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DISTILLATION OF PUREX WASTES

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CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section

DISTILLATION OF PUREX WASTES

R. G. Mansfield

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0.0 ABSTRACT

Experiments on distillation of Purex waste containing fission products showed that the activity in the distillate is due principally to volatilized ruthenium. This can be minimized by keeping the still-pot nitric acid concentration below 9 M.

[redacted]

1.0 INTRODUCTION

Concentration of Purex process waste, which contains fission products, is desirable in order to avoid storage of large volumes of radioactive materials or to simplify fission product recovery. Since the waste contains large amounts of the volatile reagent nitric acid, volume reduction by evaporation was considered to be an attractive process provided that a radioactivity-free distillate could be obtained. There would be an additional advantage in an evaporation procedure if nitric acid pure enough for reuse in the process could be obtained in the distillate.

With the exception of ruthenium, which, as the tetroxide, is volatile under certain conditions, the fission products present in the waste stream are not volatile during distillation. However, some of the other radioactive components of the waste might pass into the distillate as entrained particles in the vapor. The value of the ruthenium-to-cerium ratio in the distillate is considered to be a measure of the relative values of volatilized and entrained activity.

Preliminary experiments were carried out in a simple distillation apparatus, in a still equipped with an entrainment trap, and in a recirculating still in order to determine the amount and nature of the activity in the distillate and the conditions under which ruthenium volatilization might be minimized. No attempt has been made at this time to study recovery of nitric acid. Purex IAW raffinate, which contains the highest ruthenium concentration of any of the Purex waste streams, was used in the studies.

Acknowledgment is made of the assistance given by F. R. Bruce and W. B. Lanham, who made many helpful suggestions during the course of the work; by F. E. Harrington, who carried out the preliminary work reported in Sec. 3.1; and of W. R. Lewis and E. R. Johns, who performed most of the distillation experiments.

2.0 SUMMARY

In simple distillation experiments at atmospheric pressure, it was shown that the amount of radioactive material and the amount of nitric acid passing into the distillate increase as the distillation continues. The percentage of ruthenium in the distillate increased from about 8 percent of the gross beta activity at the beginning of the distillation to about 67 percent near the end of a 100-fold volume reduction. When the still was fitted with an entrainment trap that also acted as a reflux column, the first 75 percent of the distillate was free of both acid and beta activity, and the subsequent cuts contained beta activity that was

approximately 100 percent ruthenium. Under the reflux conditions, ruthenium did not begin to volatilize until the acid concentration of the still-pot contents reached 9 to 10 M.

Reduction of the pressure reduced the ruthenium carryover in the distillate but increased the cerium carryover. No material that was both stable under the conditions and capable of reducing ruthenium tetroxide, and thus preventing its passage into the distillate, was found.

It is recommended that Purex wastes be evaporated at atmospheric pressure, with an entrainment trap in the vapor column, and that the acid concentration in the still-pot not be allowed to go over 9 M. No recommendations are made at this time on the recovery of nitric acid for reuse.

3.0 EFFECT OF NITRIC ACID CONCENTRATION OF STILL-POT RESIDUE

3.1 Simple Distillation

In a preliminary simple distillation experiment on a diluted Purex IA raffinate, under atmospheric pressure, both the acidity and the beta activity of the distillate were shown to increase as the distillation was continued. Ruthenium comprised about 8 percent of the gross beta activity at the beginning of the distillation and about 67 percent near the end of a 100-fold volume reduction (see Table 3.1). No attempt was made to identify the elements making up the rest of the gross beta activity.

Table 3.1

Results of Simple Distillation of Purex IA Raffinate

Procedure: 220 ml of Purex IA raffinate (3 M in HNO_3) diluted to 720 ml with 3 M HNO_3; distillation continued until still-pot volume of ~8 ml reached (100-fold volume reduction); distillate collected in six fractions
Activity of feed: gross beta, 1.78×10^6 c/m/ml; Ru beta, 1.2×10^6 c/m/ml
Pressure: atmospheric

