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SOLIDIFICATION OF HIGH LEVEL WASTES
Part I
Evaporation and Calcination of Purex IWW -
Volatility and Leachability of Fission Product

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SOLIDIFICATION OF HIGH LEVEL WASTES

PART I

EVAPORATION AND CALCINATION OF PUREX IWW -
VOLATILITY AND LEACHABILITY OF FISSION PRODUCTS

By

G. B. Barton

August 4, 1959

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-2-

HW-57686

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	5
SUMMARY	9
EXPERIMENTAL PROCEDURES	11
RESULTS	19
Volume Changes	19
Volatilization of Fission Products	21
Acid IWW Salts	21
Volatilization from Modified Waste Systems	28
Leaching Studies	34
Effect of Atmosphere	44
Weight Loss	44
Kinetics	47
Calcination of Formaldehyde Treated IWW	51
REFERENCES	52

DECLASSIFIED

LIST OF FIGURES

<u>Figure Number</u>	<u>Title</u>	<u>Page</u>
1	Ratio of Iron: Aluminum: Sodium in Various IWW Compositions as Analyzed or Postulated	14
2	Volatilization of Gross Beta Activity from Various Salt Mixtures Heated to Different Temperatures	23
3	Volatility and Weight Loss on Heating; Leachability of Residue from IWW Salts (1)	24
4	Reproducibility of Volatility Loss on Heating Neutralized IWW Salts	25
5	Volatility and Weight Loss on Heating; Leachability of Residue from IWW Salts (8)	26
6	Volatility and Weight Loss on Heating; Leachability of Residue from IWW Phosphate Salts (9)	27
7	Volatilization of Ruthenium Gamma Activity from Various Salts Heated to Different Temperatures	29
8	Volatilization of Cesium Gamma Activity from Various Salts Heated to Different Temperatures	30
9	Leaching of Gross Beta Activity from the Residue of Various Salt Mixtures after Heating to Different Temperatures	31
10	Leaching of Cesium Gamma Activity from the Residue of Various Salts Heated to Different Temperatures	38
11	Leaching of Ruthenium Gamma Activity from the Residue of Various Salts Heated to Different Temperatures	41
12	Leaching of Cerium Gamma Activity from the Residue of Various Salts Heated to Different Temperatures	42
13	Volatilization and Leaching of Gross Beta Activity from IWW Salts Heated for Different Periods of Time	48
14	Volatilization and Leaching of Specific Fission Products from IWW Salts Heated at 400 C for Different Periods of Time	49
15	Volatilization and Leaching of Specific Fission Products from IWW Salts Heated at 800 C for Different Periods of Time	50

DECLASSIFIED

-4-

HW-57686

LIST OF TABLES

<u>Table Number</u>	<u>Title</u>	<u>Page</u>
I	Activity of Fission Products - Total Curies of Each	7
II	Ratio of IWW Activity to MPC	8
III	Calculated Purex IWW Compositions	12
IV	Fission Product Concentration	16
V	Composition of the Solutions from Which the Various Salts Were Prepared	18
VI	Weight Loss and Solubility of Salts from "Cold" IWW	20
VII	Per Cent Gross Beta Activity Volatilized at Different Temperatures	22
VIII	Per Cent of Ruthenium Gamma Activity Volatilized at Different Temperatures	32
XIX	Per Cent of Cerium Gamma Activity Volatilized at Different Temperatures	33
X	Per Cent of Cesium Volatilized at Different Temperatures	33
XI	Per Cent of Gross Beta Activity Leached From Solid After Heating to Different Temperatures	35
XII	Per Cent Cesium Leached From Solids After Heating to Different Temperatures	39
XIII	Per Cent of Ruthenium Gamma Activity Leached From Solids After Heating to Different Temperatures	40
XIV	Per Cent of Cerium Gamma Activity Leached From Solids After Heating to Different Temperatures	43
XV	Leaching of Strontium From Salts Heated at Different Temperatures	45
XVI	Weight Loss of Salts After Heating	46

DECLASSIFIED

-5-

HW-57686

SOLIDIFICATION OF HIGH LEVEL WASTES

PART I

EVAPORATION AND CALCINATION OF PUREX IWW -
VOLATILITY AND LEACHABILITY OF FISSION PRODUCTS

INTRODUCTION

The basic objective of the storage of radioactive wastes is to protect humanity from: (1) direct radiation, (2) contamination of food and water supplies, and (3) contamination of mineral resources.⁽¹⁾

There have been many proposals⁽²⁻⁶⁾ for the disposal of high level liquid wastes from chemical plants processing nuclear fuels. These include our present Hanford system of tank storage; disposal to deep wells, such as the oil industry uses for discard of brines they pump; storage in salt caverns; disposal to selected geological formations, such as salt domes and anticlines, or impermeable substances, such as clay, etc.; or release to the depths of the ocean. Only the use of tanks and salt caverns can be considered as storage systems. The latter is essentially a dry mine into which material would be placed as solids or packaged liquids. There is no control over the movement of activity with the other disposal methods. This is also potentially true for tank storage should corrosion or other damage cause leakage.

A number of proposed⁽²⁾ methods consider converting radioactive wastes directly to solids for storage in a form where a more permanent control could be exercised. Some of the suggested methods are: glass formation by heating with various natural substances, combining with Portland cement to form a solid body, and absorption in clays with subsequent firing of the resulting mixture.

Storage of highly radioactive wastes poses a problem in handling the heat generated by fission product decay. The calculations of Van Tuyl⁽⁷⁾ on rate of energy release from 600-MWD/T uranium at 90 days cooling

DECLASSIFIED

-6-

HW-57686

gives 1920 watts per ton of uranium processed. This drops to 305 watts at the end of one year. Coppinger⁽⁸⁾ calculated that an oxide powder generating heat at the 90-day rate, and having an assumed thermal conductivity of $0.2 \text{ Btu hr}^{-1} \text{ ft}^{-2} \text{ }^{\circ}\text{F}^{-1} \text{ ft}$, could be stored in a four-to six-inch diameter cylinder without the central temperature exceeding 500 C. By increasing the conductivity to 0.5, the diameter could be increased to eight inches. Various investigators^(9, 10) have calculated that storage of the waste from 50 to 100 tons of uranium in a compact mass would generate central temperatures of tens of thousands of degrees. Thus, it is advantageous to look for a substance of high density and high thermal conductivity to help dissipate the heat generated and preclude excessive temperature rise within the stored mass.

The present investigation is based on the assumption that the formation of a solid - particularly a "nonleachable" solid - is the preferable method for ultimate storage of these high-activity wastes. The basis for this choice is demonstrated by considering the magnitude of the hazards involved. Table I⁽⁷⁾ summarizes data on the activity associated with the waste from the processing of one ton of uranium that has been irradiated to 600 MWD/T at MW/T and then cooled for periods of 90 days, one year, and ten years. It is seen that the bulk of the activity decays away in one year. So, from the standpoint of heat generation, it is preferable to store the material in solution for one to several years and then process it to the form desired for ultimate storage.

