DP-MS-79-92

CONF-800460--1

CHARACTERIZATION OF OFF-GASES FROM A SMALL-SCALE, JOULE-HEATED CERAMIC MELTER FOR NUCLEAR WASTE VITRIFICATION

by

G. B. Woolsey and E. L. Wilhite

Savannah River Laboratory
E. I. du Pont de Nemours & Company
Aiken, South Carolina 29808

MASTER

To be presented at the 82nd Annual American Ceramic Society Meeting to be held in Chicago, IL, April 27-30, 1980.

This paper was prepared in connection with work under Contract No. DE-AC09-76SR00001 with the U.S. Department of Energy.

DISCLAIMER

DP-MS-79-92

CHARACTERIZATION OF OFF-GASES FROM A SMALL-SCALE, JOULE-HEATED CERAMIC MELTER FOR NUCLEAR WASTE VITRIFICATION

G. B. Woolsey and E. L. Wilhite

Savannah River Laboratory
E. I. du Pont de Nemours & Company
Aiken, South Carolina 29808

Savannah River Plant Waste

The Savannah River Plant has been producing plutonium and other radioisotopes for the past 26 years. About 68 million gallons of high-level radioactive waste were generated during that time and about 1.5 million gallons are now generated each year. The volume of stored high-level waste has been reduced by evaporation to 23 million gallons, and this inventory is stored in 33 underground tanks. We have a goal of immobilizing this high-level waste in such a way that it may be stored without surveillance and be safe from dispersion in the environment for up to 1000 years, the time needed for decay to activity levels of natural radioactive ores.

Savannah River liquid waste was initially acidic and contained dissolved salts. When the waste was neutralized, insoluble oxides precipitated and settled out as a sludge in a storage tank. The supernate was decanted and pumped to an evaporator. The concentrated waste was returned to a storage tank where, on cooling, soluble salts crystallized out. The remaining supernate was then recycled to the evaporators until the storage tanks contained only the insoluble sludge and a wet salt cake.

Waste Immobilization at the Savannah River Plant

We have chosen to develop vitrification in borosilicate glass as a possible means of immobilizing our waste. The intent of the process is to get all the high-level activity waste into one stream, and then capture the activity in borosilicate glass.

In order to decontaminate the supernate or salt cake portion of our waste, it is dissolved in water and its radioactive cesium and soluble strontium are removed by ion exchange. (The remaining decontaminated salt can be disposed of as low-level waste.) The ^{137}Cs and ^{90}Sr are eluted and then prepared for feeding into the glass melter.

The sludge taken from the waste tanks is washed with NaOH and water, to remove aluminum compounds and all water-soluble salts. This wash solution is combined with the supernate and decontaminated. The washed sludge is mixed with the eluted Sr and Cs, dried, and mixed with molten borosilicate glass.

In the reference process, the sludge is dried by spray-calcining. The sludge is sprayed as a slurry into a vertical cylinder heated to over 600°C. The spray droplets dry on passage through the calciner barrel, and the residual nitrates and hydroxides present in the sludge may be converted to oxides. In addition, any volatile components are evaporated if their boiling points are below 600°C. The resulting mixture of non-condensable gases, volatile but condensable gases, and dried particulates is swept onto particulate filters. The filters are 10 μ, sintered Inconel® 600.

The filters are maintained at 350°C to avoid condensing liquids on the filter surfaces. The filter cake which builds up is intermittently blown off with compressed air. When the cake falls into the molten glass at 1150°C, those components boiling below 1150°C start to evaporate.

Studies With Authentic Waste

All of the processes described so far have been demonstrated with simulated waste. Except for spray calcining, these processes have also been demonstrated with authentic waste. In general, the

authentic waste processed the same as simulated waste. Tests with sludge removed from Waste Tank 15 yielded the first direct information on the composition of off-gas when authentic Savannah River Plant waste is vitrified.

Composition of Tank 15 Waste

Waste storage Tank 15 at the Savannah River Plant has been used for sludge accumulation since 1963. When liquid process waste is neutralized and cooled, oxide sludge precipitates and settles from the liquid. The liquid is decanted and evaporated in another vessel. This process was repeated until Tank 15 contained about 5 million pounds of sludge. It has a high aluminum concentration as a result of the processes which generated the waste. Sludges with both high and low aluminum contents, prepared by carrying out or deleting the caustic wash step, were vitrified.

Analysis of the Sludge

The sludge taken from Tank 15 consisted of about 78 weight % liquid and soluble salts, and 22% insoluble solids. Compounds of sodium, aluminum, iron, silicon, NO_3, NO_2, OH^- and SO_4^{-2} were the dominant species. Mercury was abundant.

The elements present which can evaporate at calciner-melter temperatures are of primary concern to us. These are Ru, I, Cs, Hg, Cl, F, and Tc. In addition, Sb, Se, Te, and As are fission products normally found in waste which can evaporate at operating temperatures.

Strontium and cesium contribute the bulk of the radioactivity in the waste, but Ru and other radioactive elements must be immobilized as well.

Sludge Drying

Washed sludge was fed as a slurry to a 5.7 liter fluid bed dryer. Preheated air at a flow rate of about 280 liters/minute fluidized the bed material. Twelve 208V cartridge heaters mounted on the outside wall of the drier heated the bed to about 350°C. Hot air discharged from the fluidized bed carried dry sludge powder and steam from the feed slurry. A single 8 cm. diameter cyclone separated the dry powder. A heated sintered metal filter removed the fines. The air and steam mixture was then discharged to the cell environment. The dryer was fed at about 3 liters/hr. and produced about 100 g/hr. of dry sludge powder.

This equipment was not used to develop process data on sludge drying since a spray calciner is planned for the full-scale plant. A small-scale spray calciner specifically designed to couple with the melter and generate a more representative off-gas will be installed by June 1980.