Fraction No.	Distillate Vol. (ml)	Distillate Composition			
		HNO_3 (M)	Gross β (c/m/ml)	Ru β (c/m/ml)	Ratio of Ru β to Gross β
1	200	0.08	2.0×10^2	---	---
2	175	0.22	7.5×10^3	5.9×10^2	0.08
3	125	0.88	6.3×10^4	1.1×10^4	0.18
4	135	5.6	1.3×10^5	2.1×10^4	0.16
5	45	12.0	2.5×10^5	1.5×10^5	0.60
6	32	14.2	4.6×10^6	3.1×10^6	0.67

3.2 Distillation Through an Entrainment Trap

Since ruthenium is the principal fission product in the IA raffinate that is volatile under the distillation conditions, the other activity in the distillate was considered to be due to entrained particles. Results of a distillation carried out in a still attached to an entrainment column indicated this to be a correct assumption. Analyses of the distillate fractions (see Table 3.2 and Fig. 3.1) showed that, with this apparatus, there was no appreciable activity or acid in the distillate until the still-pot contents reached a nitric acid concentration of about 10 M (75 percent volume reduction). At this point, appreciable activity began to appear in the distillate, and was shown by analysis to be approximately 100 percent ruthenium. Approximately 2 percent of the total ruthenium of the raffinate was distilled over by the time the volume reduction was about 97.5 percent.

The distillations were carried out in glass apparatus at atmospheric pressure. The still-pot was an 800-ml Kjeldahl flask. The entrainment trap, which was of the type designed by Hahn[1] (see Fig. 3.2) was packed with 1/8-in. glass helices and led to a condenser. Four hundred milliliters of Purex IAW solution was evaporated to 10 ml in most of the experiments. In the experiment summarized in Table 3.2, which was run somewhat differently in order to determine more accurately the nitric acid concentration of the still-pot contents at which ruthenium began to be volatilized, the first 300 ml (75 percent volume reduction) was taken as one fraction, and 5-ml cuts were taken as the remaining 100 ml was distilled.

Since the entrainment trap also acted as a fractionating column, there was no appreciable nitric acid in the distillate during the first part of the run. Under the conditions of this experiment, therefore, 75 percent volume reduction of the waste is accomplished without contamination of the distillate, but there is no recovery of nitric acid.

Although appreciable volatilization of ruthenium did not take place until the still-pot contents reached an acidity of around 10 M, the recommendation is made that the acidity be kept below 9 M in distilling Purex wastes as an additional safety factor.

Table 3.2

Volatilization of Ruthenium from Purex IAW Solution by Distillation at Atmospheric Pressure through Hahn Entrainment Trap

Charge to Still: 400 ml of Purex IAW solution from laboratory column run X-12A

Composition of charge: HNO_3, 2.40 M; gross β, 1.43×10^7 c/m/ml; Ru β, 8.00×10^5 c/m/ml; Ce β, 8.9×10^6 c/m/ml

Distillate Fraction	Calcd. HNO_3 Conc. in Pot (M)	HNO_3 Conc. of Distillate (M)	Gross β in Distillate (c/m/ml)	Ru β in Distillate (c/m/ml)	Ru Remaining in Pot (c/m/ml)	Ratio of Ru in Distillate to Ru in Pot
1st 300 ml	9.58	0.005	19	---	3.20×10^6	6.0×10^{-6}
1st 5 ml of remaining vol.	10.09	0.01	31	---	3.37×10^6	9.2×10^{-6}
2nd 5 ml	10.65	0.01	137	---	3.55×10^6	3.9×10^{-5}
3rd 5 ml	11.15	0.01	361	---	3.74×10^6	9.7×10^{-5}
4th 5 ml	11.98	0.01	528	---	4.00×10^6	1.3×10^{-4}
5th 5 ml	12.77	0.05	935	---	4.27×10^6	2.2×10^{-4}
6th 5 ml	13.66	0.275	2.67×10^3	2.44×10^3	4.58×10^6	5.3×10^{-4}
7th 5 ml	14.62	1.23	5.66×10^3	5.66×10^3	4.93×10^6	1.2×10^{-3}
8th 5 ml	15.57	2.98	7.36×10^3	7.25×10^3	5.34×10^6	1.4×10^{-3}
9th 5 ml	16.54	4.95	9.36×10^3	9.63×10^3	5.82×10^6	1.7×10^{-3}

