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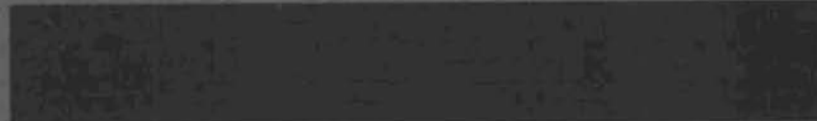
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QUARTERLY PROGRESS REPORT  
 RESEARCH AND DEVELOPMENT ACTIVITIES  
 FIXATION OF RADIOACTIVE RESIDUES  
 FEBRUARY, MARCH, APRIL, 1968

A. M. Platt

September 1968



AEC RESEARCH &  
 DEVELOPMENT REPORT

TO: <i>Prod Respt Div 63011 Med/108</i>	DATE: <i>NOV 25 1968</i>
FROM: <i>for RB H. Johnson</i>	DATE: <i>NOV 11 1968</i>
	<i>11-27-68</i>

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3 3679 00061 1378

BNWL-824  
UC-70, Waste Disposal  
and Processing

QUARTERLY PROGRESS REPORT  
RESEARCH AND DEVELOPMENT ACTIVITIES  
FIXATION OF RADIOACTIVE RESIDUES  
FEBRUARY, MARCH, APRIL, 1968

By

Members of the Staff  
of the Chemistry and Chemical Engineering Department  
and  
Environmental and Radiological Sciences Department

Edited by  
A. M. Platt  
Chemical Development and Engineering Section

September 1968

History  
1968

BATTELLE MEMORIAL INSTITUTE  
PACIFIC NORTHWEST LABORATORY  
RICHLAND, WASHINGTON

Printed in the United States of America  
Available from  
Clearinghouse for Federal Scientific and Technical Information  
National Bureau of Standards, U.S. Department of Commerce  
Springfield, Virginia 22151  
Price: Printed Copy \$3.00; Microfiche \$0.65

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\* Reference notation used in this report.

\*\* Report for the period July through October, 1967. Reporting periods are now February-April, May-July, August-October, and November-January.

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QUARTERLY PROGRESS REPORT  
RESEARCH AND DEVELOPMENT ACTIVITIES  
FIXATION OF RADIOACTIVE RESIDUES  
FEBRUARY-APRIL, 1968

INTRODUCTION

This progress report is the thirty-sixth in a series presenting research and development activities in the field of radioactive wastes.

Experimental work charged to programs other than those of the Division of Reactor Development and Technology is sometimes included for general interest and completeness; such work is identified in the headings.

SUMMARY

During the report period, approximately 3,000,000 Ci of radioactivity were successfully processed in two phosphate glass runs in WSEP. These runs represent the fourth and fifth conversion of highly radioactive wastes into glass on an engineering scale. Phosphate glass Run PG-4 was made using sulfate-containing Purex Waste 2 (PW-2) feed while PG-5 was made using sulfate-free Purex Waste 1 (PW-1) feed. Leach rates on phosphate glass solids from WSEP were  $1 \times 10^{-6}$  to  $2 \times 10^{-7}$  g/cm<sup>2</sup>/day.

Platinum corrosion was evaluated for sulfate-free phosphate glass flowsheets made with excessive phosphate, lead, and silicone antifoam agent. Significant platinum corrosion occurred only in the vapor phase with high phosphate feed and in the melt phase with feed containing lead. In no case was there evidence of cracking or embrittlement.

Testing of low-salt flowsheets was carried out on the developmental spray solidifier. Major characteristics were a reduced capacity in the calciner, reduced denitration of the powder from spray calciner, and increased difficulty in removing the calcined powder from the spray calciner filters. Batch discharge of the melt from the melter allows filling of an unheated container.



A simulated spray-solidified melt prepared from low-salt PW-4 solution corroded both 304-L and 310 stainless steel at a rate of about 15 mils/month in 100 hr tests at 800 °C.

Addition of formaldehyde or hypophosphorous acid to spray solidifier feed reduced the volatility of ruthenium significantly.

Laboratory tests with commercial silicone antifoam agents were successful in reducing DEP-induced foaming in phosphate glass runs.

Equipment is being fabricated for studying pressure buildup in high sulfate wastes stored with a molten core.

## PHOSPHATE GLASS SOLIDIFICATION

### PROCESS TECHNOLOGY

#### Foaming in Evaporator - J. E. Mendel

Laboratory tests indicated the probable source of the foaming observed during Runs PG-1, 2, and 3 in the WSEP was dibutyl phosphate (DBP) introduced with the Purex Plant waste solution. Commercial silicone antifoam agents successfully counteracted the DBP-induced foaming tendency in a laboratory test apparatus.

The test apparatus was an immersion heater surrounded by a shroud and baffle arrangement designed so that the solution movement in the WSEP evaporator was simulated on a small scale. Initial experiments established that laboratory-prepared PW-2 phosphate glass process feed solution did not foam when the evaporator was operated anywhere in the range of boiling points 125 to 140 °C. A series of possible organic contaminants which could be present in Purex waste were then tested with the laboratory evaporator operating at the boiling point 130 °C. Also tested was di (2-ethylhexyl) phosphoric acid, the extractant used in fission product recovery.

<u>Contaminant</u>	<u>Result of Foam Test</u>
Degraded NPH*	Negative
Tributyl phosphate	Negative
Dibutyl phosphate	Positive
Monobutyl phosphate	Negative
di (2-ethylhexyl) phosphoric acid	Negative

Dibutyl phosphate, a degradation product of the Purex extractant tributyl phosphate, was the only contaminant which caused significant foaming. Maximum foaming occurred with about 200 ppm DBP (the concentration at which the foam could not normally be retained in the test apparatus) and at a heat input of 240 W which was used in all tests. The foaming decreased to negligible amounts at DBP concentrations below 30 and above 1600 ppm.

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\* NPH is the Normal Paraffin Hydrocarbon currently used as diluent in the Purex solvent. It was chemically degraded by heating with  $\text{HNO}_3$ - $\text{HNO}_2$ .

Two commercial silicone-type antifoam agents and one commercial magnesium silicate antifoam agent were tested for their ability to counteract the foaming due to DBP. All tests were made at 130 °C. The silicone antifoam agents suppressed the foam, while the magnesium silicate did not. One silicone antifoam was chosen for longer term testing. At 200 ppm DBP and 100 ppm of antifoam, foaming was suppressed for approximately 2 hr, at which time more antifoam had to be added to prevent foaming out of the apparatus. As the test was continued, a tendency for successive antifoam additions to become less effective was noted, although this did not occur in the plant test, as is described elsewhere.