Volatiles From the Melt

Vitrification of Tank 15 waste provided the first opportunity for an analysis of authentic off-gas from a continuous melter. Volatiles in the sludge which were soluble in water or caustic

were removed in the washing steps; those which boiled below about 350°C evaporated in the fluid-bed drier. Other volatiles present in the sludge were evolved up to 1150°C at the melter. Thirteen off-gas runs were made with Tank 15 sludge.

The off-gas collection system consisted of a semivolatiles trap to condense high boiling components, a packed bed gas-scrubber with recirculating water, a condenser, a 90°C silica gel absorber for gaseous ruthenium compounds, a 250°C silver zeolite absorber for I_2, and a HEPA filter to catch fine particles at the exhaust. The operating flowrate was one standard liter per minute. Sampling points, which were 1M NaOH bubblers, were located both upstream and downstream of major system components for efficiency tests.

The Semivolatiles Trap Revealed the Vapor Composition Near the Melt

Materials which vaporize from the melt but boil at high temperatures can condense in places that affect the coupled calciner-melter's performance in the DWPF. The description of the behavior of semivolatiles was a major objective of the actual waste vitrification experiments.

The semivolatiles trap was a stainless steel 9/16 in. ID tube containing a stack of concentric 1/2 in. OD tube segments (rings). Off-gas from the melter passed through the stacked rings and the

inside walls of the rings provided a surface for deposition of condensing volatiles or reaction products. After an experiment, the rings were sequentially leached with aqueous solutions (including H_2O, H_2SO_4, and HNO_3-HF) to quantify deposition on each ring. For the first six off-gas runs, the entrance-ring was about six inches above the melt surface. The tube was packed with 16 one-inch long rings. Beginning with the seventh off-gas run, the semivolatiles trap was modified to place its entrance within one inch from the melt and to contain 17 rings. Thermocouples were installed at each end of the ring-stack. Each ring between was assigned a temperature based on an assumed linear gradient of 800°C to 130°C.

The vitrification runs were of various durations. The results which I will show are based on the cumulative collection of the elements on each ring. For example, the ^{137}Cs collected on ring number 7 for several runs has been combined. The result is the same as a graph of the percent of the total Cs which was collected on ring number 7, and so on for each ring.

There are a number of elements in defense waste which form compounds boiling between 1150°C and 350°C. Because of their abundance or their special properties, we focused on these elements.

Element	Properties of Interest
Ruthenium	Isotope 106 is radioactive. RuO_4 is volatile and unstable.
Chlorine	Chlorides are corrosive to many alloys. Mixtures of alkali halides may form eutectics which blind particulate filters.
Fluorine	Same as chlorine.
Cesium	Isotope 137 is radioactive. Oxides of cesium boil in the operating range of the calciner-melter.

All are so soluble in borosilicate glass that it is a suitable waste form for them.

The objective of these experiments was to confirm multicomponent thermodynamic analysis of the vapor above the melt. This study had predicted cesium would evaporate and condense in the melter, and that halogens would volatilize as HCl and HF if the sodium concentration were low. In addition, ruthenium should be present as RuO_4 vapor.

Cesium-137 Will Reflux in the Calciner Melter

About 70% of the ^{137}Cs that vaporized from the melt surface deposited on the rings at temperatures greater than 350°C, the off-gas exit temperature in the waste vitrification process. This confirmed the thermodynamics study which predicted that volatile Cs compounds would vaporize from the melt but plate out on the walls of the calciner melter. Cesium-137 will gradually bleed off in the glass as its activity increases in the vapor.

Chlorine Deposited at Low Temperatures

Chlorides condensed primarily on the rings farthest from the melt when caustic washed sludge was vitrified. This was consistent with thermodynamic predictions that HCl would be evolved at these temperatures. The preliminary wash steps removed the soluble chloride and the remaining chloride evaporated as HCl.

We found that if we deleted the caustic wash step, thus leaving the aluminum in the slurry, the chlorides which evolved were higher boiling as shown on this slide in a dashed line.

Fluorine Deposited at Low Temperatures

This slide shows the results for fluorine. The fluorine compounds condensed at temperatures below 400°C, indicating that much of the fluorine will pass through the particulate filters and enter the off-gas treatment system. This result was also predicted by the theremodynamic study.

Ruthenium Deposition did not Depend on Temperature

Except for the fact that all the Ru deposited above 130°C, no discernible pattern emerged from the ruthenium analysis. It seems to collect at random spots in different runs, though sometimes a distinct maximum was observed. The elusive performance of ruthenium will come as no surprise to those who have worked with it. We think in this case it simply decomposed to the solid dioxide homogeneously and stuck wherever it encountered a hospitable surface, either liquid or solid. Separate studies had predicted such behavior. When RuO_4 was passed through a heated chamber, we determined that it decomposed to RuO_2 according to this slide. Another interesting finding was that the RuO_2 produced was so finely divided that much of it passed through two successive caustic wash bottles and exited as the solid entrained in air. This observation is consistent with the known particle sizes of <0.05 μ as found by Rimshaw, for RuO_2 resulting from homogeneous thermal decomposition of Ruo_4.

Conclusions

We have confirmed with actual nuclear waste the thermodynamic predictions of the fate of some of the semivolatiles in off-gas. In addition, we have determined that ruthenium behaves erratically and postulated that it migrates as a finely divided solid, rather than as a volatile oxide. Provisions for handling these waste off-gases will be incorporated in the design of facilities for vitrifying SRP waste.