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FIGURE 3.1

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RUTHENIUM VOLATILITY AS A FUNCTION OF STILL-POT ACID CONCENTRATION

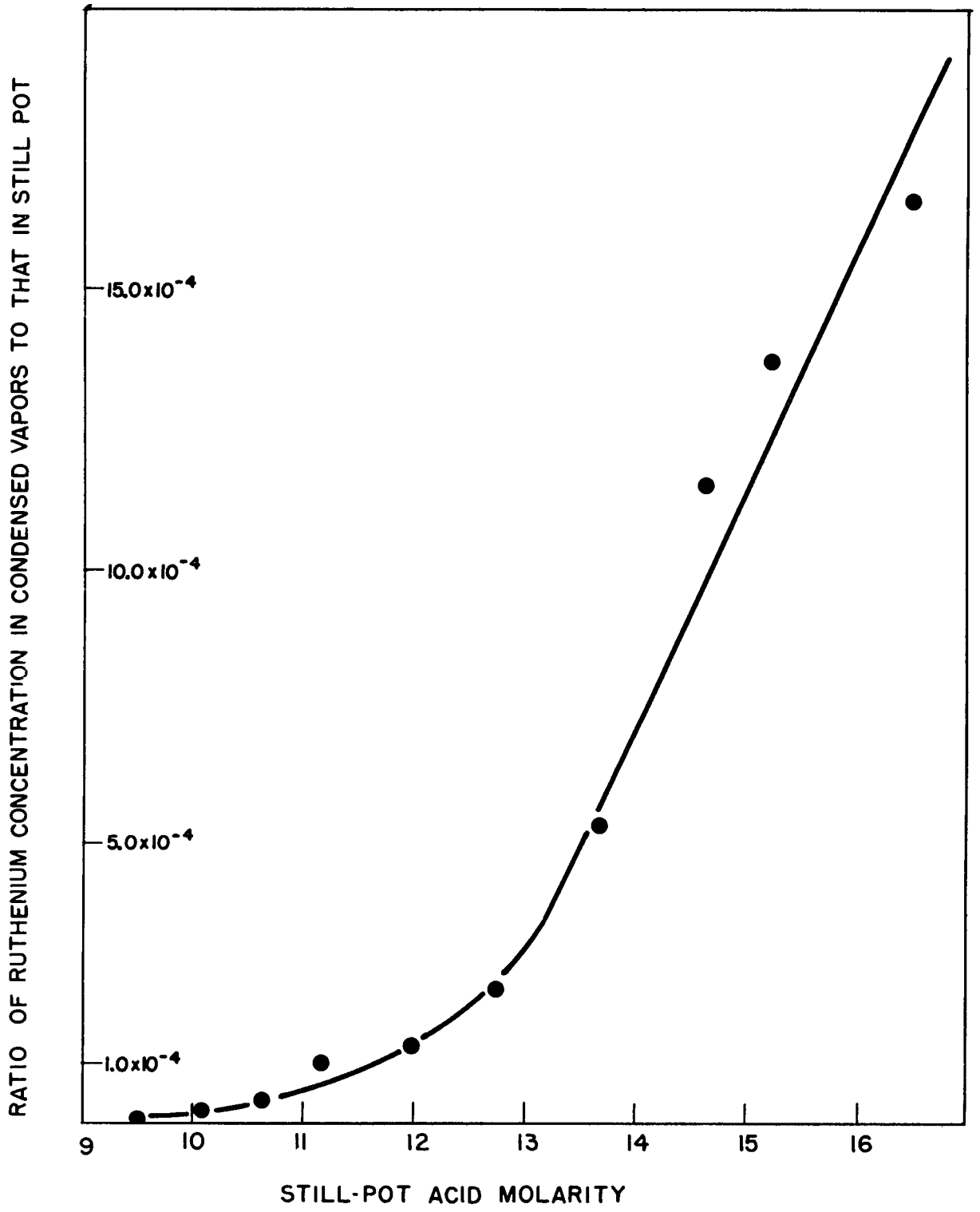

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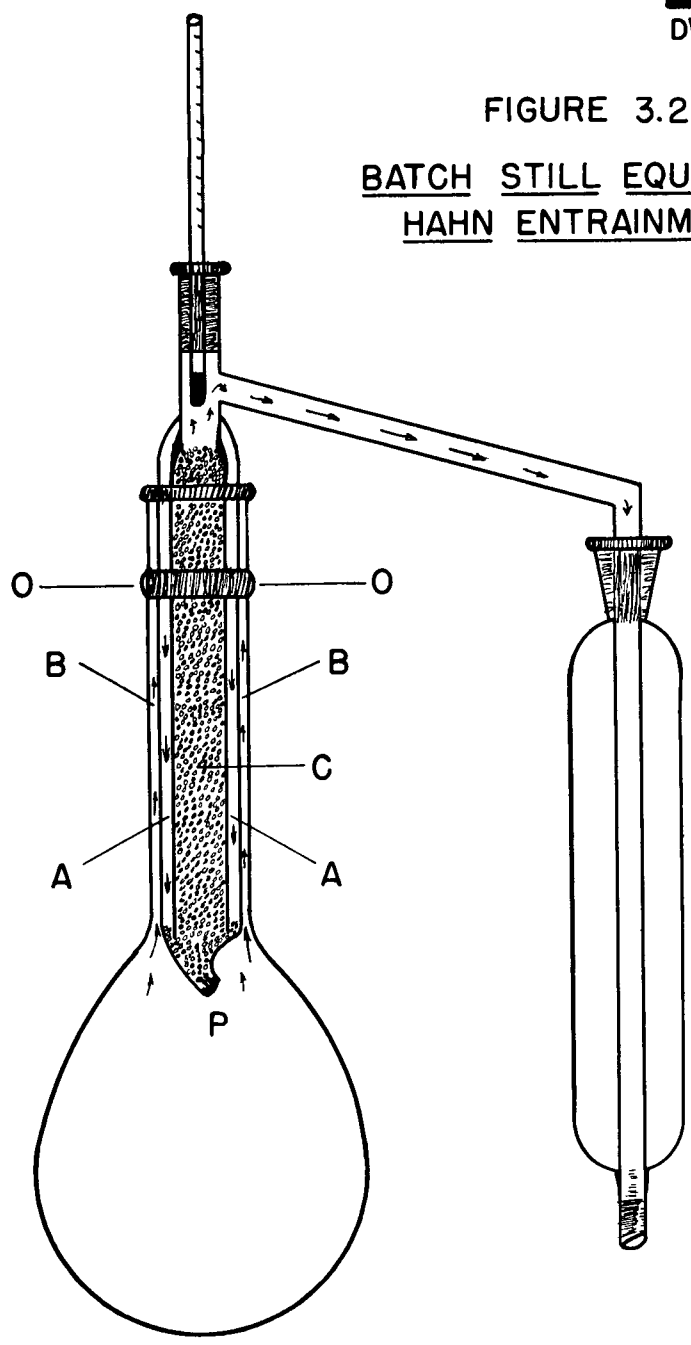
FIGURE 3.2

BATCH STILL EQUIPPED WITH HAHN ENTRAINMENT TRAP



A B – Annular vapor spaces

C – Central packed section

O – Holes thru which vapor enters trap

P – Drain

Arrows indicate path of vapor.

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3.3 Equilibration Distillation

A modified[2] Gillespie[3] recirculating equilibrium still (see Fig. 3.3) was used to determine more accurately the amount of ruthenium distilled at various pot nitric acid concentrations under equilibrium conditions. The results (see Table 3.3) confirmed the above observations, namely, that significant volatilization of ruthenium does not occur at pot acid concentrations below about 10 M.

Heat to the boiler was furnished by a 250-watt pyrex-jacketed immersion heater instead of by external heating coils. The volumes of the condensate trap and boiler were 10 and 100 ml, respectively. With the condensate trap of smaller volume than that of the original design, the time required to reach equilibrium should be less than the 3 hr reported by Gillespie as sufficient, but, in all runs, 4 hr was allowed to ensure equilibrium. Results with radioactive solutions indicated that entrainment in the apparatus was less than 0.05 percent, the value established for the original design.[3]

Boiler charge solutions were made up by spiking 98 ml of pure nitric acid with 2 ml of a Purex IAW solution that had a gross beta activity of 10^8 c/m/ml. The nitric acid concentration was varied to give boiler charge solutions ranging from about 7 to 13 M in final concentration, while the level of radioactivity remained practically the same. A trap containing 10 ml of 10 percent sodium hydroxide solution was attached to the vent of the condensate trap to catch any RuO_4 vapors escaping condensation. Analysis of the trap solution never showed more than a trace of activity.