Table II records the activities contained in the Purex-type waste at a nominal volume of 40 gal/ton after the material has been stored for one year, ten years, and fifty years following reactor discharge. These activities are expressed relative to the recommended maximum permissible concentration in potable water (MPC)⁽¹¹⁾ to be ingested by those living in the neighborhood of controlled areas. That is, if we were to assume that the IWW* were to be discharged directly to our water supply, it would have to be decontaminated or diluted by the indicated factors. Dilution is thus not a realistic

* Bottoms from the first cycle waste concentrator, Purex plant.

DECLASSIFIED

-7-

HW-57686

TABLE I
ACTIVITY OF FISSION PRODUCTS* -
TOTAL CURIES OF EACH

<u>Nuclide</u>	<u>90 d</u>	<u>1 y</u>	<u>10 y</u>
Sr ⁸⁹	51,000	1,460	---
Sr ⁹⁰	2,050	2,010	1,610
Y ⁹¹	66,000	2,620	---
Zr ⁹⁵	75,400	3,760	---
Nb ⁹⁵	119,000	8,230	---
Ru ¹⁰³	25,600	234	---
Ru ¹⁰⁶	4,320	2,590	5
Sb ¹²⁵	88	72	7
Te ¹²⁷	850	150	---
Te ¹²⁹	2,200	7	---
Cs ¹³⁴	89	67	2
Cs ¹³⁷	1,960	1,920	1,560
Ba ¹⁴⁰	2,100	---	---
Ce ¹⁴¹	34,700	98	---
Pr ¹⁴³	3,100	---	---
Ce ¹⁴⁴	53,400	27,300	9
Pm ¹⁴⁷	9,010	420	670
Sm ¹⁵¹	39	38	35
Eu ¹⁵⁵	76	56	1.4
Total	452,900	58,300	3,900
Total Energy in watts	1,923	305	17

* 600 MWD/T at 5 MW per ton of uranium (from Reference 7).

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-8-

HW-57686

TABLE II*

RATIO OF IWW** ACTIVITY TO MPC⁽¹¹⁾

Nuclide	MPC $\mu\text{c/l}$	1 y	10 y	50 y	Time to Decay to MPC
Fe ⁵⁵	0.8	2×10^4	2×10^3	---	---
Co ⁶⁰	0.05	$< 1 \times 10^8$	$< 6 \times 10^7$	$< 1 \times 10^5$	$< 140 \text{ y}$
Sr ⁹⁰	1×10^{-4}	1.3×10^{11}	1.1×10^{11}	4×10^{10}	1030
Y ⁹¹	0.03	6×10^8	---	---	---
Zr ⁹⁵	0.06	4×10^8	---	---	---
Nb ⁹⁵	0.1	5×10^8	---	---	---
Ru ¹⁰⁶	0.01	2×10^9	3×10^6	---	---
Sb ¹²⁵	0.1	5×10^6	5×10^5	20	---
Te ¹²⁷	0.06	2×10^7	---	---	---
Cs ¹³⁷	0.02	6×10^8	5×10^8	2×10^8	875
Ce ¹⁴⁴	0.01	2×10^{10}	6×10^6	---	---
Pm ¹⁴⁷	0.2	2×10^8	2×10^7	400	72
Sm ¹⁵¹	0.4	6×10^5	6×10^5	2×10^5	1540
Eu ¹⁵⁵	0.2	2×10^6	5×10^4	---	---
U ²³⁸	0.02	100	100	100	3×10^{10}
Pu ²³⁹	0.005	3×10^4	3×10^4	3×10^4	3.6×10^5
Am ²⁴¹	0.004	2×10^5	2×10^5	2×10^5	8300
Cm ²⁴²	0.02	7×10^5	---	---	---

* Adapted from Van Tuyl⁽¹²⁾ with the appropriate adjustment for the changes in MPC recommended in Handbook 69⁽¹¹⁾ for internal dose to persons in the neighborhood of controlled areas.

** 600 MWD/T uranium irradiated at 5 MW/T. 1WW volume 40 gal/T uranium.

DECLASSIFIED

-9-

HW-57686

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solution to the problem. Decontamination by the indicated factors is a formidable problem, and the recovered nuclides would still require storage.

Another way to achieve decontamination is to allow the material to decay. The last column in Table II shows how long the material must be held to allow decay to MPC-level activity. There are four fission products that require storage of more than a century and two for the order of a millenium. Since there has been no continuity of company or government for this long, great precautions must be taken to retain the materials in a form that cannot be readily dispersed. Further, the actinide elements, not the fission products are the controlling factor. These elements require storage for even longer periods to permit safe contact at the presently accepted MPC.

Perhaps the simplest and most attractive process for converting an already concentrated aqueous waste to a compact high-integrity solid is simple calcination. This has been investigated at several AEC sites, primarily, however, for the high-salt, aluminum nitrate-type solutions. Accordingly, an experimental program has been undertaken to evaluate the suitability of this approach for Purex waste. The program will consider the effects of pertinent variables such as temperature, time of calcination, atmosphere, composition of the waste, effect of added chemicals, etc. It is particularly important to know: (1) to what extent volatilization of specific fission products will be a problem, and (2) to what extent fission product activities will leach from the resultant solid.

SUMMARY

From various chemical analyses and flow sheet calculations of probable IWW compositions, two were selected as representative. They were used as the base for preparation of salt systems for investigation of the loss of activity by volatilization during calcination and by leaching of the calcined residue. The following tracer-containing salt systems were used: (a) salts from evaporation of synthetic IWW; (b) gross salts from [REDACTED]

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-10-

HW-57686

neutralization of IWW with sodium hydroxide and evaporation to dryness; (c) the precipitate from neutralized IWW; (d) a sulfate-free IWW of the same cation composition as (a); (e) the phosphates prepared by adding the stoichiometric quantity of phosphoric acid to form the orthophosphates of the metallic cations; (f) similar to (e), but with the substitution of boric acid for part of the phosphoric acid (to form sodium metaborate instead of sodium phosphate); and (g) silica-containing salt system (by adding a micron-sized commercial silica powder before evaporating). Calcinations were performed at temperatures ranging from 200 to 1400 C. The following conclusions were drawn from the experiments:

1. The volume reduction that could be expected by drying material produced by current two-cycle plant operation is about a factor of seven.
2. The dry salts from IWW have a bulk density of about one gm/cc. This is reduced to about 0.6 by calcination, which causes a loss of 40 to 50 per cent in weight when heated to temperatures of 700 C or higher. The bulk density of this powder can be increased by pressing to about 1.8 gm/cc. This would result in a final volume reduction factor of approximately 13.
3. The phosphate and phosphate-borate systems could be melted at or below 900 C to a glass whose density exceeded 2.3 gm/cc.
4. The volatility of ruthenium during calcination will present the biggest problem in handling the off-gases.
5. The presence of sulfate or phosphate reduces the volatility of both ruthenium and cesium.
6. Leaching the dried or calcined IWW salts with water would remove most of the gross beta activity unless the solid was heated to 800 C or more. This apparently results because of thermal stability and high solubility of the fission product sulfates, since a calcined sulfate-free system was relatively non-leachable.