SLIDE 1

CHARACTERIZATION OF OFF-GASES

FROM A SMALL-SCALE, JOULE-HEATED CERAMIC

MELTER FOR NUCLEAR WASTE VITRIFICATION

SLIDE 2

VOLUME OF WASTE AT SAVANNAH RIVER

- 68 MILLION GALLONS GENERATED FROM OPERATION OF SEPARATIONS PLANTS
- VOLUME REDUCED TO 23 MILLION GALLONS

SLIDE 3

CHARACTERISTICS OF LIQUID

WASTES AT SAVANNAH RIVER

- 10% AS SLUDGE (^{90}Sr, ^{239}Pu)

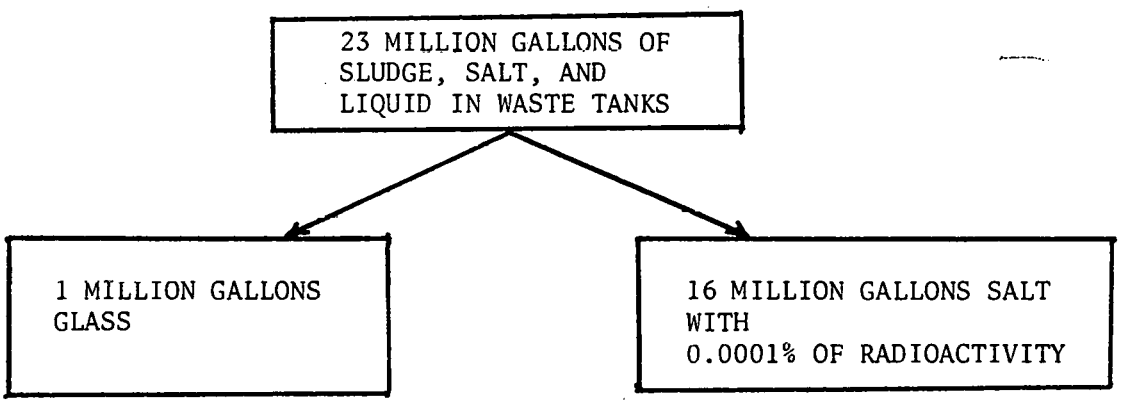
  IRON
  MANGANESE
  ALUMINUM

- REMAINDER AS LIQUID AND SALT CAKE (^{137}Cs)