#### Platinum Melter Corrosion - R. F. Maness

Three laboratory scale phosphate glass runs were made with semicontinuous addition of feed to an alumina crucible equipped with an overflow weir. A high phosphate feed was used in the first run. This was prepared from a sulfate-free (PW-1) waste solution containing 783 ml of 85 wt%  $H_3PO_4$  and 209 g of  $NaNO_3$  per liter of PW-1 solution. Feed for the second and third runs was prepared from a PW-1 solution containing 406 ml of 85 wt%  $H_3PO_4$  and 168 g of  $NaNO_3$  per liter of PW-1 solution. In addition, feed for the second run contained 0.01M Pb (II), while feed for the third run contained 0.5 g of silicone antifoam agent per liter of PW-1 solution. The first and second runs were made at 1000 °C, whereas the third run was made at 1100 °C. Platinum specimens were exposed to the liquid and to the vapor phase. Platinum corrosion in the liquid phase was essentially zero in the run made with high phosphate feed, but significant corrosion, 0.3 mils/month, occurred on the specimen exposed to the vapor phase. In the run made with feed containing Pb(II), platinum exposed to the melt corroded at a measurable rate, 0.12 mils/month, whereas vapor phase corrosion was nil. Both liquid and vapor phase corrosion were nil in the run made with feed containing the antifoam agent. In no case was there evidence of cracking or embrittlement.

#### Corrosivity of Feed Solution - R. F. Maness

Corrosion rates of titanium, 304L SS, and Hastelloy C\* were determined in a simulated low-salt waste (PW-4) solution boiling at 125 °C.

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\* Registered trademark of Union Carbide Company

Corrosion rates were less than 0.1, 34, and 14 mils/month respectively, as determined by weight loss after five, 24 hr exposures.

#### Condenser Corrosion - R. F. Maness

Nionel\* and Carpenter 20 Cb-3\*\* specimens were evaluated for corrosion resistance in  $\text{HNO}_3$ - $\text{H}_2\text{SO}_4$ - $\text{H}_3\text{PO}_4$  systems simulating the condensate from the melter of the phosphate glass process. The condensate composition, when not diluted with steam, is about 10M  $\text{HNO}_3$ -5M  $\text{H}_2\text{SO}_4$ -0.1M  $\text{H}_3\text{PO}_4$ . This system, at the boiling point, corroded Nionel at a rate of 2.2 mils/month. A 50% dilution of the system with water reduced the corrosion rate to 0.2 mils/month. Reducing only the nitric acid concentration, or only the sulfuric acid concentration, by a factor of two reduced Nionel corrosion by a factor of 2. In all cases, corrosion of Carpenter 20 Cb-3 was higher than that of Nionel by a factor of 1.5 to 2.5.

#### RADIOACTIVE DEMONSTRATION - J. N. Hartley and J. L. McElroy

##### Run PG-4

During Run PG-4, wastes equivalent to 1.3 tonnes of 1.6 year-old 20,000 MWd/tonne power reactor fuel were processed to produce 213 kg of glass product. The 73 liters of radioactive glass produced a self-generating heat density of 57 W/liter (4200 W total).

The denitrator was fed 725 liters of adjusted sulfate containing PW-2 type feed (540 liters/tonne) in 77 hr at an average feed rate of 9.4 liters/hr (see Table I for composition). The feed contained 1,160,000 Ci of radioactivity including 33,000 Ci of radioruthenium. The feed was concentrated in the denitrator-evaporator by a factor of 5.1. The continuous addition of a commercial silicone antifoam agent to the denitrator at a rate of about 100 ppm/hr (3.9 liters solution/hr) and top entry feeding into the vapor space of the denitrator were sufficient to control foaming. Denitrator foaming was allowed to occur prior to the start of the antifoam addition. None of the denitrator contents foamed over into the melter condensate. Additional operating parameters and collected data for Runs PG-4 and PG-5 are listed in Table II. Also see Figure 1 for Mode A equipment arrangement.

\* Registered trademark of International Nickel Company

\*\* Registered trademark of Carpenter Steel Company

TABLE I. Feed Composition for PG-4 and PG-5

Component	PW-2 for PG-4		PW-1 for PG-5	
	Molarity, M <sup>(a)</sup>	Lab Analysis, M	Molarity, M <sup>(a)</sup>	Lab Analysis, M
H <sup>+</sup>	---	4.3		
Fe <sup>+3</sup>	0.184		0.93	0.4
Cr <sup>+3</sup>	0.024		0.012	
Ni <sup>+2</sup>	0.01		0.005	
Al <sup>+3</sup>	0.262 <sup>(b)</sup>		0.001	
Na <sup>+1</sup>	0.95	0.99	0.138	
UO <sub>2</sub> <sup>+2</sup>	0.01		0.010	
NO <sub>2</sub> -NO <sub>3</sub> <sup>-1</sup>	5.37	4.15	7.5	
SO <sub>4</sub> <sup>-2</sup>	0.86	0.97	---	
PO <sub>4</sub> <sup>-3</sup>	0.006		0.003	
SiO <sub>3</sub> <sup>-2</sup>	0.01		0.01	
Cs <sup>+</sup> (added K)	0.42		0.42	
Sr <sup>+2</sup>	0.0155		0.0155	
Ba <sup>+2</sup>	0.0195		0.0195	
(Y + Re) <sup>+3</sup>	0.12		0.12	
ZrO <sup>+2</sup>	0.065		0.065	
MoO <sub>4</sub> <sup>-2</sup> + Tc as MoO <sub>4</sub> <sup>-2</sup>	0.079		0.079	
Ru <sup>+2</sup>	0.0032		0.0032	
Ru <sup>+2</sup> (added Fe <sup>+3</sup> )	0.0288		0.0288	
Rh <sup>+2</sup> (added Co <sup>+2</sup> )	0.0074		0.0074	
Pd <sup>+2</sup> (added Ni <sup>+2</sup> )	0.0172		0.0172	
Ag <sup>+2</sup> + Cd <sup>+2</sup> (added Cu <sup>+2</sup> )	0.0016		0.0016	
Te <sup>+4</sup> (added SO <sub>4</sub> <sup>-2</sup> )	0.0064		0.0064	
<u>Additive to Feed</u>				
Na <sup>+1</sup>	---	---	2.46	---
M <sub>T</sub> <sup>+</sup>	3.48		3.77	
PO <sub>4</sub> <sup>-3</sup>	3.36	3.2	3.77	---
M <sub>T</sub> <sup>+</sup> /P		1.09		1.0
Specific gravity at 25 °C		1.43		1.38
% Solids		10% solid 56% slurry		65% slurry
Final Volume, liters/tonne		540		666
<u>Radioactivity</u>				
Total, Ci/liter		1590		3000
Ru, Ci/liter		46		53.4
Heat, W/liter		7		12.1

(a) Molarities are at 378 liters/tonne.