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-11-

HW-57686

7. By heating to 900 C, all of the systems tested could be converted to solids losing less than six per cent of their gross beta activity when leached in boiling water for one hour.
8. The precipitate from neutralized IWW loses least activity when leached. Next in stability is the phosphate system, then the gross salts from neutralized IWW.
9. Volatilization of fission product activity from IWW salts reaches a constant value in five minutes at 400 C and in 30 minutes at 800 C.
10. The fraction of the activity removed by leaching decreases with time of heating at 800 C from about 70 per cent at five minutes heating to five per cent at four hours. However, leachability increased with time at 400 C and reached a maximum at two hours.

EXPERIMENTAL

The first problem in this study was to determine what composition of IWW to use as a basis for the various experiments. Some few analyses had been made earlier for Van Tuyl which indicated that the flow sheet composition was not obtained in actual plant practice. Since the composition is critical both for waste treatment and fission product recovery studies, it was very desirable to determine more closely what the actual plant composition was. A sampling program was set up on a series of plant samples and, based on these results,⁽¹³⁾ a synthetic IWW was prepared as indicated in Table III, column 1. Later sampling and analyses indicated that the plant composition was not that presented for three-cycle operation, but would more nearly approximate that indicated for two-cycle composition. Operation of the plant on a two-cycle flow sheet was also planned (and accomplished since this work was started). Therefore, the later work was directed toward the two-cycle material which is expected to be processed. In addition, Table III, column 3 lists a possible composition from the plant if iron and sulfamic acid are eliminated as process reagents. It is also possible to eliminate

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TABLE III
CALCULATED PUREX IWW COMPOSITIONS

Component	Molarity From			
	3-Cycle	2-Cycle	"No Fe"	"Ultimate"
HNO ₃	6.2	6.2	6.2	6.2
Fe ₃	0.86	0.35	0.05	0.005
Cr	0.12	0.009	0.006	0.0006
Ni	0.054	0.009	0.006	0.0006
Al	0.20	0.10	0.01	0.01
Na	0.32	0.60	0.60	0.05
U	0.03	0.02	0.02	0.02
SO ₄	0.60	0.75	0	0
PO ₄	0.02	0.04	0.02	0.02
FP ₄	0.01	0.03	0.03	0.03
Volume gal/ton	90	40	40	40

Wt. of Salts from One Ton*

Direct				
Evaporation	57 kg	19 kg	5.4 kg	2.2 kg
Neutralization-				
Evaporation	270	122	88.7	83.3
Phosphate	---	18.7	8.6	2.7
Phosphate-				
borate	---	19.7	9.6	2.8
Silicate	---	15.6	7.4	2.6

* Conditions of calcination given in text, page 13.

Note: Under the conditions of irradiation indicated in Table IV approximately 700 grams of fission product oxides would be produced. At a theoretical density of 5.7 these would occupy 125 ml.

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-13-

HW-57686

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sodium nitrite as a process reagent by substitution of gaseous nitrogen IV oxide and to reduce corrosion iron by the use of titanium tube bundles in the concentrators. This should result in an almost salt-free system with very low corrosion products. The resulting IWW would be largely an impurity and fission product solution. This is indicated as the "ultimate" composition in Table III. In addition to the compositions, Table III lists the weights of salts which would be obtained by: (1) direct calcination of the acid solution, (2) from neutralization followed by evaporation and calcination, and (3) by the addition - prior to evaporation and calcination- of: (a) phosphoric acid, (b) a mixture of phosphoric acid and boric acid, or (c) an addition of silica. It can be seen that neutralization of the solution with caustic results in formation of a large quantity of salt, principally sodium nitrate. The salt calculated from direct evaporation is a mixture of sulfates and oxides. If higher temperature calcination, for instance 900 C, is used, most of the sulfate is eliminated and the weight would be correspondingly less (about one-half the indicated value). The equivalent weights of phosphate and silicate are less than that of sulfate so the calculated weight of these salts from two-cycle material would be correspondingly less.

Because of the uncertainty of the composition of plant IWW, several compositions have been used in these studies, but the bulk of the work has been based on the salt composition indicated in Table III, column 1. Composition of the individual samples is discussed later and listed in Table V.

The wide variability of the waste may be illustrated by plotting the various analyzed and calculated compositions of IWW, as shown on Figure 1. This figure is based only on the major constituents of aluminum, iron, and sodium and is a plot of the relative amounts of these three elements. It can be seen that a wide variety of compositions have been proposed and are quite possible from plant operation. Therefore, it will be necessary to define a composition range over which any proposed disposal scheme will be satisfactory.

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-14-

HW-57686

FIGURE 1

Ratios of Iron: Aluminum: Sodium in Various IWW Compositions
as Analyzed or Postulated

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The expected concentration of individual fission products is given in Table IV as taken from the calculations of Van Tuyl.⁽⁷⁾ The data are for fission product production in 600 MWD/T uranium irradiated at 5 MW/T, cooled 90 days, and concentrated into a volume of 40 gallons.

The experimental procedure consisted of the following steps:

1. The salt mixture was prepared by combining the various major salt constituents indicated in Table III with the appropriate amount of nitric acid. To this was added a synthetic fission product mixture, prepared from laboratory reagents, in the proportions indicated in Table IV. The solution was traced with a small quantity of plant IWW to a level suitable for analytical purposes. It was then evaporated to dryness under an infrared lamp and, when the salts were thoroughly dry, the solids were ground in a mortar so a uniform sample could be taken.
2. A one gram portion of the mixed salt was weighed into a ceramic boat which was then inserted in a Vycor combustion tube (already heated in a tube furnace to the desired temperature). The experimental temperature range was 200 to 900 C using the Vycor tube. Later, a few experiments were performed using a zirconia tube at temperatures of 1000 to 1400 C. A stream of air (or other gas) was drawn over the samples and through a bubbler containing sodium hydroxide. This was to trap volatilized fission products. After the desired heating period, the bubbler was disconnected and the Vycor combustion tube rinsed into the bubbler solution. (The zirconia tubes could not be rinsed because the thermal shock caused breakage.) The heating period was arbitrarily set at one hour for samples heated at temperatures up to and including 500 C and one-half hour for samples heated above this temperature.

DECLASSIFIED

-16-

HW-57686

TABLE IV

FISSION PRODUCT CONCENTRATION

600 MWD/T, 5 MW/T, 90 Day Cooled, 40 gal/ton

<u>Element</u>	<u>g/T</u>	<u>Molarity x 10⁴</u>
Se	0.88	0.79
Br	0.29	0.26
Rb	9.2	7.6
Sr	25	20
Y	12	9.6
Zr	82	64
Nb	3.0	2.2
Mo	62	46
Tc	17	12
Ru	34	24
Rh	7.8	5.3
Pd	5.4	3.5
Cd	0.22	0.14
Sn	0.20	0.09
Sb	1.15	0.67
Te	9.5	5.3
I	4.5	2.5
Cs	53	28
Ba	23	12
La	24	12
Ce	67	34
Pr	23	12
Nd	74	36
Pm	9.7	4.8
Sm	10.0	4.7
Eu	0.78	0.36
Gd	0.39	0.18
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-17-

HW-57686

3. The solution from the bubbler and the tube rinse was diluted to 50 ml and a suitable aliquot was taken for gross beta counting. The remaining solution was then evaporated to 10 ml for gamma spectrometry.
4. The powder or solid remaining in the boat was leached by adding 100 ml of water to the sample and heating this at approximately boiling for one hour. The solution was then filtered to remove the solid material and diluted to 200 ml. Aliquots of this solution were mounted for beta counting, and a fraction was evaporated to 10 ml and analyzed by gamma spectrometry. This standard procedure was followed for all samples that could be removed from the boat. In a few cases, the material fused into a solid cake that could not be removed. In these cases the entire boat was immersed in water and heated in a water bath for one hour.