  SODIUM NITRATE
  SODIUM ALUMINATE
  SODIUM HYDROXIDE

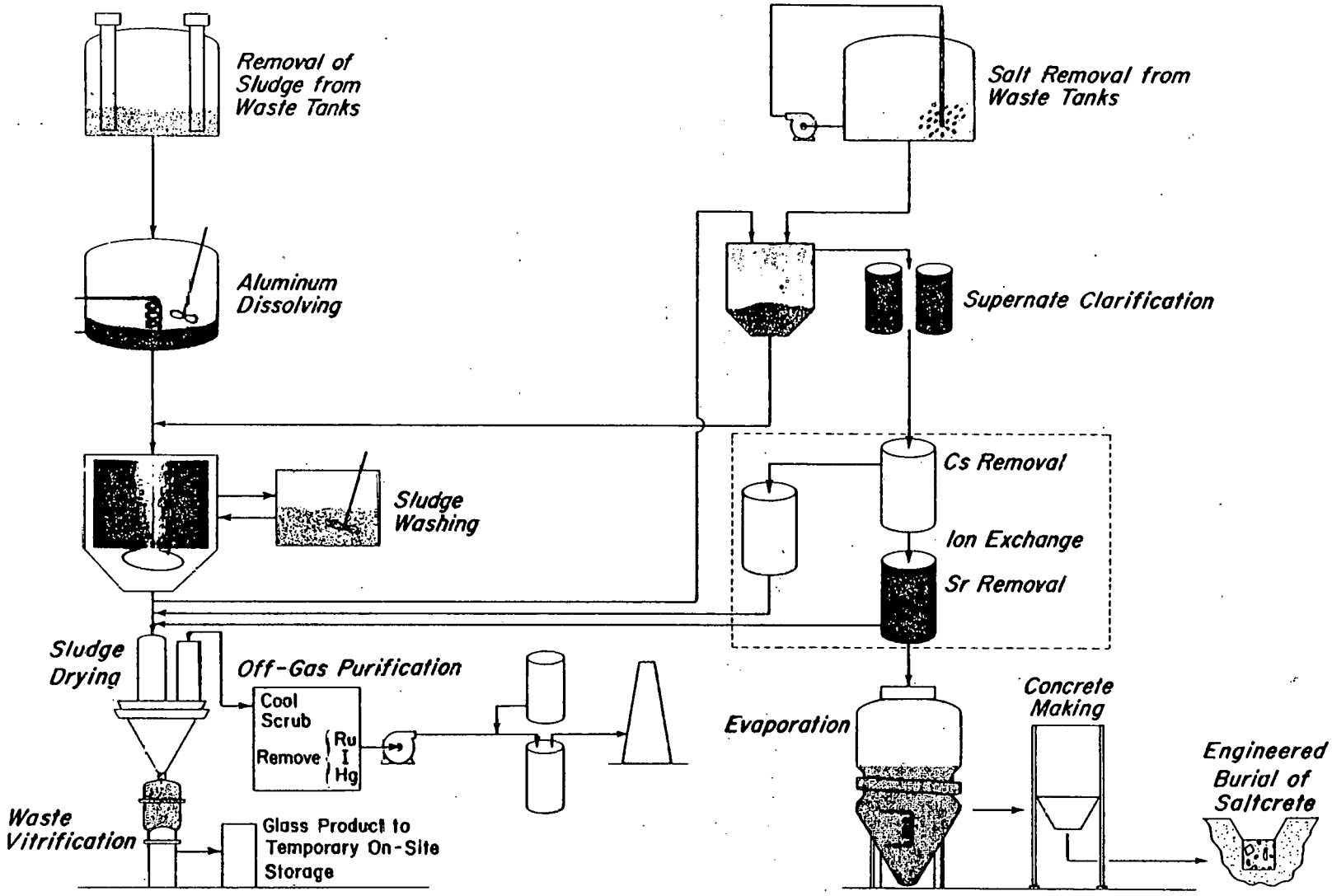
SLIDE 4

DISPOSITION OF WASTE INVENTORY

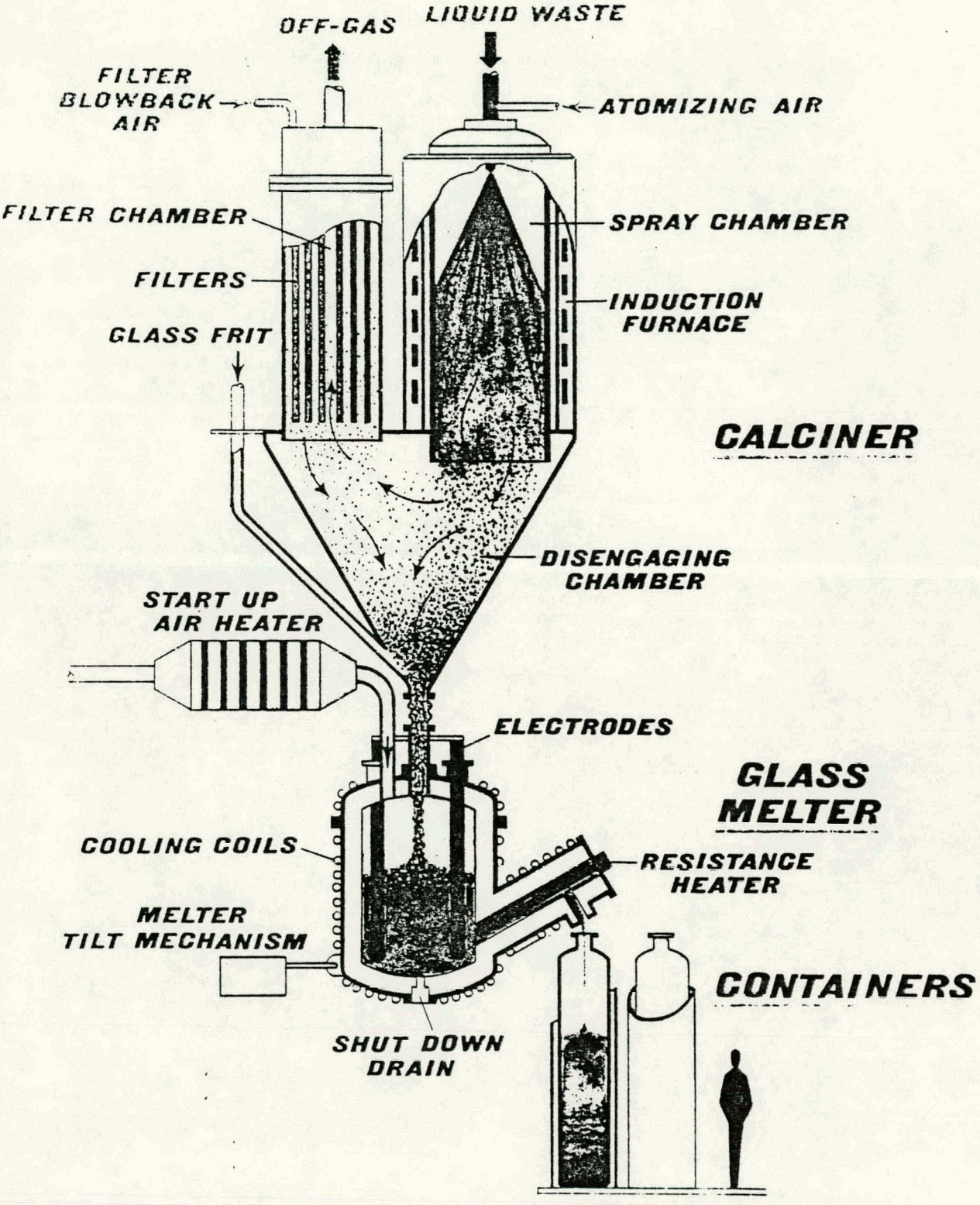


SLIDE 5

SRP DEFENSE WASTE PROCESSING REFERENCE FLOWSHEET



SLIDE 6


OFF-GAS
LIQUID WASTE
FILTER BLOWBACK AIR
ATOMIZING AIR
FILTER CHAMBER
SPRAY CHAMBER
FILTERS
INDUCTION FURNACE
GLASS FRIT
CALCINER
DISENGAGING CHAMBER
START UP AIR HEATER
ELECTRODES
GLASS MELTER
COOLING COILS
RESISTANCE HEATER
MELTER TILT MECHANISM
CONTAINERS
SHUT DOWN DRAIN

SLIDE 7

GENERAL COMPOSITION OF THE 25 LITER TANK 15 SLUDGE SAMPLE

Component	kg/Liter	Wt %
Water	0.84	56
Soluble Salts	0.33	22
Insoluble Solids	0.34	22
Total	1.50	100

SLIDE 8

MAJOR METALS IN TANK 15 SLUDGE

	Grams/Liter of Sludge			