(b) Aluminum is considered as a substitute for part of the iron.

**TABLE II. WSEP Phosphate Glass Solidification Operating Parameters and Results**

Operation Data	PG-4	PG-5
<u>Run Number</u>		
Date	2/68	4/68
Feed Type	PW-2 <sup>(a)</sup>	PW-1
Feed, liter/tonne	540	666
Pot Diameter, in.	8	12
Pot Material	Mild Steel	Mild Steel
Run Feed Time, hr	77	104
Average Feed Rate, liter/hr	9.4	8
Average Steady State Feed Rate, liter/hr	7.5	NA <sup>(c)</sup>
Cooling, hr	2 <sup>(b)</sup>	NA
Total Feed, liters	725	825
Total Feed, tonne equivalent	1.3	1.2
Feed: Solid Volume Ratio	9.1	2.1
Operating Mode	A	A, B
<u>Problems</u>	1. Overfed melter causing high level of foam in melter.	1. Continuous plugging problems in airlift pot recirculation line, melter feed line, and denitrator dip tubes.
<u>Fraction of Activity in Condensate, Total Less Ru and /Ru</u>		
Through Melter Condenser	$\sim 2 \times 10^{-3} / 1.2 \times 10^{-2}$	$3.2 \times 10^{-3} / 9.9 \times 10^{-2}$
Through First Condenser	$3.5 \times 10^{-3} / 2.2 \times 10^{-2}$	NA/NA
Through Evaporator Condenser	$3.1 \times 10^{-7} / 8.5 \times 10^{-4}$	$4.6 \times 10^{-6} / 2.7 \times 10^{-3}$
Through Fractionator Condenser	$2 \times 10^{-9} / 2 \times 10^{-6}$	$3 \times 10^{-8} / 8.4 \times 10^{-7}$
Off-Gas to Scrubber	$4 \times 10^{-9} / 7 \times 10^{-7}$	$9.4 \times 10^{-10} / 1.6 \times 10^{-6}$
Off-Gas to Stack	$2 \times 10^{-12} / \text{NA}$	$1 \times 10^{-12} / \text{NA}$
Ratio Activity <sup>(e)</sup>	$4 \times 10^2 / 7.8 \times 10^3$	$1.8 \times 10^3 / 1.8 \times 10^3$
<u>Filled Pot Data</u>		
Total Curies in Feed to Pot	$1.2 \times 10^6$	$2.5 \times 10^6$
Curies of Ru in Feed	$3.3 \times 10^4$	$4.4 \times 10^4$
Solid in Pot, liters	73.3	115
Solid in Pot, kg	213	400
Solid in Pot, liter/tonne	56.4	95.8
Heat in Pot, W	4200 <sup>(d)</sup>	8300
Equivalent Aging Time, years	1.6	0.5
☉ Temperature in Good Furnace, °C	510	740
☉ Temperature in Water, °C	NA	NA
Δ Temperature ☉ to Wall, °C	175	340
Total Corrosion, mm	NA	NA
Welded Lid	Yes	Yes
Pot Self Pressurizer, psi	NA	NA
Pot Leakage, atm cm <sup>3</sup> /sec	NA	NA
Radiation Reading, R/hr at 6 in.	$3.7 \times 10^4$	$4.7 \times 10^4$

(a) Aluminum substituted for ~50% of nominal 0.445 iron

(b) Values are with pot sitting in cool furnace.

(c) Not available

(d) By pot calorimetry data

(e) Ratio of activity concentration in the fractionator condensate to that in 10CFR20