For some experiments, the original IWW composition was modified in the following fashions:

1. Phosphate mixtures were prepared by adding a stoichiometric quantity of phosphoric acid to form the orthophosphates of the metallic cations. Some of these phosphate mixtures contained sulfate (Table V, No. 9) and some were sulfate free (Table V, No. 5).
2. A mixed phosphate-borate was formed by adding boric acid equivalent to the formation of sodium metaborate and phosphoric acid equivalent to the remaining cations (Table V, No. 6).
3. A silicate system was formed by adding micron-sized silica (Davison D72) equivalent to formation of the ortho silicates (Table V, No. 7).
4. A sulfate-free system was prepared from the nitrate salts of the various cations (Table V, No. 4).
5. In addition, the gross salts obtained by neutralizing and drying IWW (Table V, No. 2) and the dried precipitate filtered from a neutralized IWW (Table V, No. 3) were carried through the same measurements.

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TABLE V
COMPOSITION OF THE SOLUTIONS FROM WHICH
THE VARIOUS SALTS WERE PREPARED

Component	Molarity of Ion in Composition No.							
	1 & 8	2*	3**	4	5	6	7	9
H ⁺	6.2	0	0	1	1	6.2	1	6.2
Na ⁺	0.32	10	N. D.	0.43	0.40	0.32	0.40	0.32
Fe ⁺⁺⁺	0.86	0.86	0.25	0.25	0.25	0.86	0.25	0.86
Al ⁺⁺⁺	0.20	0.20	0.17	0.17	0.17	0.20	0.17	0.20
Cr ⁺⁺⁺	0.12	0.12	0.006	0.006	0.006	0.12	0.006	0.12
Ni ⁺⁺	0.054	0.05	0.006	0.006	0.006	0.054	0.006	0.054
UO ₂ ⁺⁺	0.03	0.03	0.015	0.015	0.015	0.03	0.015	0.03
F. P.	0.01	0.01	0.033	0.033	0.033	0.01	0.033	0.01
SO ₄ ⁼	0.60	0.60	N. D.	0	0	0.60	0.51	0.60
PO ₄ ⁼	0.02	0.02	N. D.	0.015	0.57	1.13	0.015	1.24
BO ₂ ⁻	0		0	0	0	0.32	0	0
SiO ₂	0		0	0	0	0	1.08	0
NO ₃ ⁻	to balance composition							

* Calculated composition from neutralization of No. 1 with no change in volume.

** Calculated precipitate remaining after neutralizing IWW solution and filtering.

Designation in text: 1 and 8 - acidic IWW salts
2 - salts from neutralized IWW
3 - precipitate from neutralized IWW
4 - sulfate free
5 - phosphate (sulfate-free)
6 - phosphate-borate
7 - silicate
9 - phosphate

DECLASSIFIED

-19-

HW-57686

All these salt mixtures were prepared in a manner similar to the initial IWW, i. e. -the fission product-traced solution was dried under an infrared lamp and the salt cake ground to a powder and thoroughly mixed before sampling. Table V lists the composition of the solutions from which the various salts were prepared.

Two other variables examined briefly were the atmosphere in which the calcination occurred and the kinetics at two different temperatures. Since ruthenium is the major element volatilizing, presumably as the tetroxide, it was assumed that atmosphere might play an important part in controlling its volatilization. So, some measurements were made using either steam or air saturated with formalin as alternates to a straight air atmosphere. These results will be subsequently presented. As work progressed, a question arose as to the rate at which volatilization and leachability might be altered as the sample was heated at constant temperature. To determine this, measurements were made at 400 and 800 C using heating periods ranging from five minutes to 24 hours.

RESULTS

Volume Changes

The volume reduction that occurs on evaporating the acidic IWW solution to a solid was measured on "cold" solutions. Two samples (3-cycle composition, Table III), when evaporated to dryness under a heat lamp, gave a volume reduction of approximately six. A sample of the salt was prepared by drying in an oven at 110°. This was then used for the experiments reported in Table VI, where the weight loss after heating to the indicated temperature and the solubility of the calcined solid are indicated. Using a bulk density of one and the weights in Table III, the final volume on going from IWW to a solid is calculated to be 16, 13, 3.8, and 1.5 percent of the initial volume, respectively, for the four compositions. The bulk density is a function of the method of calcination and the composition of the solid, so these figures should be taken merely as an indication.

TABLE VI

WEIGHT LOSS AND SOLUBILITY OF SALTS FROM "COLD" IWW

One gram sample heated in combustion tube at indicated temperature for 1 hour. Air drawn through tube.

	Temperature ° C							
	150	203	203	250	500	900	250*	500*
% wt loss on calcining	2.90	9.25	6.91	14.7	27.2	43.2	20.6	26.9
% wt loss on leaching	54.6	56.2	56.1	55.2	57.4	53.9	52.9	57.3
Bulk density of leached solid (g/ml)	0.46	0.56	0.54	0.60	0.61	0.66	0.59	0.57
Apparent calcine density** (g/ml)	0.99	1.16	1.14	1.14	1.04	0.83	1.0	0.98

* Atmosphere = air saturated with formalin, air alone in all other cases.

** Apparent calcine density = $\frac{\text{weight of ignited solid}}{\text{Volume of leached solid}}$

B. M. Johnson, Jr., in his experiments with radiant heat spray calcination, has produced products with bulk densities of 0.1 to 1.2 g/ml. Some of the phosphate compositions when melted have given glasses with a density greater than 2.3 g/ml. Compaction of the dried IWW salts with a hand press gave a pellet with a bulk density of about 1.8 g/ml. Thus, it appears possible to reduce the volume of the current-type IWW to 5.3 per cent of its volume before neutralization if it is converted to a phosphate glass, or to 7.5 per cent by calcining and pressing.

Another advantage in going to a glassy solid is the probable increase in thermal conductivity. The data in the Handbook of Chemistry and Physics⁽¹⁵⁾ for sand and glass indicate that a possible increase of about three in thermal conductivity might be experienced. This would be of considerable advantage in increasing the permissible size of the storage container if current wastes were being processed.