In the operation of the still, boiling liquid is forced by vapor-lift action up the Cottrell pump tube. Vapor separates in the disengagement chamber and collects in the condensate trap, from which it overflows and drains slowly back into the boiler. Samples may be taken through stopcocks at the base of the boiler and condensate trap.

4.0 OTHER APPROACHES TO THE SOLUTION OF THE RUTHENIUM VOLATILITY PROBLEM

As shown in Sec. 3.0, control of the pot acidity throughout the evaporation can be used to minimize distillation of ruthenium. Other possible methods of preventing ruthenium contamination of the distillate are: (1) passage of the vapors through a trap packed with a material that will reduce the RuO_4 and cause the reduced compound to deposit on the packing, (2) evaporation under reduced pressure to lower the boiling point and thereby retard ruthenium oxidation, and (3) control of the distillation time.

Table 3.3

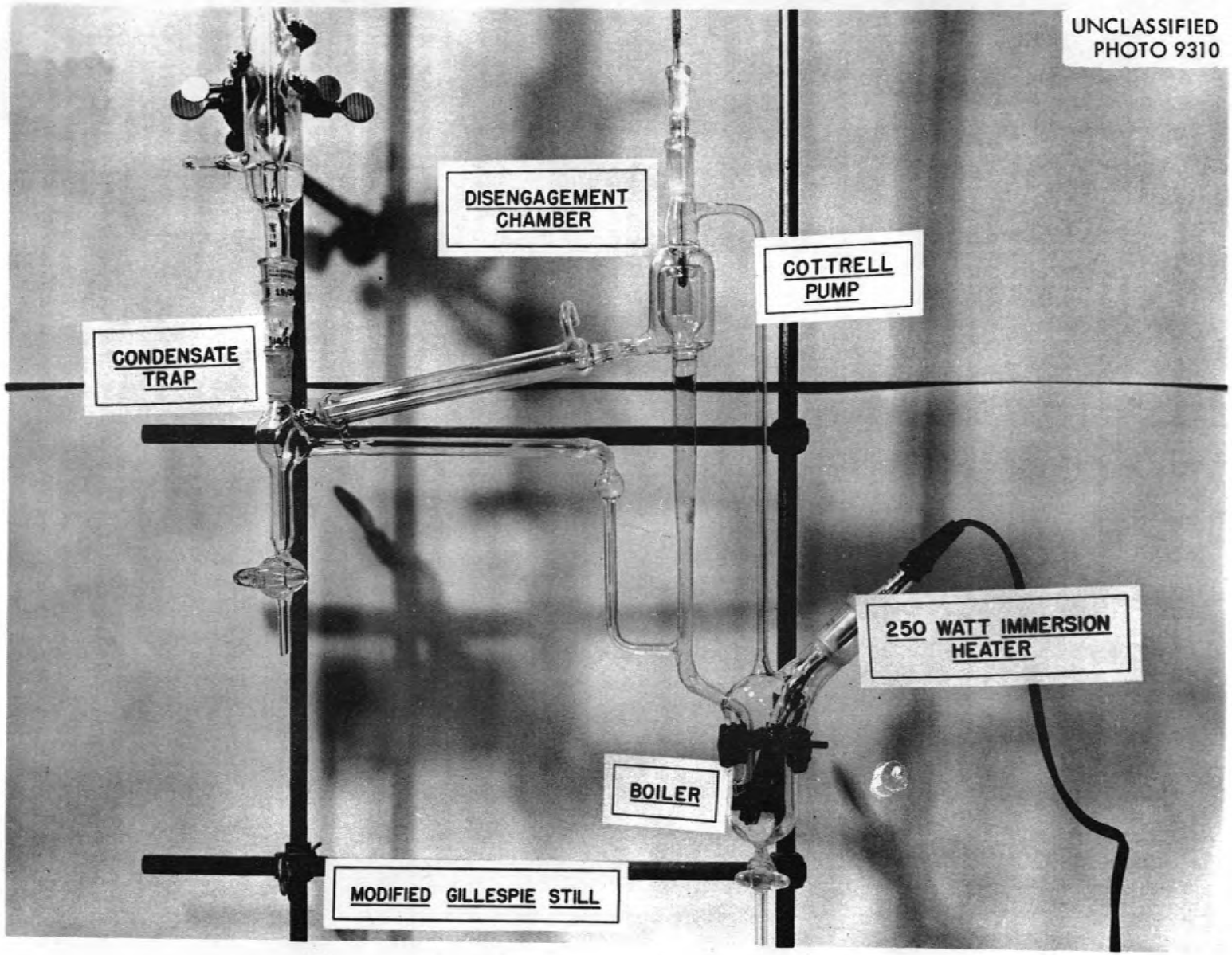
Distribution of Radioactivity between Residue and Condensate in Gillespie Equilibrium Still