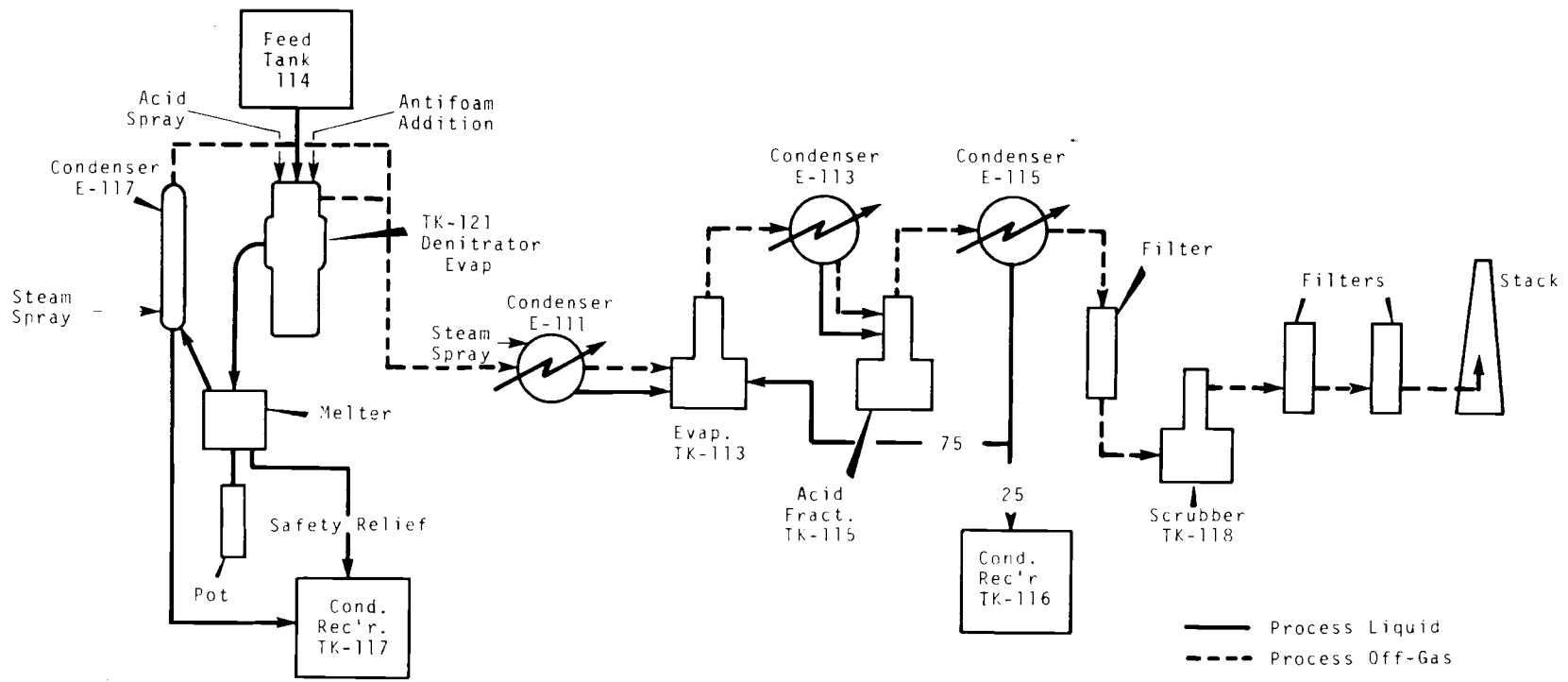


FIGURE 1. Mode A Arrangement for PG-4

Prior to the run, laboratory investigations on nonradioactive feed (discussed above in the Process Technology section of this report) and on actual radioactive feed from the previous Run PG-3 were made to determine the cause of and methods for prevention of foaming. It was established that dibutyl phosphate (DBP) is an effective foaming agent in the evaporator concentrate and was probably the cause of the foaming during previous Runs PG-1, 2, and 3. The silicone antifoam agent was found to counteract the DBP-induced foaming in the laboratory test apparatus during short-term tests, but was less successful in tests lasting several hours. The radioactive feed tests were conducted in B-Cell on the feed from PG-3 to investigate foaming in a glass scaled-down test apparatus similar in geometrical shape to that of the denitrator. It was found that foaming was time-dependent with some foam-making material accumulating in the denitrator. Subsequently, it was found that the antifoam agent would successfully subdue foam and prevent its recurrence if the antifoam was added continuously to the system. In the full-scale denitrator, a continuous addition of approximately 100 ppm/hr was required for adequate control.

Startup and shutdown for the denitrator required 12 and 13 hr respectively, thereby leaving 65 hr of steady-state operation. The average feed rate during steady-state was 7.5 liters/hr limited by a maximum liquid level of 27 in. in the denitrator. Of the 725 liters of adjusted feed (540 liters/tonne) fed to the denitrator, 669 liters of equivalent feed was airlifted to the melter. After the final dumping of the melter, cooling the pot to where the steady-state wall temperature in the "cool" furnace would not exceed 425 °C required 2 hr. These conditions gave an average processing rate of waste from 0.35 tonnes of power reactor waste per day. This includes startup, steady-state operation, shutdown, and cooling time. The steady-state processing rate was 0.48 tonnes of power reactor waste per day.

The 57 W/liter of self-generating heat density in the glass was sufficient to produce a pot centerline temperature of 510 °C and a centerline-to-wall  $\Delta T$  of 175 °C with the pot in the "cool" furnace.



These values indicate an effective thermal conductivity of the glass of 0.44 Btu/(hr)(ft)(°F) [0.76 W/(m)(°C)]. The product had a glassy, dark, greenish-brown color and a measured density of 2.9 kg/liter.

With the melter operating at 1220 °C, the internal melt temperature ranged from 840 to 1100 °C, depending on feed rate to the melter. The melt was overflowed through the unheated melter weir until the end of the run when it was batch-dumped through the freeze valve into the receiving pot. This was done to completely empty the melter. Receiving pot temperatures were controlled at 550 to 590 °C to prevent stalagmite formations.

As a result of using a 4 year-old radiocerium solution as the main heat contributor for the feed, the rare earth content in the feed was approximately 6 times the nominal 0.12M. Additional phosphoric acid and sodium (2.17M and 0.5M respectively) were added to form a good melt.

Aluminum was substituted for about 50% of the nominal 0.445M iron in the PW-2 feed because of excess aluminum in the sulfate-free waste stock from the Purex Reprocessing Plant. This aluminum produced no noticeable change in the expected processing characteristics.

During PG-4, 2.2% of the total ruthenium and 0.35% of other radioactive species that were fed to the denitrator were volatilized or entrained. Likewise, 1.3% of the total ruthenium and 0.22% of all other radioactive species that were fed to the melter were volatilized or entrained. Figure 2 shows the fission product accumulation in the melter condensate.

The ruthenium decontamination factor (DF)<sup>\*</sup> (cumulative for the entire run) across the WSEP condensate evaporator was 32. The cumulative DF for nonvolatiles across the evaporator was  $3.1 \times 10^5$ . The fractionator had a DF\*\* for ruthenium and nonvolatiles of 400 and 300, respectively. Figure 3 shows the ruthenium volatility from the WSEP evaporator.

The fraction of feed activity in the final condensate stream from the acid fractionator was  $2 \times 10^{-6}$  for ruthenium and  $2 \times 10^{-9}$  for other

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\* Total curies in evaporator at end of run from any source/total curies gained in fractionator.

\*\* Total curies in fractionator at end of run from any source/total curies gained in fractionator condensate.