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Volatilization of Fission Products

The volatility of fission products was measured by: (a) gross beta activity and (b) gamma spectrometry for cerium, ruthenium, cesium, and zirconium-niobium. The results for gross beta measurements are tabulated in Table VII and graphically summarized by Figures 2, 3, 4, 5 and 6. In interpreting these results, two sources of variation need to be considered. These are the experimental variation and the differing "ages" of the tracers used to prepare different batches of solids. The magnitude of the experimental variation can be estimated from the duplicate results presented in Table VII and by Figures 3, 4, 5, and 6. The different "age" tracers influence the results because of the varying ratios of a given activity to the whole. For example, ruthenium was a larger fraction of the activity in the IWW salts used for the experiments listed in columns 8, 8a, 9 and 9a of Table VII and by Figures 5 and 6 than in the other samples. The tracers used with compositions 1 through 7 (see Table VII) were of approximately the same age and compositions 8 and 9 were prepared from a single lot of tracer.

Because these were scouting experiments, not all the experimental variables that could produce a spread in the data were investigated. It seems likely that some of the variation could arise from incomplete recovery of activity from the combustion tube. The first column of data in Table VII was only for the activity carried into the bubbler. The remaining data are for the activity recovered from the combustion tube in addition to that in the bubbler. On a number of occasions the activity was found to be firmly attached to the walls of the combustion tube. Such drastic reagents as HCl - HF mixtures were required to remove it. Under these conditions, incomplete recovery of the activity would not be unexpected.

Acidic IWW Salts

The results of heating the acidic IWW salts at various temperatures can be generalized as follows:

- (1) There is no strong temperature dependence for volatility. The low results at 200 C (Figure 5) are probably significant and those at 900 C possibly so, but the intermediate "wiggles" are not outside the

DECLASSIFIED

HW-57686

- 22 -

TABLE VII

PER CENT GROSS BETA ACTIVITY VOLATILIZED AT DIFFERENT TEMPERATURES

Temp. C	1**	1a	2	2a***	3	4	5	6	7	8	8a***	9	9a***
200	0.74	3.4	0.009		N.D. +	2.7	0	1.3	2.2	17	16	6.4	7.8
300	0.99	5.3	N.D.	0.016	0.0007	4.1	0.5	1.9	3.9	37	42	12	14
400	0.76	7.0	0.026	N.D.	N.D.	4.7	1.5	0.36	5.5	40	41	20	11
500	1.2	7.3	N.D.	N.D.	0.0007	4.6	1.9	1.7	6.0	40	40	15	16
600	0.45	2.8	0.28	0.067	0.003	4.7	2.5	1.7	6.9	45	46	17	17
700	0.23	4.2	0.18	0.11	N.D.	2.8	2.4	17	3.4	39	32	13	15
800	0.74	4.1	0.77	0.62	N.D.	2.2	3.0	4.8	3.6	38	38	13	6.4
900	1.4	5.7	0.67	2.1	0.027	1.9	1.1	3.9	2.8	23	Lost	14	8.4
1000	0.51		0.52			0.055	0.18		0.33				
1300	0.78		1.2			0.10	0.11	0.31					
1400	0.092		1.04	1.42		0.18	0.068		12				

* Compositions listed in Table V.

** 1a was a rerun, using same salt as 1 three months later and rinsing combustion tube into scrubber sample. Rinse omitted on series 1.

+ N.D. = not detected.

*** Duplicates of 2, 8 and 9, respectively. Samples run consecutively.

DECLASSIFIED

-23-

HW-57686

FIGURE 2
Volatilization of Gross Beta Activity from Various Salt Mixtures
Heated to Different Temperatures

DECLASSIFIED

-24-

HW-57686

FIGURE 3

Volatility and Weight Loss on Heating; Leachability of Residue from IWW Salts(1)

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-25-

HW-57686

FIGURE 4
Reproducibility of Volatility Loss on Heating Neutralized IWW Salts

DECLASSIFIED

-26-

HW-57686

FIGURE 5

Volatility and Weight Loss on Heating; Leachability of Residue from IWW Salts(8)

DECLASSIFIED

-27-

HW-57686

FIGURE 6

Volatility and Weight Loss on Heating; Leachability of
Residue from IWW Phosphate Salts(9)

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-28-

HW-57686

experimental variation. This material behaves differently from acidic aluminum nitrate as reported by workers at Argonne⁽¹⁴⁾; i. e., they reported ruthenium volatility decreased sharply when the calcination temperature was raised from 400 C to 500 C, whereas little change or an increase was found in the present work.

2. The activity volatilized is primarily ruthenium. Comparison of the results for ruthenium, cerium, and cesium volatility, as measured by gamma analysis (Figures 7, 8, and 9, and Tables VIII, IX, and X), with the gross beta results indicates close parallelism (except for one 200 C point) between the beta and ruthenium data. The cerium results appear to parallel the gross beta results also, but are considerably lower than the ruthenium results. Thus, it appears that ruthenium volatilization will be the major problem.

The data collected for measurements at temperatures above 900 C are presented with reservations because of uncertainty introduced by deposition of "activity" on the zirconia tubes. As explained in the description of experimental procedure, these tubes could not be rinsed. Checks with GM survey instruments indicated the presence of "activity" in the tubes, but it did not appear to represent gross amounts as would have been the case if most of the ruthenium from the sample had volatilized and redeposited in the tubes. Thus, it is probable that volatilization does indeed decrease at these higher temperatures. However, the difficulty of realizing such temperatures in large scale calciners may make such a trend of academic interest only.

Volatilization from Modified Waste Systems

Comparison of the results for the acidic IWW salt with those for the modified salts indicates the following:

1. The modified salt systems display a generally lower volatility at temperatures of 500 C and below (Figure 2).
2. Above 500 C the silicate, sulfate-free, and phosphate-borate systems showed somewhat higher losses than the acidic IWW.

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FIGURE 7

Volatilization of Ruthenium Gamma Activity from Various Salts
Heated to Different Temperatures

DECLASSIFIED

-30-

HW-57686

FIGURE 8

Volatilization of Cesium Gamma Activity from Various Salts
Heated to Different Temperatures

FIGURE 9

Leaching of Gross Beta Activity from the Residue of Various Salt Mixtures After Heating to Different Temperatures

TABLE VIII

PER CENT OF RUTHENIUM GAMMA ACTIVITY VOLATILIZED AT DIFFERENT TEMPERATURES

Temp. (° C)	Salts of Composition *												
	1	1a	2	2a	3	4	5	6	7	8	8a	9	9a
200	10	62	N.D.		N.D.	5.4	0	14	16	23	11	9.7	13
300	9.6	0.11	N.D.	N.D.	N.D.	77	0.62	30	8.5	64	68	17	20
400	6.4	15.6	N.D.	N.D.	N.D.	91	17	4.9	12	66	71	27	17
500	11	13	N.D.	N.D.	0.024	83	27	16	13	66	66	16	24
600	4.5	5.9	2.4	0.13	0.037	83	24	19	65	61	61	21	21
700	3.5	8.6	2.3	1.4	0.049	47	28	170?	34	60	56	21	20
800	7.3	8.9	5.2	5.7	0.0075	33	33	57	44	60	60	19	9.5
900	18	9.6	7.9	19	0.072	28	14	41	52	40		11	17
1000	0.25		4.1			0.75	1.35		2.4				
1400	0.08		0.17	2.5		1.04	N.D.		21				

* Compositions listed in Table V.