Boiler charge: 98 ml of nitric acid spiked with 2 ml of Purex IAW solution having a gross β activity of 10^8 c/m/ml

HNO_3 Conc. of Boiler Solution (M)	HNO_3 Conc. of Condensate (M)	Boiling Point (°C)	Activity (c/m/ml at 10% geometry)					
			Gross β	Ru β	Ce β	Gross β	Ru β	Ce β
6.90	0.95	108	3.3×10^{6}*	1.9×10^{5}	1.7×10^{6}	110	12	13
7.30	1.40	109	6.4×10^{6}	3.6×10^{5}	3.0×10^{6}	152	18	21
8.50	2.28	111	5.8×10^{6}	3.9×10^{5}	2.8×10^{6}	54	12	25
9.05	2.70	111.5	5.8×10^{6}	3.2×10^{5}	2.8×10^{6}	46	17	22
9.95	3.85	113	6.3×10^{6}	3.3×10^{5}	3.0×10^{6}	370	319	27
10.85	5.20	114	6.3×10^{6}	3.5×10^{5}	3.3×10^{6}	456	434	14
12.25	8.05	116	5.8×10^{6}	3.3×10^{5}	2.9×10^{6}	144	141	9
12.65	8.70	117	5.6×10^{6}	3.4×10^{5}	3.2×10^{6}	993	1000**	22

*Only 1 ml of spike added to boiler charge.

**Owing to analytical error, Ru β appears slightly greater than gross β.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COTTRELL PUMP
CONDENSATE TRAP
250 WATT IMMERSION HEATER
BOILER
MODIFIED GILLESPIE STILL

4.1 Reduction of RuO_4 and Deposition of Reduced Compound on Various Solid Packing Materials

Distillations of IAW solution were made with various reducing materials packing the Hahn column. With the inert glass packing used in the experiments described in Sec. 3.0, the activity in the distillate was lower than that in the original waste by a factor of about 10^3. None of the materials tested gave a decontamination factor enough higher than this to make them of interest.

The distillations were carried out at atmospheric pressure in the apparatus described in Sec. 3.2. The reducing material being tested was placed in the inner tube of the trap (part C in Fig. 3.2) in place of the glass helices. Four hundred milliliters of IAW solution (see Table 3.2 for composition) was evaporated to 10 ml in each run. The materials tested, in the order of their decreasing affinity for the ruthenium compound, were:

1. Tygon packing: An average gross beta decontamination factor of 7.8×10^4 was obtained. Deterioration of the plastic started when the nitric acid concentration of the vapors reached about 3 M.

2. Duriron chips: A gross beta decontamination factor of 10^4 was obtained.

3. Stainless steel Fenske rings: When the packing was rinsed with chloroform to remove grease, the decontamination obtained with it was 1.8×10^3, comparable to that obtained with glass packing. When the packing was not cleaned prior to use, an overall gross beta decontamination factor of 3×10^5 was obtained. Use of uncleaned rings is, however, considered to be of no interest.

4. Graphite rods: No decontamination of the RuO_4 was apparent; the decontamination factor obtained was about the same as that obtained with glass packing.