Metal	Water Soluble	Acid Soluble	Insoluble Residue	Total
Na	86	5.5	1	93
Al	4.0	52.5	20	76
Fe	<0.01	23.2	4	27
Mn	--*	2.5	--	2.5
Hg	0.13	23.2	--	23.3
Cr	0.08	0.9	--	0.98
Ca	--	1.0	0.5	1.5
Ni	--	1.1	--	1.1
Th	--	6	3	9
Si	--	0.1	11	11
Zr	--	--	1	1

*None detected

SLIDE 9

ANIONS IN TANK 15 SLUDGE

Anion	g/liter of Tank 15 Sludge	
	Water Soluble	Acid Soluble
NO_3^-	147	25
NO_2^-	32	--
OH^-	23	--
Cl^-	2.8	--
F^-	0.10	0.56
SO_4^{-2}	21	1.3
$C_2O_4^{-2}$	0.18	0.31

SLIDE 10

TRACE ELEMENTS IN TANK 15 SLUDGE

	Concentration Range, g/Liter of Sludge	
	0.1-0.5	<0.1
Water Soluble:	I, Mo, K, B	Ag, Ru, ^{99}Tc
Acid Soluble:	Nd, Ba, Cu, K, Si, Mg, ^{238}U/Pu	Y, Co, V, ^{147}Pm/Sm Pr, Ce, La, Ag, Ru
Insoluble Residue:	Nb, Mg	B

- Insoluble residue apparently a mixture of refractory oxides and aluminum silicates.