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TABLE IX

PER CENT OF CERIUM GAMMA ACTIVITY VOLATILIZED
AT DIFFERENT TEMPERATURES

Temp. (° C)	Salts of Composition										
	1	1a	2	2a	3	4	5	6	7	8	9
200	N. D.	0.01	N. D.		N. D.	N. D.	N. D.	N. D.	0.55	N. D.	N. D.
300	0.46	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.
400	0.41	0.05	N. D.	N. D.	N. D.	N. D.	N. D.	0.008	N. D.	N. D.	N. D.
500	0.37	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	0.03	N. D.	N. D.	N. D.
600	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.
700	N. D.	0.012	N. D.	N. D.	0.01	N. D.	N. D.	0.069	N. D.	N. D.	N. D.
800	0.03	0.015	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.
900	N. D.	0.030	N. D.	N. D.	N. D.	N. D.	N. D.	0.12	N. D.	N. D.	N. D.
1000	0.20		1.02			0.14			0.025		
1400	0.27		N. D.			0.05	N. D.		N. D.		

TABLE X

PER CENT OF CESIUM VOLATILIZED AT DIFFERENT TEMPERATURES

Temp. (° C)	Salts of Composition										
	1	1a	2	2a	3	4 *	5	6	7	8	9
200	0.17	0.06	N. D.		N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.
300	N. D.	0.097	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.
400	N. D.	0.13	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.
500	N. D.	0.20	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.
600	N. D.	0.25	0.19	0.32	N. D.	N. D.	N. D.	0.31	N. D.	N. D.	N. D.
700	N. D.	0.096	1.2	0.99	N. D.	N. D.	N. D.	2.3	N. D.	N. D.	N. D.
800	N. D.	0.12	24	14	N. D.	13	N. D.	0.88	N. D.	N. D.	N. D.
900	N. D.	0.15	9.6	29	N. D.	22	N. D.	0.95	N. D.	N. D.	N. D.
1000	0.20		9.0			N. D.			0.004		
1400	0.07		N. D.			0.03			N. D.		

* Relative to leaching results at 200° as 100%.

3. The gross neutralized waste and the separated precipitate from it gave exceptionally low losses (Figure 2).
4. Ruthenium, the major loss through evolution, is suppressed by the addition of phosphate or sulfate. This is demonstrated by comparing the sulfate-free curves with those for other salts plotted in Figure 7, and the volatility curve for IWW salts (Figure 5) with one for IWW phosphate salts (Figure 6). Ruthenium is almost entirely retained by treatment with sodium hydroxide.
5. As the temperature reaches 800 C both ruthenium and cesium begin to volatilize significantly from the neutralized waste. Apparently, the excess sodium nitrate oxidizes the ruthenium.
6. Cesium volatilizes from the sulfate-free system as well as from the neutralized salts at 800 C and higher. This is probably a result of the decomposition of cesium nitrate to give the volatile oxide. The sulfate and phosphate of cesium are more stable than the nitrate.
7. It appears that volatilization of ruthenium or entrainment of other activity will require an efficient gas cleaning system even with any of the additives tested. The smallest removal problem would be from neutralized waste or precipitate heated at 400 to 500 C.
8. For suppression of volatilization from an acidic system, phosphate appears a somewhat better choice. Addition of borate is advantageous in reducing the melting point of the system, but not in reducing volatility.

Leaching Studies

The leaching results were examined for indications of a particular advantage of one system over the others. First, the gross beta results (Figure 9 and Table XI) for the unmodified IWW salts were considered as a function of heating to various temperatures. It can be seen that a large fraction of the gross beta activity (80 per cent or greater) is leached from

TABLE XI
PER CENT OF GROSS BETA ACTIVITY LEACHED FROM SOLID AFTER
HEATING TO DIFFERENT TEMPERATURES

Temp. (° C)	Salt of Composition *												
	1**	1a	2***	2a	3	4	5	6	7	8	8a	9	9a
200	88	79	1.6		0.023	71	36	42	97	45	44	22	20
300	92	78	1.3	1.2	0.055	49	3.2	43	97	25	26	10	9.4
400	94	80	1.1	1.5	0.063	8.6	5.2	48	97	33	32	19	19
500	104	87	0.51	1.1	0.11	2.2	0.44	49	99	42	41	29	29
600	93	88	0.96	0.98	0.14	1.9	0.80	39	75	36	34	29	31
700	82	77	1.8	1.8	0.079	1.7	1.9	15	82	22	22	0.46	4.33
800	23	17	0.56	0.54	0.083	0.74	0.38	0.3	18	3.8	2.6	.053	.055
900	5.7	5.7	1.1	0.76	0.081	0.28	0.07	0.2	2.5	0.18	0.22	.022	.031
1000	14		0.078			0.42	0.063		0.54				
1300	4.2		0.18			0.20	0.002	0.03					
1400	0.074		0.045	0.054		0.016	0.060		0.085				

* See Table V
** See Table VII
*** See Table VIII

these salts when they are heated at any temperature up to 700 C. For composition 8 (Table XI and Figure 9), the fraction of gross beta activity leached was considerably reduced by the large amount volatilized. At 800 and 900 C the solubility of the radioactive species greatly decreased. This behavior is interpreted as being due to the sulfate content of the IWW solution.

Ferric and aluminum sulfate decompose at temperatures in the neighborhood of 600 C. Sulfates of the alkaline earths do not decompose until 900 C in the case of magnesium sulfate, and greater than 1200 C for barium and calcium. Data are not available for rare earth sulfates but the temperature of decomposition of lanthanum sulfate is 1150 C.⁽¹⁵⁾ These data indicate that the stability of the rare earth and alkaline earth sulfates are sufficient to permit them to be leached away from the bulk oxides of iron and aluminum. The experiments performed on the sulfate-free system would seem to bear out these conclusions. Examination of Figure 9 and Table XI indicates that the sulfate-free system solubility decreases very markedly at 400 C, and at 500 C drops to only a few per cent.

The most effective additive in reducing the solubility of the fission products from the calcined material is sodium hydroxide. Neither the calcined material from the gross neutralized waste nor the calcined precipitate are significantly leached. This statement should be advanced with reservations, since if the one per cent or so of gross activity were largely strontium and cesium, and were to enter a public water supply, the amount would greatly exceed MPC. However, if gross solubility of the material can be reduced to the indicated levels, a considerable step toward preventing dispersal of activities by accidental means has been made.

Phosphate is the most effective of the other additives. It reduces the solubility of the gross activity to less than half that for the untreated IWW when heated at 200 C. At 300 C, the leachability becomes less than four per cent. The addition of phosphate plus borate does not parallel this path, but is similar to the acid IWW salt behavior except that gross leachability is reduced to approximately one-half that found with no additives.