4.2 Effect of Reduced Pressure on Volatilization of Ruthenium

A 6-hr distillation of the diluted IAW solution at a boiler acid concentration of 11.8 M was carried out at 380 mm Hg (0.5 atm) pressure in the Gillespie still. The distillation rate was adjusted to approximately that obtained at atmospheric pressure. Ruthenium carryover into the condensate was reduced by a factor of about 4, but cerium carryover (entrainment) was approximately doubled (Table 4.1). Reduced pressure, although it reduces volatilization of ruthenium, appears to offer no advantages since it increases the entrainment.

Table 4.1

Effect of Evaporator Hold-Up Time and Boiler Nitric Acid Concentration at Atmospheric Pressure

HNO_3 Conc. in Boiler (M)	Distillation Time (hr)	Activity (c/m/ml at 10% Geometry)						Ratio of Condensate Ru to Boiler Ru
		Gross β	Ru β	Ce β	Gross β	Ru β	Ce β	
7.55	1	5.0×10^{7}	2.9×10^{6}	2.1×10^{7}	422	32	170	1.1×10^{-5}
7.20	2	5.2×10^{7}	3.0×10^{6}	2.0×10^{7}	310	30	170	1.0×10^{-5}
7.40	3	5.2×10^{7}	7.3×10^{6}	2.3×10^{7}	189	20	79	2.8×10^{-6}
7.60	4	4.9×10^{7}	3.7×10^{6}	2.3×10^{7}	359	30	146	8.0×10^{-6}
7.10	5	4.9×10^{7}	3.0×10^{6}	2.1×10^{7}	307	30	173	1×10^{-5}
7.45	6	5.2×10^{7}	3.0×10^{6}	2.4×10^{7}	292	50	120	1.7×10^{-5}
9.80	1	6.8×10^{7}	2.2×10^{6}	2.9×10^{7}	466	39	411	1.8×10^{-5}
9.60	2	6.6×10^{7}	2.5×10^{6}	2.8×10^{7}	546	89	205	3.6×10^{-5}
9.80	3	6.5×10^{7}	3.9×10^{6}	3.0×10^{7}	421	136	Trace	3.5×10^{-5}
9.75	4	6.8×10^{7}	4.0×10^{6}	3.0×10^{7}	805	230	261	5.7×10^{-5}
9.65	5	6.6×10^{7}	3.7×10^{6}	3.1×10^{7}	685	454	104	1.2×10^{-4}
9.45	6	6.3×10^{7}	3.2×10^{6}	2.7×10^{7}	2.4×10^{3}	1.2×10^{3}	161	3.8×10^{-4}
11.70	1	6.6×10^{7}	3.5×10^{6}	2.9×10^{7}	7.8×10^{3}	3.5×10^{3}	411	1×10^{-3}
11.60	2	6.2×10^{7}	3.8×10^{6}	3.1×10^{7}	2.4×10^{4}	1.7×10^{4}	2800	4.5×10^{-3}
11.50	3	6.0×10^{7}	3.6×10^{6}	2.8×10^{7}	4.4×10^{3}	4.1×10^{3}	163	1.1×10^{-3}
11.80	4	6.5×10^{7}	4.4×10^{6}	3.3×10^{7}	1.7×10^{4}	1.6×10^{4}	170	3.6×10^{-3}
11.60	5	6.4×10^{7}	3.0×10^{6}	2.5×10^{7}	4.3×10^{4}	3.7×10^{4}	120	1.2×10^{-2}
11.80	6	6.4×10^{7}	4.1×10^{6}	3.3×10^{7}	4.6×10^{4}	4.3×10^{4}	436	1.0×10^{-2}
11.80*	6	5.9×10^{7}	3.3×10^{6}	2.7×10^{7}	1.1×10^{4}	9.8×10^{3}	760	3×10^{-3}

*The results of one run made at reduced pressure (380 mm Hg) are included for comparison with data obtained at atmospheric pressure.