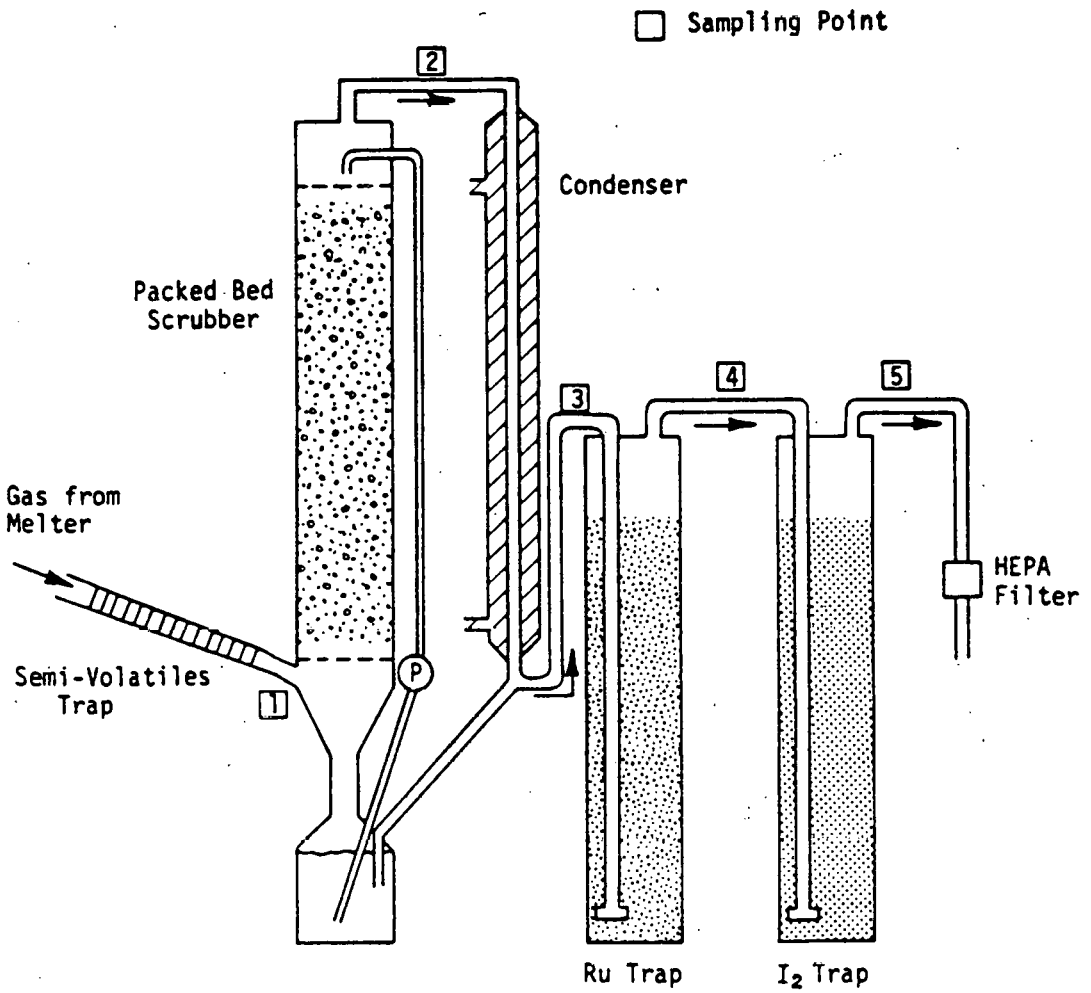
SLIDE 11

RADIONUCLIDES IN TANK 15 SLUDGE

	mCi/Liter of Sludge	mg/Liter of Sludge
^{137}Cs	450[a]	5.2
^{90}Sr	9600	66
^{106}Ru	5.9	0.0018
^{239}Pu	0.51	8.3
^{238}Pu	10	0.60
^{154}Eu	23	0.16
^{125}Sb	5.6	0.0047
^{144}Ce	37	0.012
^{60}Co	33	0.029