It is possible that this behavior is a function of the formation of soluble borates which become insoluble at temperatures of 800 C and above. For the compositions used, strong sintering or melting did not occur until a temperature of 800 or 900 C was reached. Similarly, silica addition does not appear attractive for reduction of the solubility of the contained activities unless a temperature of at least 900 C is used. This result is not unexpected, since the addition would not conceivably result in true silicate formation unless a temperature of the order of 900 C (where solid state reactions become important) was attained. The silica was added in the form of a micron-sized silica powder. This would probably not be very reactive. Some qualitative experiments were performed with a more active silica (Ludox*) which formed a strong gel. These experiments were performed after the tracer work had been completed and no measurements were made as to the comparative fission product leachability behavior of this material. Another promising gel was achieved using silicic acid prepared from sodium silicate by ion exchange methods. Some waste calcination work has been done in a radiant heat spray calciner and in a paddle trough calciner by B. M. Johnson, Jr.⁽¹⁶⁾ who has found the phosphate, or phosphate plus borate, additions valuable in reducing dusting and increasing the density of the powder product.

Of the various fission products, the two of greatest concern from the standpoint of biological hazard and probable high solubility are cesium and strontium. The results from gamma spectrometry on the leach solution (Figure 10 and Table XII) indicate that cesium may leach from the calcined, unmodified IWW salts almost completely. However, there is some uncertainty since the first two sets of experiments did not give concordant results and later sets (8 and 8a) unfortunately did not contain enough cesium for measurement. In the first case, approximately quantitative leaching was achieved from material calcined at temperatures up to 700 C. In the second, approximately 20 per cent of the activity was leached for materials heated

* Product of the Grasselli Chemical Dept. of E. I. duPont De Nemours and Co. (Inc.), Wilmington, Del.

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-38-

HW-57686

FIGURE 10
Leaching of Cesium Gamma Activity from the Residue of Various Salts
Heated to Different Temperatures

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TABLE XII
PER CENT CESIUM LEACHED FROM SOLIDS
AFTER HEATING TO DIFFERENT TEMPERATURES

Temp. (° C)	Salt Composition *										
	1	1a	2	2a	3	4**	5	6	7	8	9
200	94	21	90		57	100	13	64	24	N. D.	N. D.
300	98	23	47	45	94	44	24	39	8.4	N. D.	N. D.
400	82	22	25	20	37	50	23	33	23	N. D.	N. D.
500		22	14	38	57	49	33	42	3.7	N. D.	N. D.
600	113	21	10	12	12	45	25	58	48	N. D.	N. D.
700	91	22	1.2	0.99	100	36	100	54	9.0	N. D.	N. D.
800	65	15	1.3	0.98	89	15	26	7.1	1.8	N. D.	N. D.
900	44	11	3.5	0.08	N. D.	3.7	2.6	0.86	20	N. D.	N. D.
1000	73		N. D.			N. D.	0.11		N. D.		
1400	N. D.		1.5	0.46		N. D.	0.08		N. D.		

* Compositions listed in Table V.

** Relative to 200°. Starting sample analysis faulty.

to 300 C or above. Most samples indicated that less than 50 per cent of the cesium would leach under tested conditions. After heating to 900 C all salt systems, except the acidic IWW, lost less than five per cent of the cesium by leaching.

The ruthenium results (Figure 11 and Table XIII) indicate that generally only a small fraction of the ruthenium is leached. The IWW acid salt used in the first series of measurements generally gave greatest ruthenium solubility. However, all the second measurements on this salt indicated less than one per cent ruthenium solubility. This discrepancy merits further study. The silica-containing system and the phosphate-borate system both gave one inconsistently high result. The leaching of cerium was variable and surprisingly high from the phosphate-borate system (Figure 12 and Table XIV). Otherwise the results followed the expected pattern when stability

TABLE XIII

PER CENT OF RUTHENIUM GAMMA ACTIVITY LEACHED FROM SOLIDS
AFTER HEATING TO DIFFERENT TEMPERATURES

Temp. (° C)	Salts of Composition *												
	1	1a	2	2a	3	4	5	6	7	8	8a	9	9a
200	20	0.63	2.0		N.D.	4.8	0.09	15	N.D.	7.9	8.3	1.3	1.1
300	5.3	0.43	2.0	2.4	N.D.	1.4	0.11	4.8	N.D.	0.19	0.19	0.64	0.76
400	17	0.39	1.0	1.6	0.24	1.4	0.10	3.0	13	N.D.	N.D.	0.16	0.15
500		0.61	1.3	2.3	N.D.	N.D.	0.05	3.0	N.D.	N.D.	N.D.	N.D.	N.D.
600	1.2	0.21	0.52	0.97	0.10	1.6	N.D.	19	N.D.	N.D.	N.D.	N.D.	N.D.
700	7.1	0.63	2.3	1.4	0.088	1.7	0.27	1.9	N.D.	N.D.	N.D.	N.D.	N.D.
800	0.69	0.28	1.1	1.2	0.057	0.6	0.09	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
900	3.5	0.90	1.9	1.0	0.14	0.2	0.04	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
1000	0.44		2.2			N.D.	N.D.		N.D.				
400	N.D.		4.0	N.D.		N.D.	0.09		0.11				

* Compositions listed in Table V.

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FIGURE 11

Leaching of Ruthenium Gamma Activity from the Residue of Various Salts
Heated to Different Temperatures

DECLASSIFIED

-42-

HW-57686

FIGURE 12

Leaching of Cerium Gamma Activity from the Residue of Various Salts Heated to Different Temperatures

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-43-

HW-57686

TABLE XIV
PER CENT OF CERIUM GAMMA ACTIVITY LEACHED FROM SOLIDS
AFTER HEATING TO DIFFERENT TEMPERATURES

Temp. (° C)	Salt of Composition *												
	1	1a	2	2a	3	4	5	6	7	8**	8a**	9	9a
200	91	18	N.D.		N.D.	144	54	51	26	89	86	5.3	49
300	72	17	N.D.	N.D.	0.024	0.47	1.6	51	9.5	55	58	25	22
400		17	N.D.		0.084	0.13	0.3	57	24	58	73	43	55
500		19	0.22	2.7	0.060	0.07	0.28	68	3.6	94	100	69	68
600	111	19	0.05	0.07	0.14	0.34	0.15	48	99	100	98	68	92
700	104	15	N.D.	N.D.	0.049	0.19	0.14	13	91	65	66	9.8	9.0
800	29	2.2	0.29	0.35	0.0075	0.13	0.16	N.D.	122	9.0	4.2	N.D.	N.D.
900	0.033	0.017	0.76	0.20	0.072	0.13	0.18	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
1000	0.43		N.D.			N.D.	0.44		0.18				
1400	0.49		0.38	0.39		0.075	0.012		0.04				

* Compositions listed in Table V.

** Relative to highest concentration as 100%.

DECLASSIFIED

-44-

HW-57686

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of the rare earth sulfates was considered. The high results for the silica-containing system at 600, 700, and 800 C are questionable.

Leaching of strontium was determined for acidic IWW salt compositions 1 and 8, phosphate compositions 5 and 9, sulfate-free salt composition 4, and phosphate-borate composition 6. The data (Table XV) indicate that strontium could be largely leached from the oxide powder heated at 400 to 600 C. The difference in strontium leaching between compositions 5 and 9 cannot be explained on the basis of work done to date.