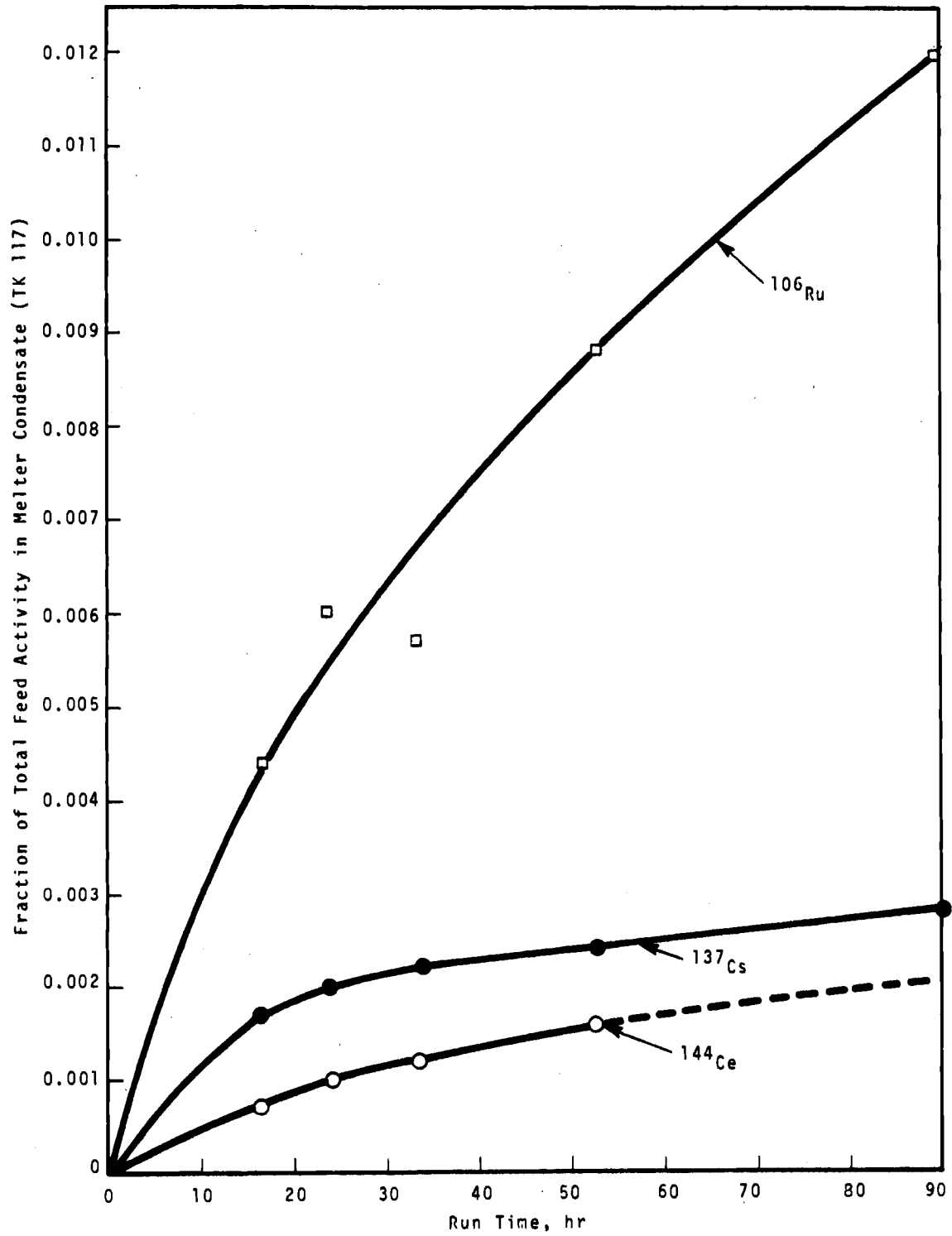


FIGURE 2. Fission Product Accumulation in Melter Condensate (WSEP Run PG-4)

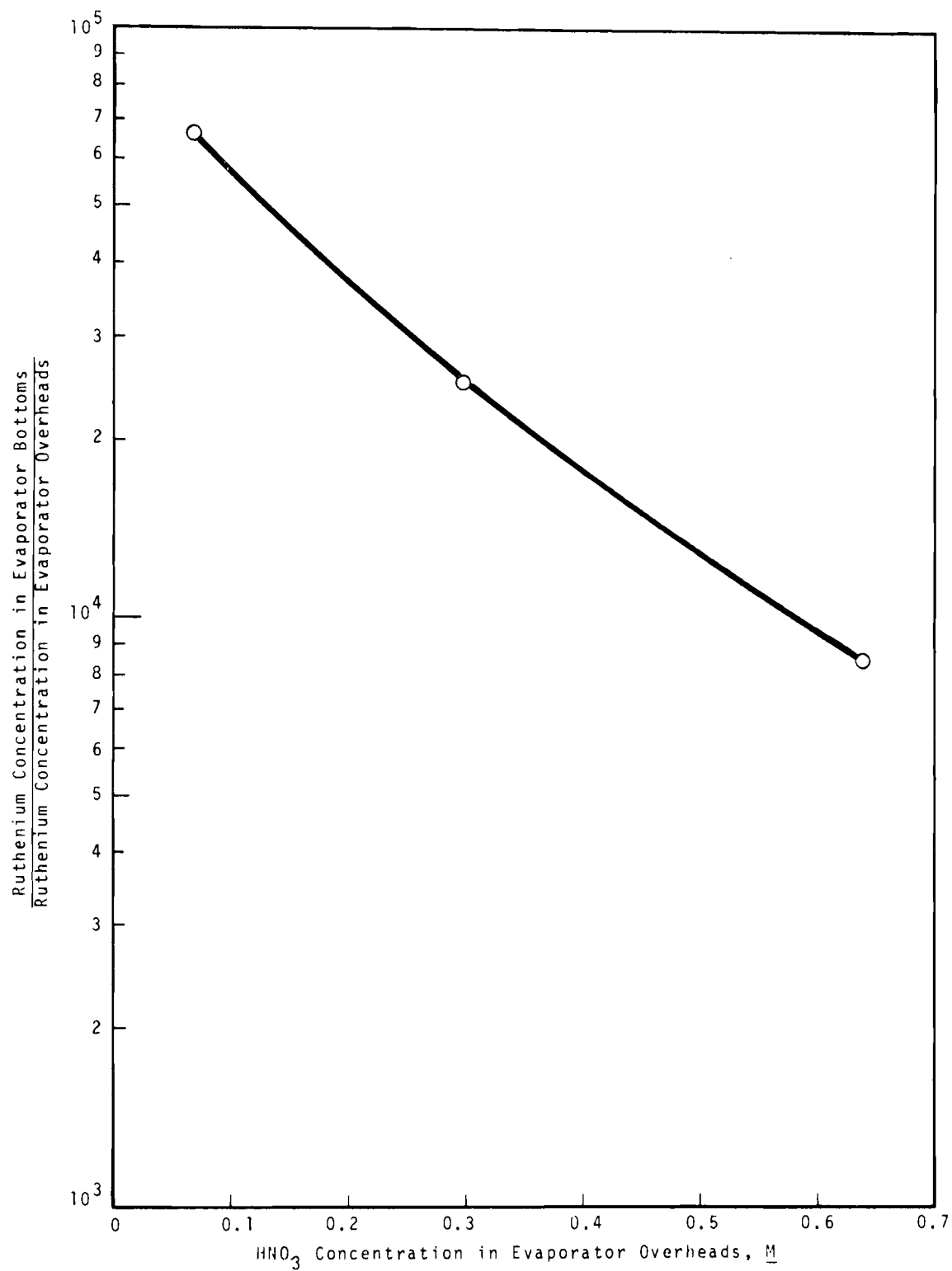


FIGURE 3. Ruthenium Volatility from Evaporator  
(WSEP Run PG-4)

combined fission products. This represents activity which is above CFR20 limits\* by factors of 7800 and 400.

A test that was conducted to investigate the effects of air sparging the melter on melter capacity was inconclusive.

#### Run PG-5

Phosphate Glass Run PG-5 was completed in WSEP using a sulfate-free PW-1 type feed containing 2.46M sodium additive as a melt-making flux. During PG-5, wastes equivalent to 1.2 tonnes of 0.5 year-old 20,000 MWd/tonne power reactor fuel were processed to produce 315 kg of glass product. The 115 liters of radioactive glass produced a self-generating heat density of 77 W/liter (8800 W total).

The denitrator was fed 825 liters of adjusted sulfate-free PW-1 type feed (666 liters/tonne) in 104 hr at an average feed rate of 8 liters/hr (see Table I for composition). The feed contained 2,500,000 Ci of radioactivity (10,000 W) including 44,000 Ci of radoruthenium. The feed was concentrated in the denitrator-evaporator by a factor of approximately 3. Continuous addition of a silicone antifoam agent was used throughout the run at an average rate of 11 g/hr (1 1/2 liters/hr solution). The antifoam addition completely suppressed any foaming in the denitrator.

