
10	----	40.4	35.7	23.9	1.54	95
11	Min.	36.9	34.5	28.6	1.42	50
12	Min.	49.7	30.4	19.9	1.68	150
13	Min.	50.1	31.5	18.4	1.67	130
14	Min.	31.8	36.1	32.0	1.44	50
15	Min.	56.7	29.6	13.8	1.68	175

(a) The maximum water composition is that composition in which any additional water added will produce free liquid directly corresponding to the amount added. The minimum water composition is that composition in which there is just sufficient water to mix the cement; this composition may vary for different mixers.

## The Mechanical Strength and Leach Resistance of Digester Glass

The relative mechanical strength and integrity of digester glass was checked with a 10 meter drop test. A 30 foot (9.14 meter) drop test is generally used to test impact resistance of waste transport containers. The drop test gives a conservative indication of the potential radionuclide dispersion due to transportation accidents. A container and/or waste product that shows very little damage in a drop test is expected to sustain negligible damage in a credible transport accident.

The canister of digester glass tested measured 15 cm in diameter by 15 cm high (shown in Fig. 13). The glass product weighed 5.6 kg and was vitrified directly in a thin wall stainless steel can. The can was sealed with a paint can lid that was tape sealed to the main canister. The canister was dropped from the roof of the Hanford 300-Area fire station to a metal pan lying 10 meters below on a concrete sidewalk. The set-up is shown in Fig. 14. The canister landed flat on its bottom with no resultant damage to either the canister nor its glass product. The canister was dropped a second time at an angle so as to impact a fragile edge. The thin walled canister was bent at the point of impact and some glass was dislodged within the container. At no time was the canister, lid, or seal breached. Examination of the inner glass product contents showed that 52 grams of the 5600 gram product had been broken up, or less than 1 wt.% of the bulk glass exhibited structural damage. Figures 15 and 16 show the results of the test on the canister and the contained glass.

In comparison, an un-contained six-inch cube of concrete exhibiting a compression strength of about  $110 \text{ kg/cm}^2$  (1500 psi) was dropped from the same 10 meter height. The concrete block broke up upon impact as shown in Fig. 17.



Fig. 13. Small Glass Canister Prepared for Drop Test.

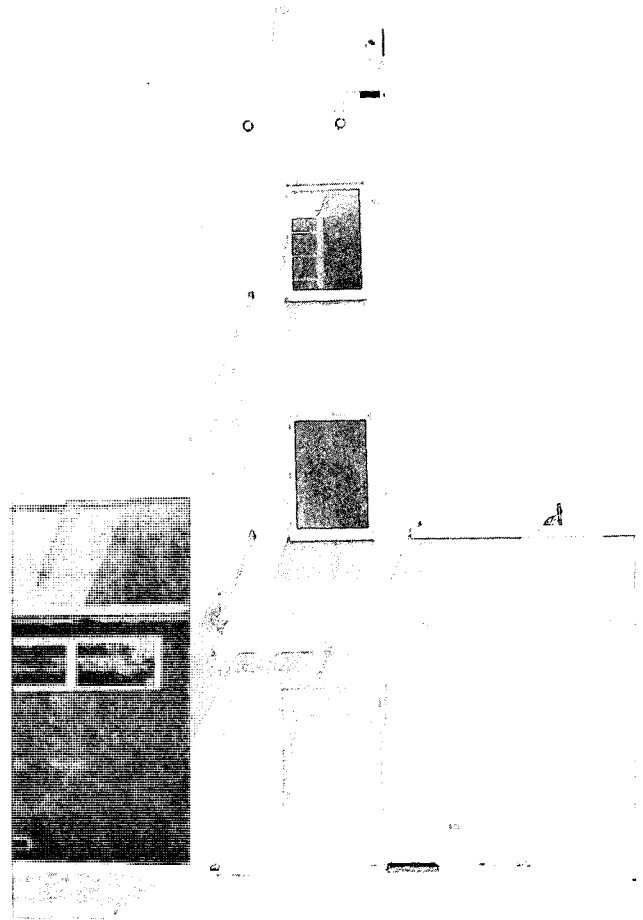


Fig. 14. Drop Test Location and Setup.



Fig. 15. Glass Canister After Drop Test.



Fig. 16. Examination of Dropped Glass Canister.



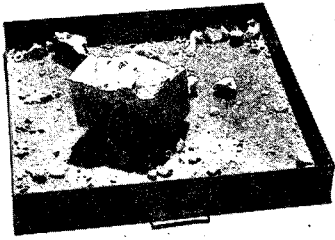


Fig. 17. Examination of Dropped Concrete Cube.

In conjunction with mechanical tests, uranium spiked digester type glass buttons approximately 1 inch dia. by 1/2 inch high were leach tested using an agitated distilled water leachant. The leachant was sampled daily for about two weeks and the uranium leach rate of the tested buttons was determined to be about  $2 \times 10^{-5}$  g/cm<sup>2</sup>/day. TRU elements such as plutonium is expected to exhibit even lower leach rate values.

The digester glass was judged to have mechanical properties and leach resistance properties suitable for a candidate transuranic waste form.

#### CONCLUSIONS

Acid digestion residue can be successfully immobilized in both portland cement and borosilicate glass waste forms. Cementation of the dried residue increases the volume of the waste unless the residue has been treated to remove the sulfate fraction. Pilot plant data shows that the residue represents about 6 vol. % of the original waste; cementation of that residue increases the waste fraction to about 13% unless the residue is desulfated which reduces the waste fraction to 5%. Vitrification of the residue which includes sulfate removal can decrease the volume fraction to 2-1/2% of the original. The borosilicate glass form exhibits the best overall waste product characteristics.

#### REFERENCES

1. R. V. Subramanian and R. A. V. Raff, "Immobilization of Low Level Radioactive Wastes," AICHE Symposium Series, Vol. 72, No. 154, pp. 62-64.
2. R. E. Lerch, Ed., Division of Waste Management, Production and Reprocessing Programs Progress Report for Jan. - Dec. 1976, HEDL-TME 77-40, Hanford Engineering Development Laboratory, Richland, WA, April 1977.