Calcination followed by leaching would appear to be one way of reducing the bulk of solids associated with the fission products. Both materials (the solid and solution) would have to be stored, but much of the heat generation would be eliminated from the bulk solid by a leaching step.

Effect of Atmosphere

The effect of changing the atmosphere in which the calcination was conducted was studied in two sets of experiments. It was postulated that a reducing atmosphere, such as one containing formalin vapors, would reduce the volatilization of ruthenium. Qualitatively, this was observed to be the case. Samples of acidic IWW salts were calcined in atmospheres of air saturated with formalin vapor, and steam. The latter would resemble conditions in the radiant heat spray calciner when steam is employed as the atomizing fluid. The major effect seems to have been for steam to prevent the formation of insoluble cerium compounds at the highest temperatures employed. The data on volatility did give some indication of enhancement by steam, particularly for ruthenium, but this may be merely a flushing action to remove ruthenium that was otherwise deposited in the tube under the other conditions.

Weight Loss

Weight loss measurements were made on nearly all the samples calcined. Table XVI gives information on the stability of the various compositions examined and indicates the general temperature range over which certain changes occur. The data for composition 1 are in reasonable

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TABLE XV

LEACHING OF STRONTIUM FROM SALTS HEATED
AT VARIOUS TEMPERATURES

Temp. (° C)	Salt Composition *					
	1	4	5	6	8	9
200	78 %	120 %	2.1%	6.4 %	38 %	19 %
300	75	92	6.5	8.9	52	23
400	85	0.09	0.04	13	87	25
500	94	0.04	0.06	14	82	52
600	98	0.09	1.2	12	69	67
700	93	0.26	4.2	5.9	68	36
800	59	0.04	0.29	0.15	26	3.5
900	33	0.04		0.69	17	0

* Compositions listed in Table V.

agreement with that given in Table VI for the "cold" IWW salts. This is interpreted as indicating that denitration will be largely complete at 400 C and that relatively little decomposition of the remaining compounds occurs below 600 C. At 700 C and above, sulfate begins to be eliminated and its destruction is essentially complete at 1000 C. For the neutralized salt, it appears that the sodium nitrate is only slightly decomposed at 500 C or less. At 700 C decomposition becomes very extensive, and it is likely that sodium oxide is evaporated at the higher temperatures. Decomposition is essentially complete at 600 C with the sulfate-free system. The sulfate-free phosphate system should have completed decomposition at a rather low temperature, since there was no sulfate to be driven off at higher temperatures and the phosphates are quite stable. The low weight losses measured at the three highest temperatures may have been due to samples melting (thereby dissolving a component that evaporated from the porous solid heated at lower temperatures). The mixed

TABLE XVI

WEIGHT LOSS OF SALT AFTER HEATING

Temp. (° C)	Salt of Composition *												
	1	1a	2	2a	3	4	5	6	7	8	8a	9	9a
200	13.5%	10.7%	2.3%		9.0%	12.4%	6.3%	12.9%	21.6%	10.5%	8.6%	8.9%	8.6%
300	20.8	20.0	3.2		16.3	18.1	49.3	19.2	26.5	19.7	18.9	19.2	19.6
400	30.2	27.4	2.8	4.5%	16.0	28.4	41.1	21.4	29.1	24.5	24.8	22.7	22.5
500	28.4	29.9	6.2	6.1	14.2	33.7	60.3	22.6	28.3	27.2	27.5	24.0	23.7
600		33.1	17.3		16.9	49.6	50.9	25.9	32.7	31.5	33.6	27.8	27.2
700	40.6	42.2	47.5	50.4		49.8	63.3	34.9	39.6	40.5	40.9	37.9	37.5
800	40.4	43.9	50.6	51.4	18.4	50.8	65.6	40.3	44.5	43.0	43.5	41.5	38.7
900	45.5	43.4		58.9	15.0	51.6	30.2	40.3	44.9	44.0	45.6	43.6	43.6
1000	50.0		53.7			50.9	33.7		45.7				
1400	50.7		61.2			54.7	34.9		49.7				

* Compositions listed in Table V.

REF ID: A63170

HW-57686

DECLASSIFIED

-47-

HW-57686

phosphate-borate and silica-containing systems behaved somewhat like the untreated salts. However, the silica-containing system lost weight faster at the lower temperatures. A higher water content would explain this behavior.

The reversal of weight loss with increasing temperature between 400 and 500 C by samples 3 and 7 is probably due to the oxidation of chromium to chromate at temperatures up to 400° and its decomposition at higher temperatures. This chromate behavior was observed in the leachate from the various residues. Some volatility of the metal oxides at the higher temperatures would not be unexpected.

Kinetics

The heating period used in the early measurements was arbitrarily chosen. To determine whether the period was sufficient to reach the volatility end point, a series of measurements were made at temperatures of 400 and 800 C. Both volatility and leachability were measured. The salt was the acid IWW salt listed as composition 1 in Table V. Heating periods from 5 minutes to 24 hours were employed. The furnace was at temperature when the boat was inserted. The same experimental procedure was applied for collection of the volatilized activity and leaching of the residue as in the previous experiments. The results (Figures 13 through 15) indicate that the volatile material comes off rapidly at 400 C, five minutes apparently being sufficient time. At 800 C there appears to be a slower process that does not reach completion for about half an hour. The gamma analyses for ruthenium, cerium, and cesium indicate that ruthenium accounts for the bulk of activity. The increase with time, of solubility of the gross beta-emitting elements heated to 400 C was surprising. No change, or at most a slight decrease, had been expected. The decrease observed at 800 C indicates slow decomposition, or metathesis, at this high temperature.

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FIGURE 13

Volatilization and Leaching of Gross Beta Activity from IWW
Salts Heated for Different Periods of Time

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FIGURE 14
Volatilization and Leaching of Specific Fission Products from IWV Salts Heated at
400 C for Different Periods of Time

FIGURE 15

Volatilization and Leaching of Specific Fission Products from IWW Salts Heated at 800 C for Different Periods of Time

DECLASSIFIED

-51-

HW-57686

It appears that the original choice of time was satisfactory for volatility measurement for this salt system. However, the solubility measured is probably higher than would be found for the optimally heated sample. At temperatures high enough for melting, equilibrium would probably be reached rapidly.

Calcination of Formaldehyde-Treated IWW

Since consideration is being given to removal of a major part of the nitric acid remaining in IWW by reaction with formaldehyde, a few comments will be made relative to this material. One of the principle advantages of the technique (apart from interim storage considerations) would be the reduction of the evaporative heat load on the calciner. This is possible since the low acid solution can be evaporated further before deposition of the bulk salts begins. Thus, a more concentrated salt solution is fed to the calciner. The salt produced should be very similar in character to the salt produced from calcination of the high acid IWW. The same volatility and leachability should be experienced.

Another advantage, if it is desired to calcine on the basic side, is that the sodium nitrate content of a neutralized solution is reduced to about one half if formaldehyde treatment precedes neutralization. This material would accordingly be somewhat more attractive to calcine and store.

DECLASSIFIED

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DECLASSIFIED

-53-

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