During the run approximately 2,000,000 Ci of radioactive waste was concentrated along with the denitrator condensate in the WSEP evaporator for use during the next run, PG-6. Figure 4 shows the Mode B equipment arrangement for performing this operation.

After 38 hr of operation the melter feed line became plugged with solids from the denitrator concentrate. The run was temporarily shut down until the melter feed line was unplugged. This was finally done by heating the feed line with 130 °C steam while the line was lightly tapped. The line was then flushed with nitric acid, and the run was later restarted. Plugging difficulties with specific gravity and weight factor dip tubes of the denitrator did not occur until approximately 50 hr had elapsed during both parts of the run. During this time, continuous

\* AEC's Rules and Regulations, 10-CFR 20, Table II Column II.

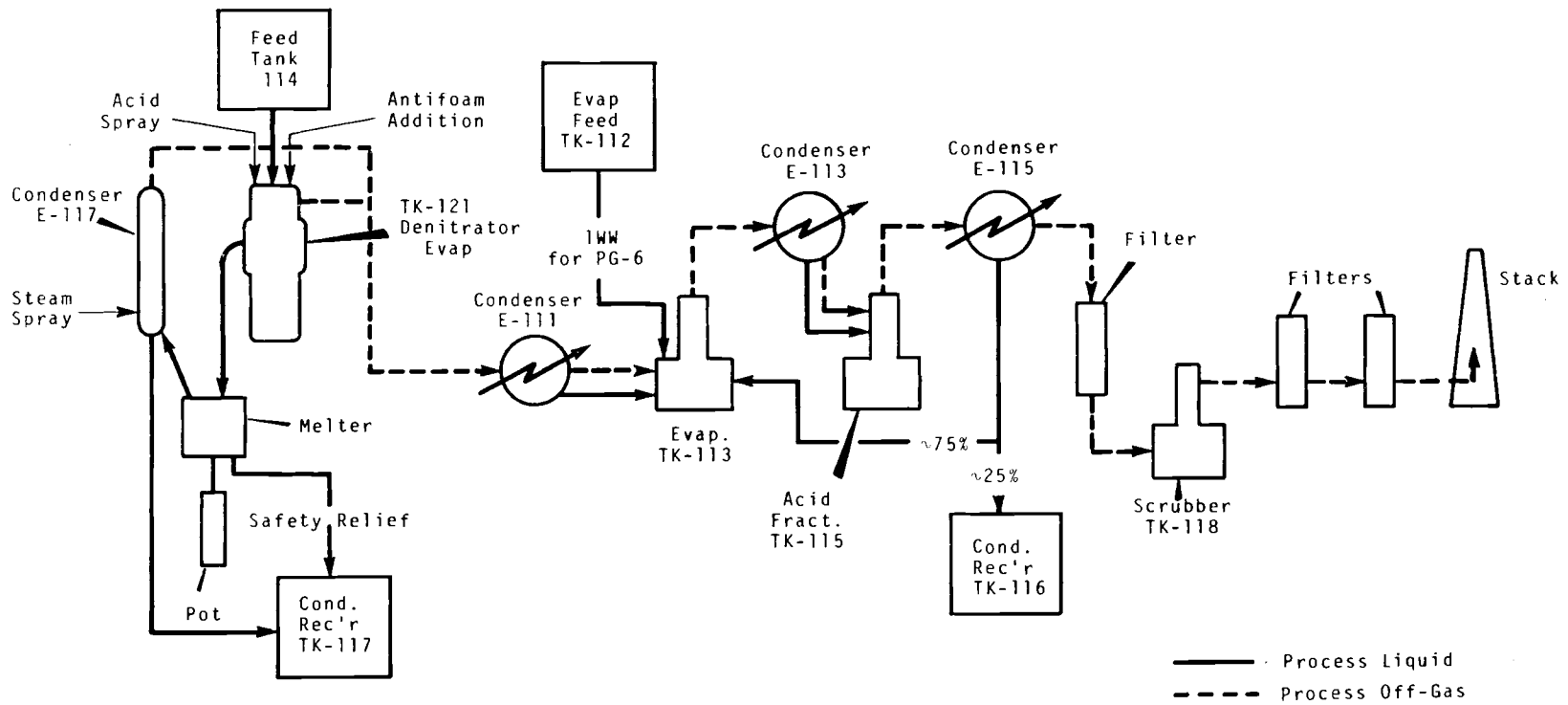


FIGURE 4. Mode B Arrangement for PG-5

steam purges were being used to prevent plugging. Following this, a steam purge of the dip tube once every 2 hr satisfactorily prevented plugging. Some plugging difficulties in the airlift pot recirculation line to the denitrator were encountered and were overcome by using the remote features of the newly installed airlift pot and by acid spraying the entire pot. The remote feature that was used to help unplug the recirculation line was the adjustable recirculation plug valve which was extended in and out of the recirculation line.

Excessive foaming in the melter occurred only once and was generally prevented by maintaining the melt above 950 °C. The rate of discharge of radioactive glass from the melter to the 12 in. diameter mild steel pot was approximately 1 liter of glass per hour. With the pot in the cool furnace, the 8800 W of internal heat produced a centerline temperature of 700 °C and a centerline-to-wall temperature difference of 375 °C. These values give an effective thermal conductivity of 0.58 Btu/(hr)(ft)(°F). No plugging of the dip tubes occurred in the WSEP auxiliary evaporator, in contrast to several previous runs. This lack of plugging was attributed to a thorough flushing of the dip tubes with alternating flushes of caustic and nitric acid prior to PG-5.

The only other difficulty that occurred during the run was when the Number 1 feed pump developed a leak after 92 hr of feeding; the run was completed using the Number 2 feed pump.

### SPRAY SOLIDIFICATION

#### SPRAY CALCINER DEVELOPMENT - W. R. Bond

During the quarter, Runs DSC-15, 16, and 17 were made using a simulated low-salt (PW-4) feed to the spray calciner and platinum melter. Additives used in the first two runs were 1.5M NaNO<sub>3</sub> and 1.1M H<sub>3</sub>PO<sub>4</sub> at 100 gal/tonne, while the third run additives of 1.1M NaPO<sub>3</sub> and 0.4M NaOH at 100 gal/tonne were used. In all three runs the ratio of metal equivalents to phosphorus atoms was 2.3. This formulation had a melting point of 900 °C and a calcine stick point of 750 °C which are compatible with spray calciner and platinum melter operation.