a. 417 mCi Water Soluble

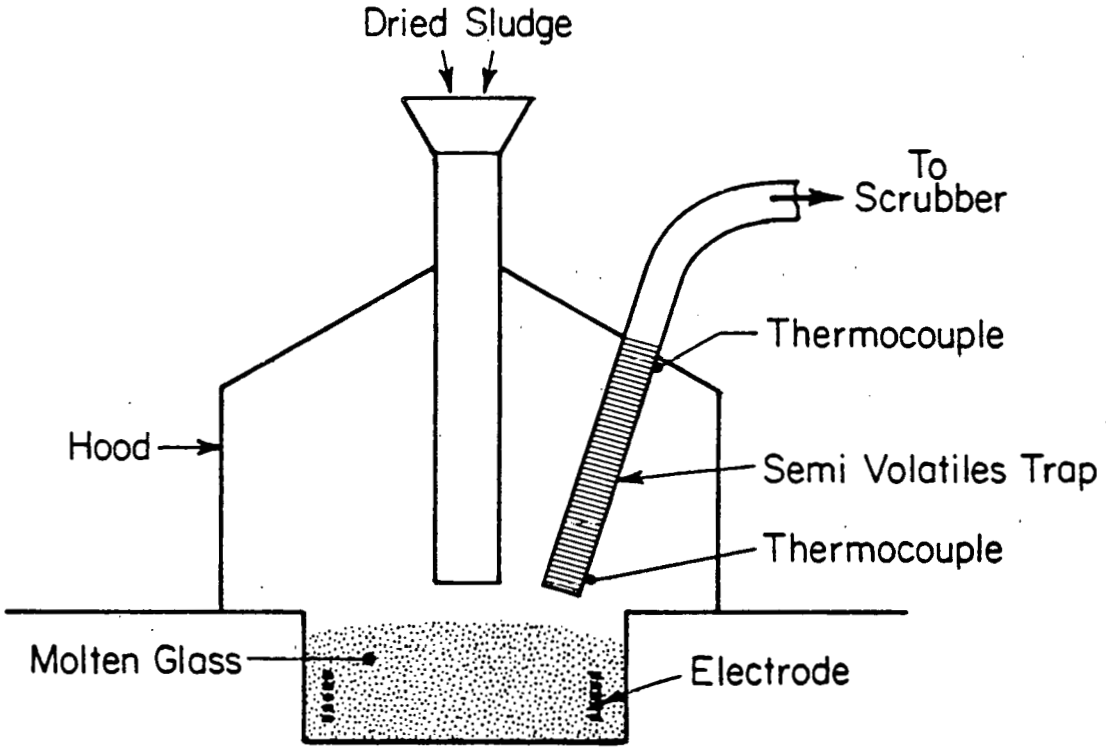
SLIDE 12



Schematic of Hot Cell Off-Gas System

SLIDE 13

SCHEMATIC OF LAB-SCALE MELTER

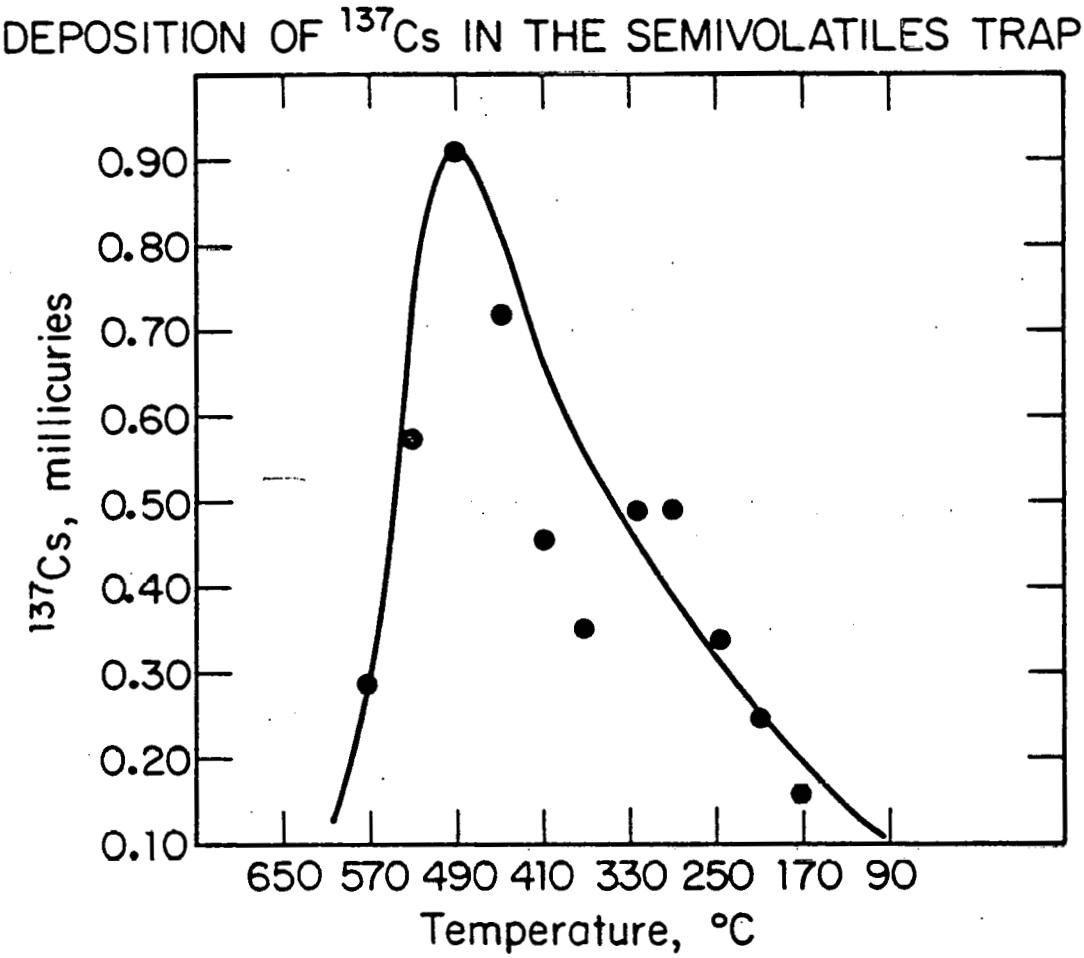


SLIDE 14

SEMIVOLATILES IN THE OFF-GAS

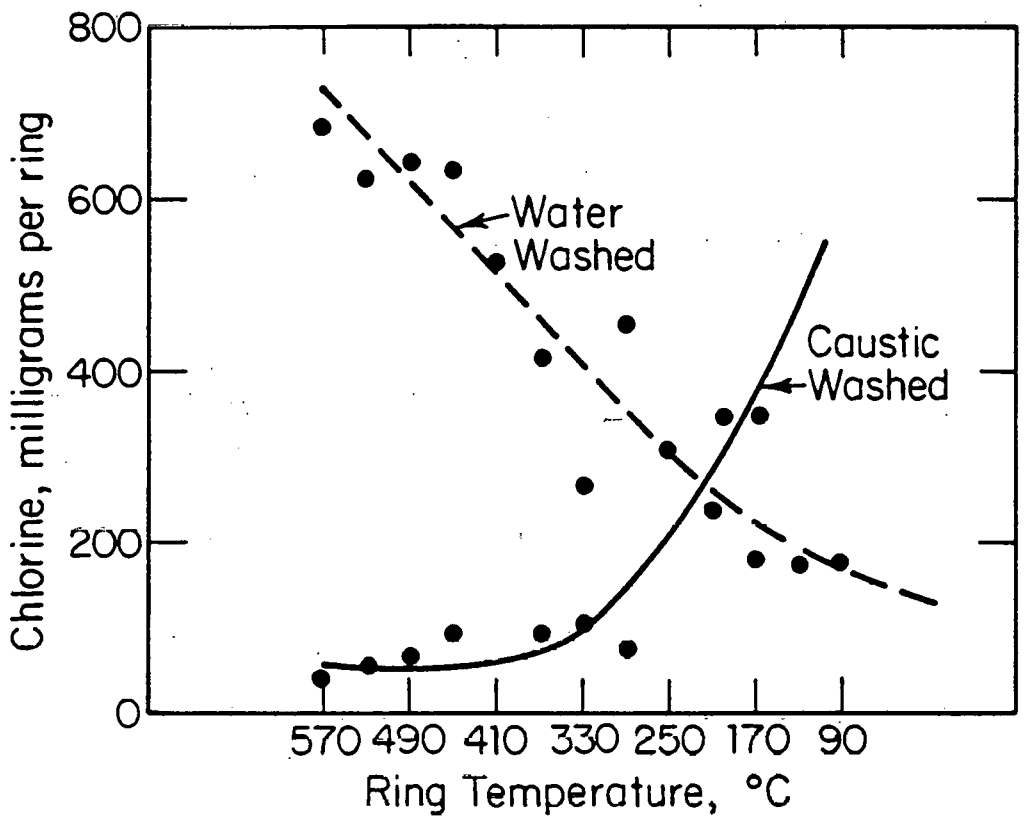
ELEMENT	PROPERTIES OF INTEREST
RUTHENIUM	ISOTOPE 106 IS RADIOACTIVE. RuO_4 IS VOLATILE AND UNSTABLE.
CHLORINE	CHLORIDES ARE CORROSIVE TO MANY ALLOYS. MIXTURES OF ALKALI HALIDES MAY FORM EUTECTICS WHICH BLIND PARTICULATES FILTERS.
FLUORINE	SAME AS CHLORINE.
CESIUM	ISOTOPE 137 IS RADIOACTIVE. OXIDES OF CESIUM BOIL IN THE OPERATING RANGE OF THE CALCINER-MELTER.