Pertinent run conditions and results for the runs are presented in Table III. After Run DSC-15 the calciner barrel was caked badly with a

1/2 to 3/4 in. thick calcine scale the full length of the barrel. The calcine apparently had been wet, and after contacting the hot walls it dried there as a cake. There was no indication that the calcine had sintered, and the deposition was apparently the result of exceeding the drying capacity of the calciner. The total of 9 kg of calcine was removed from the calciner barrel. For Runs DSC-16 and 17, lower feed rates (see Table III) were used than in DSC-15. Although inspection of the calciner after run DSC-16 revealed some scale, less than 2 kg of calcine were removed from the barrel. The calciner barrel was relatively clean after run DSC-17. No significant deposition occurred in the calciner cone during any of the runs.

TABLE III. Run Conditions and Results

<u>Run No.</u>	<u>DSC-15</u>	<u>DSC-16</u>	<u>DSC-17</u>
Feed Type	PW-4	PW-4	PW-4
Atomizing Gas	Air	Air	Air
Calciner Furnace Temperature, °C	675 to 700	690 to 700	700
Melter Furnace Temperature, °C	1000 to 1025	1025 to 1060	1025 to 1110
Pot Furnace Temperature, °C	--	--	800
Feed Consumed, liters	164	174	154
Feed Concentration, liters/tonne	379	454	454
Feed On-Time, hr	9	12	10
Average Feed Rate, liters/hr	17.2 first half 19.2 second half	14.5	15.4
Product Collected, kg	20.9	19.8	18.7
Product Concentration, liters/tonne	27.2	27.4	26.4
Pot Material	304-L SS	304-L SS	304-L SS
Pot Diameter, in.	8	8	8

The filter pressure drop during DSC-15 ranged between 10 and 11 in. of H<sub>2</sub>O at a blowback steam pressure of 30 psig. The blowback pressure was increased to 50 psig for one hour midway through the run. The filter pressure drop was reduced to 7 in. of H<sub>2</sub>O during this period, and chunks of filter coat were noted falling into the melter. The filter pressure drop rose back to the previous range after the blowback pressure was reduced to 30 psig.

Inspection of the filters after the run revealed that the bottom half of the filters was relatively clean with a filter coat approximately 1/16 in. thick. The top section of filters had a very dense filter coat 1/8 to 1/4 in. thick with large chunks of calcine lodged between the filters. Apparently, the filter coat broke loose in chunks during the use of 50 psig blowback steam, and the chunks were unable to fall clear of the filter because of their size. The application of 90 psig blowback air failed to remove any calcine from the filters. The filters were cleaned in-place by injecting nitric acid directly into the blowback steam.

During the first 5 hr of Run DSC-16, the filter pressure drop rose from 0.5 to 8 in. of H<sub>2</sub>O while 30 psig blowback steam was used. It was necessary to increase the blowback pressure to 40 psig to level the filter pressure dropout at 8.5 in. of H<sub>2</sub>O. Inspection of the filters after the run revealed them to be covered with a dense filter coat 1/8 to 3/16 in. thick. There was no holdup of calcine between the filters. The application of 90 psig blowback air reduced the filter coat to less than 1/16 in. thick. The filters were then cleaned by back flushing with water.

Difficulty was experienced with excessive filter pressure drop during Run DSC-17. The filter pressure drop rose from 0.5 to 2.5 in. of H<sub>2</sub>O during the 15 min that water was fed and rose to 7.0 in. of H<sub>2</sub>O within 5 min after the feed was turned on. Despite the fact that the blowback steam pressure was raised progressively from 35 to 65 psig and the blowback cycle was reduced from 2 to 1 min, the filter pressure drop increased to 15 in. of H<sub>2</sub>O after 7 hr of feeding. The feed and atomizing air were turned off at this point, and the filters were blown back with 70 psig steam for 20 min. Restart of the run revealed that the filter pressure drop was reduced to only 12 in. of H<sub>2</sub>O, and increased to 15.3 in. of H<sub>2</sub>O at the end of the run despite the use of 70 psig blowback steam. Postrun inspection of the filters revealed them to be coated, as in the previous runs, with a very dense coat of fine calcine approximately 3/16 in. thick.



The PW-4 melt was discharged by batch from the melter via the freeze valve during both DSC-15 and 16. Melt batches ranged from 2 to 4 liters and were discharged in 1 to 2 min. The dump procedure involved reduction of the calciner vacuum to 1 to 2 in. of H<sub>2</sub>O just prior to the dump so as to essentially empty the melter. The calciner vacuum was increased back to normal immediately after the dump and in some cases reduced again briefly to reseal the freeze valve. During one dump, the calciner vacuum was not reduced, and the melter continued to drip after the dump. It was then necessary to completely empty the melter by reducing the calciner vacuum in order to reseal the freeze valve. The drip discharge of the melter at the end of this dump was erratic and caused partial blockage of freeze valve port. In general, the melter drained during a dump in a straight steady stream. One exception occurred when the freeze valve thermocouple stuck out into the melt stream and caused a stalagmite that completely filled the freeze valve port. Although the receiver pot was unheated during both these runs, the melt dumps filled the pot evenly. Sectioning of the pot revealed some void space between the batches and gas pockets within the batches. The bulk density of the product as measured in the receiver was 2.6 kg/liter, or approximately 83% of theoretical.

The melt was discharged continuously during DSC-17 from the melter via the weir which drained both by drop and in a steady stream as a result of pressure fluctuations in the melter caused by the filter blow-back. Immediately following a pressure increase in the melter, the steady stream melt discharge became quite erratic just prior to the transition to dropwise discharge, and as a result, considerable melt splattered against the sides of the weir port and formed stalactites. Several of these had to be broken off during the run, and one of these almost completely filled the weir port. The weir quit discharging 1 1/2 hr before the end of the run as a drop of melt solidified just off the end of the weir tip. At the end of the run it was necessary to raise the freeze valve temperature to 1020 °C before the melt could be drained from the melter. The freeze valve quit discharging with about a 1/2 liter of

melt remaining in the melter, and it was found that a drop of melt had also solidified off its tip. The drip point of the melt was determined to be 860 °C, which was comparable to that of previous runs. There was some splatter on the walls and thermowell of the receiver pot as a result of the erratic weir discharge, but there was no gross deposition. The bulk of the melt had laid out evenly in the bottom of the heated receiver pot.

Denitration of the calcine was noted in the melter during the first two runs. Analyses of calcine samples indicated that calcine from DSC-15 contained as much as 18 wt% nitrate, and that from DSC-16 contained as much as 10 wt%. Under similar operating conditions, the nitrate contents of PW-1 and PW-2 calcines were routinely less than 2 wt%. Analytical data on ruthenium volatility during Run DSC-16 indicated that instantaneous ruthenium losses to the condensate ranged from 4 to 20% during the run with an overall loss of 12%. However, analyses of calcine and melt samples indicated losses of ruthenium ranging from 80 to 90%. This discrepancy has not been resolved. The effect on the calcine denitration and ruthenium volatility as a result of using  $\text{NaPO}_3$ , and NaOH as additives during Run DSC-17, instead of  $\text{H}_3\text{PO}_4$  and  $\text{NaNO}_3$ , is not yet known because of the unavailability of analytical results.

#### MELT CONTAINER CORROSION - R. F. Maness

A simulated spray-solidified phosphate melt prepared from PW-4 solution (Meq/P = 2.3) corroded both 304-L and 310 SS at a rate of about 15 mils/month in 100 hr tests at 800 °C.

#### PRODUCT CHARACTERIZATION AND STORAGE

##### PRODUCT MEASUREMENTS, TESTING AND STORAGE

#### A-Cell Modifications for SSETF - V. P. Kelly

Beneficial occupancy of A-Cell for the Solids Storage Engineering Test Facility (SSETF) was achieved as scheduled with the completion of in-cell modifications by mid-March. Completed items included installation of the second floor window and the stainless steel wall liner. Items remaining to complete the project are design and fabrication of a wall transfer mechanism, fabrication of a shielded ion chamber, and completion of miscellaneous gallery items.

SSETF Equipment and Systems Fabrication and Installation - V. P. Kelly

Fabrication and installation of SSETF equipment proceeded at a vigorous pace. Items of equipment include:

1. The pot storage rack: a stainless-steel pipe structure to be installed in the cell to support test pods and pots during assembly.
2. Sixteen test pods (ten completely assembled).
3. The third-floor TV plug required for viewing upper level remote operations.
4. The remotely operated mirror unit as additional viewing aid.
5. Electrical, instrument, mechanical drive, welding, leak test, and air supply wall plugs.
6. Three test pod heater control units, providing a total of seven of the required ten units.
7. The 300-point digital data acquisition system for temperature monitoring is about 50% complete.

Pot transfer hardware and incell tool systems are required to activate the cell.

Remote Handling Tests - V. P. Kelly

Remote handling design verification testing is required to verify operability of in-cell components. The first phase of these tests was completed with the transfer of four storage pods from the fabrication shop to the cell, and remote installation of the first pod in a second-floor cubicle opening. Placement of handling pods into third-floor cubicle openings, removal of lights and filters, and assembly of a pot and pod will complete remote handling tests.

LABORATORY STUDIESPG-1 and PG-2 Leach Rate Measurements - J. E. Mendel

Leach rates on a grab sample of a phosphate glass product from WSEP Run PG-1 have been measured in room-temperature water on a weekly basis for 4 1/2 months. The leach rate, based on the amount of

$^{137}\text{Cs}$  found in the leach water, has leveled off at about  $9.0 \times 10^{-7} \text{ g/cm}^2/\text{day}$ . The leach rate, based on  $^{144}\text{Ce}$  is about  $1.8 \times 10^{-7} \text{ g/cm}^2/\text{day}$ .

A grab sample of phosphate glass product from WSEP Run PG-2 has been leached 2 3/4 months. The leach rates are  $1.4 \times 10^{-6}$  and  $2.4 \times 10^{-7} \text{ g/cm}^2/\text{day}$ , based on  $^{137}\text{Cs}$  and  $^{144}\text{Ce}$  respectively, and may still be decreasing slowly. Because of the higher activity in Run PG-2,  $^{95}\text{ZrNb}$  and  $^{106}\text{Ru}$  were also detected in the leach water.  $^{95}\text{ZrNb}$  leached at about the same rate as  $^{137}\text{Cs}$ , while  $^{106}\text{Ru}$  leached at a lower rate, about the same as  $^{144}\text{Ce}$ .

#### Study of Molten Core Storage of Solidified Waste Containing Sulfate -

D. W. Brown

Decomposition of sulfate gas resulting in pressure buildup is most probable under conditions of high-temperature, molten core storage of melt-solidified waste products that have a high sulfate content. A vessel has been designed and built whereby molten core storage can be simulated and pressure buildup due to sulfate decomposition can be followed. This will be accomplished by centering a heater in a 12 in. diameter storage pot about 30 in. high and filled with a simulated spray solidifier sulfate-containing PW-2 waste.

#### INTERMEDIATE AND LOW LEVEL WASTE

#### WSEP CONDENSATE TREATMENT - ENGINEERING DEVELOPMENT -

W. T. McKean

All major components have been received for the Distillation Demonstration Unit for pilot scale distillation of melter condensate from the phosphate glass process. Exceptions are the tantalum tank and piping and the Sihi\* vacuum pump. Installation of vessels, piping, and instruments is in progress.

Preliminary work with laboratory-scale apparatus similar to that used at BNL is proceeding in C-Cell. Preliminary results indicate that ruthenium evolution can be minimized by using semicontinuous operation and nitrogen sparge. Current BNL efforts are to determine the effect of acid ratios and concentrations on the decontamination factors.

\* A product of Heraeus-Englehard Vacuum, Inc.

The results of the laboratory scale runs will be used to direct tests with the Distillation Demonstration Unit. Tentatively, nitrogen sparge will be employed, and semicontinuous feed operations will be tested.

### SUPPORTING ACTIVITIES

#### RUTHENIUM VOLATILITY STUDY - D. W. Brown

Investigations have begun to determine ways to reduce ruthenium volatility or remove ruthenium from the off-gas to levels acceptable in waste solidification. One trap tried was an electrical capacitor arrangement 2 in. long with a 1/2 in. diameter and one lead into a wool plug; the other lead was wrapped around the glass. This was run at 115 °C with 1500 V, and 0 current across the trap. The result was about 5% of the ruthenium input past the trap compared to about 20% of the ruthenium input past the trap with 30 V and a bed temperature of 170 °C. This should be investigated further at higher potentials and different bed temperatures, using tracer ruthenium for analytical purposes.

Formaldehyde additions to the feed lowered ruthenium volatilized to 4.3% as compared to 37% ruthenium volatilized when no formaldehyde was used. However, formaldehyde is too reactive to handle easily, and a large quantity is apparently needed; 18.5% formaldehyde by volume was added to the feed solution to effect this decrease.

A more satisfactory additive was hypophosphorus acid,  $\text{H}_3\text{PO}_2$ . When 1M  $\text{H}_3\text{PO}_2$  and 0.097M cold ruthenium was used in PW-1 spray solidifier feed, the ruthenium volatilized was less than the minimum detection limit of 2.75% compared to 37% volatilized when no  $\text{H}_3\text{PO}_2$  was used. On heating PW-1 spray solidifier feed solution with 1M  $\text{H}_3\text{PO}_2$  present, visible  $\text{NO}_3^-$  decomposition started at about 80 °C. Analyses indicate that 0.25M  $\text{H}_3\text{PO}_2$  has little effect on ruthenium volatility with PW-2 (without sulfate) spray solidifier or pot calcination feeds.

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