SLIDE 15


DEPOSITION OF ^{137}Cs IN THE SEMIVOLATILES TRAP
^{137}Cs, millicuries
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
650 570 490 410 330 250 170 90
Temperature, °C

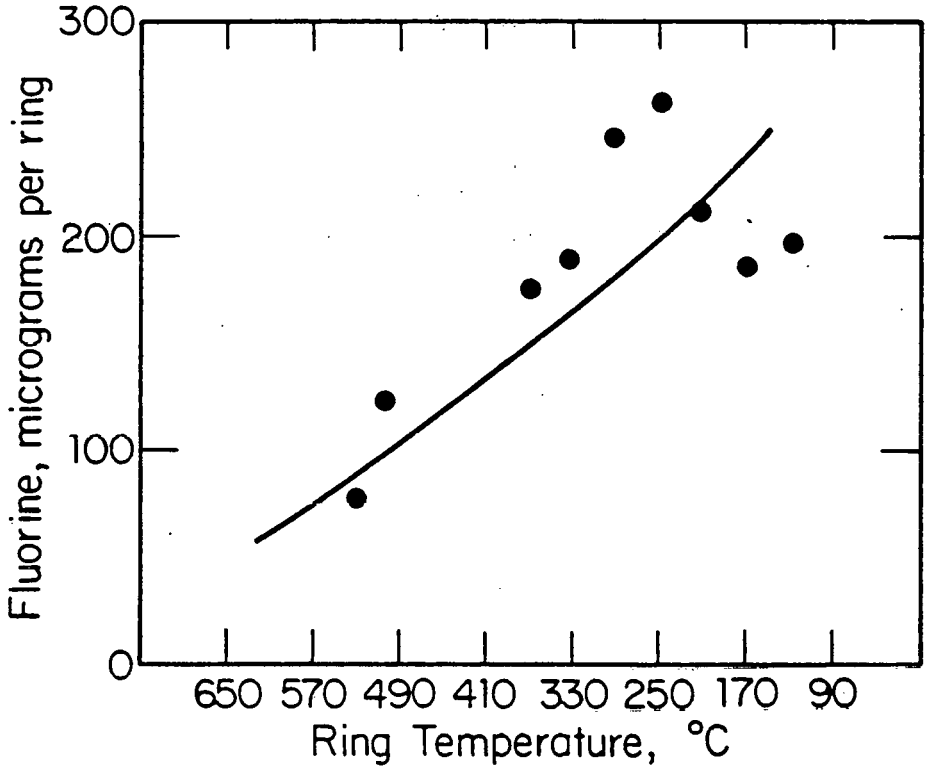
SLIDE 16

DEPOSITION OF CHLORINE IN THE SEMIVOLATILE TRAP



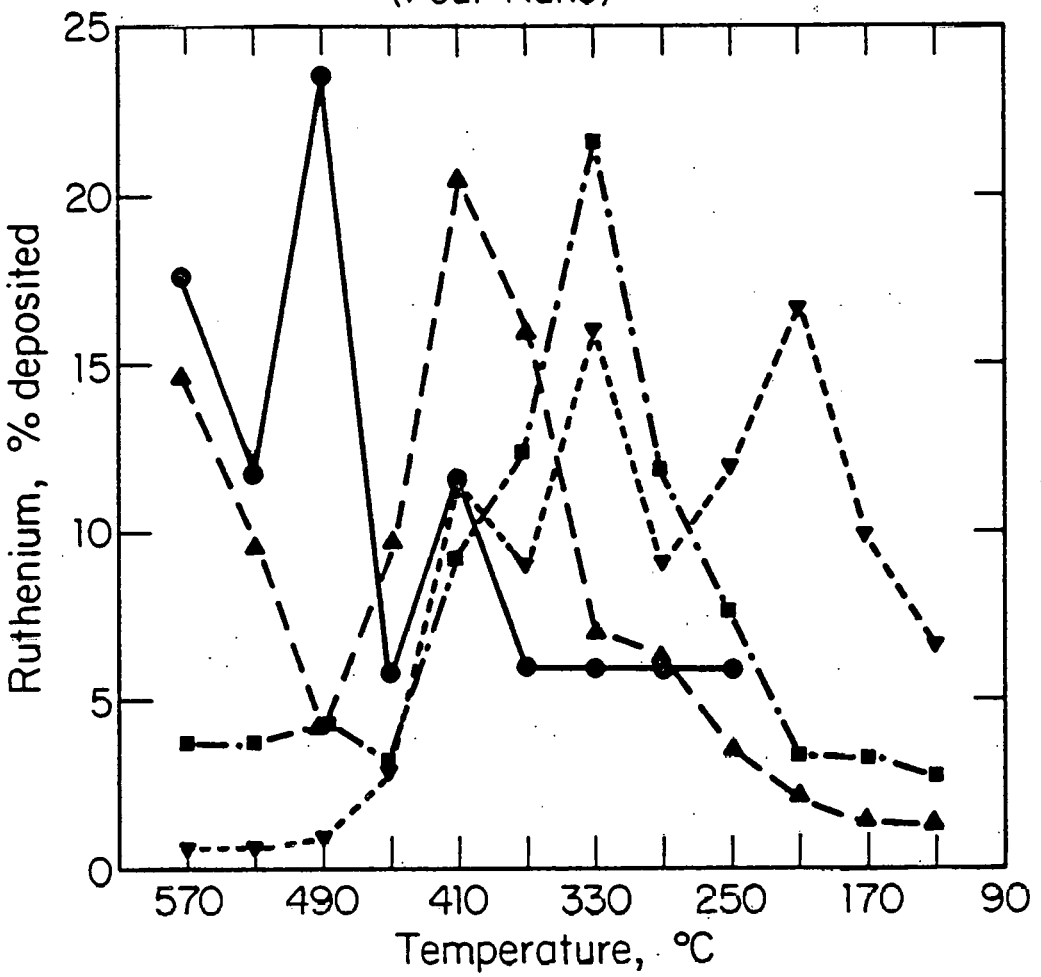
SLIDE 17

DEPOSITION OF FLUORINE IN THE SEMIVOLATILE TRAP

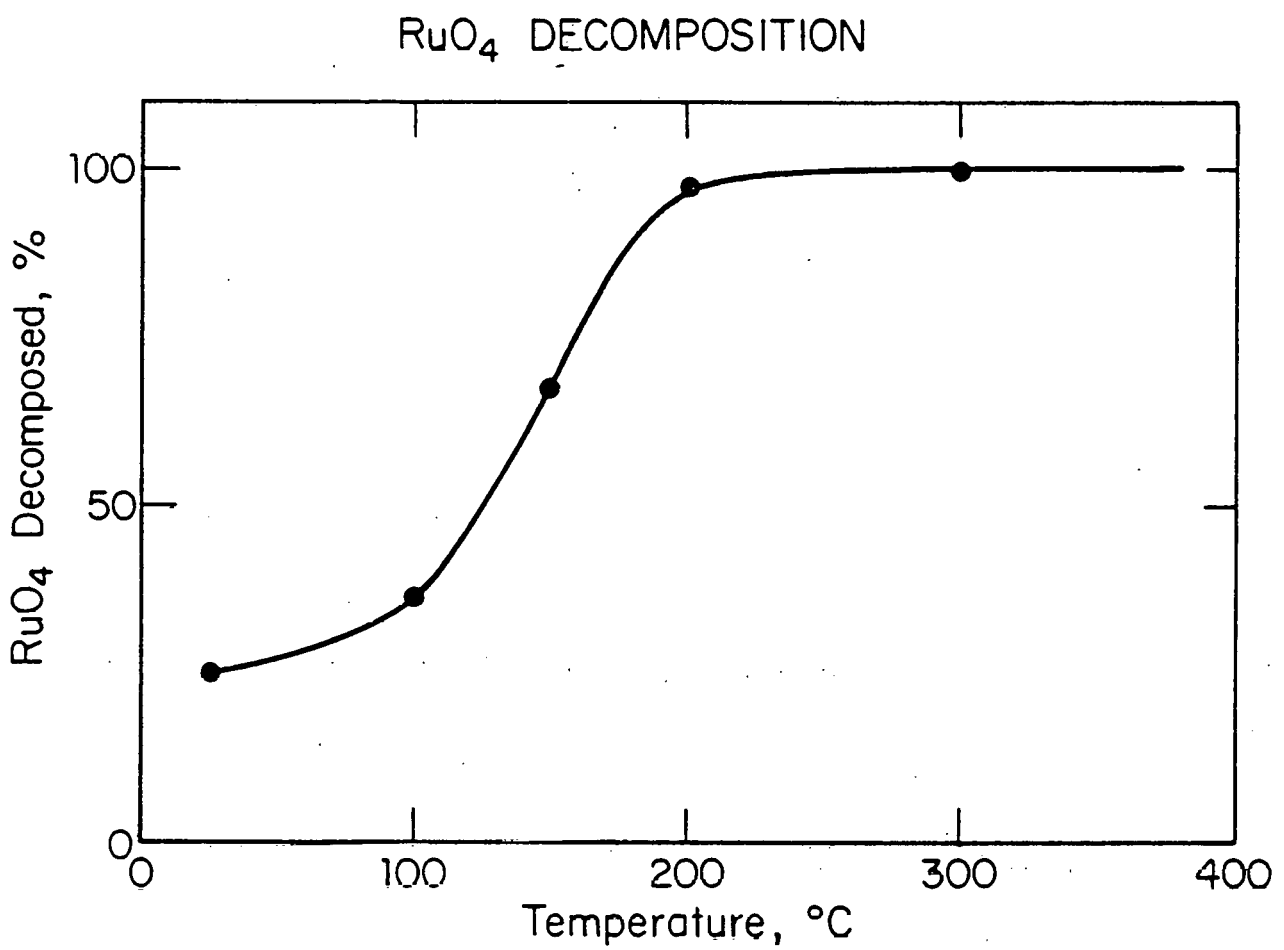


SLIDE 18

DEPOSITION OF Ru IS NOT TEMPERATURE DEPENDENT
(Four Runs)



SLIDE 19


RuO4 DECOMPOSITION
RuO4 Decomposed, %
100
50
0
0
100
200
300
400
Temperature, °C