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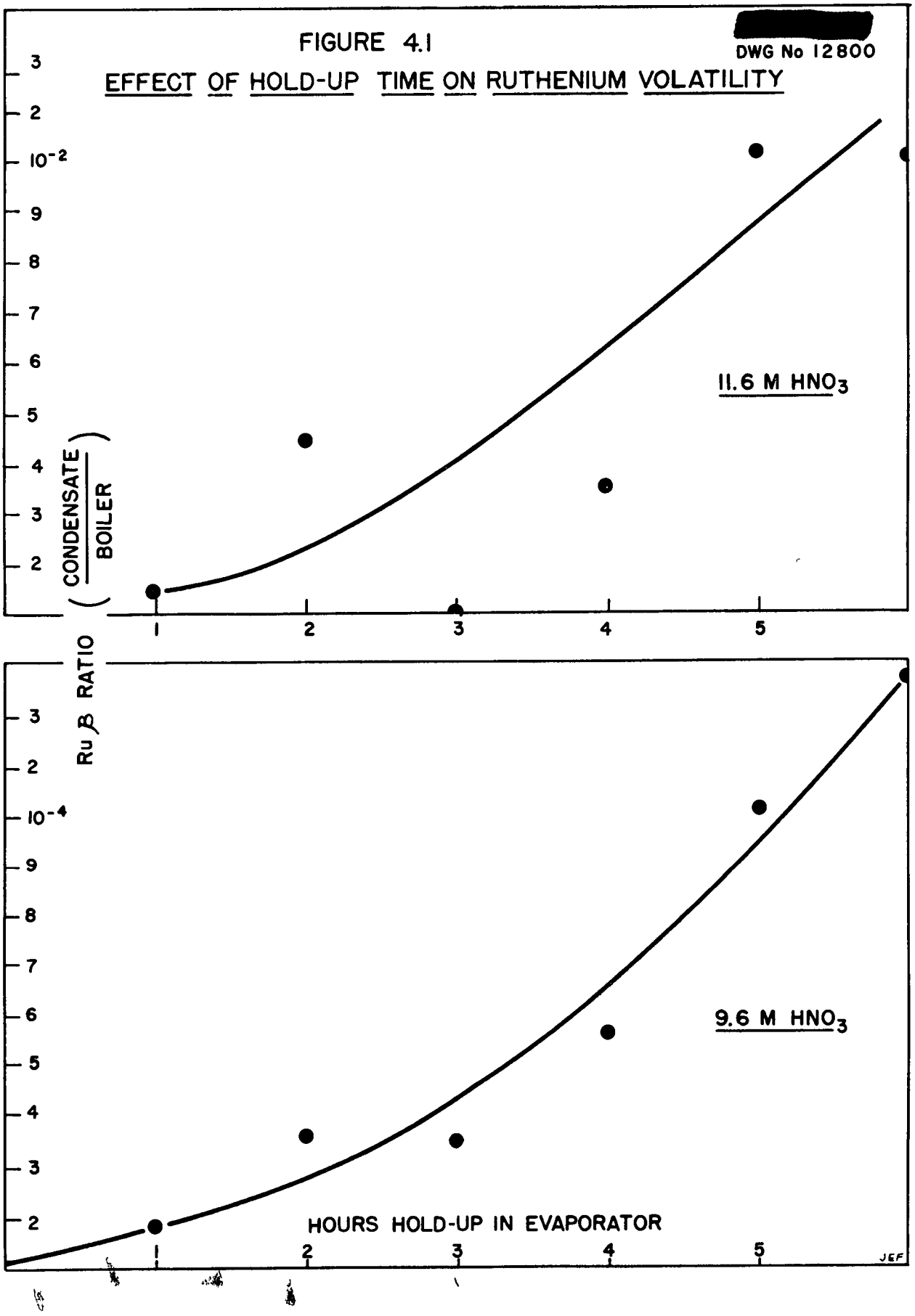
FIGURE 4.1

EFFECT OF HOLD-UP TIME ON RUTHENIUM VOLATILITY



4.3 Effect of Evaporator Hold-Up Time

In order to determine the effect of evaporator hold-up time on ruthenium volatilization from boiling IAW solution, distillations were carried out at atmospheric pressure in the Gillespie still at boiler acidities of about 7, 10, and 11.6 M. The distillation time was varied by 1-hr increments over a range of 1 to 6 hr. The results (Table 4.1) suggest a trend toward increased volatility of ruthenium with increase in nitric acid concentration and hold-up time. This behavior is illustrated in Fig. 4.1, where the ratio of ruthenium in the condensate to that in the boiler is plotted against boiler acidity and hold-up time. The results indicate that if the distillation could be carried out before there was time for the ruthenium to be oxidized to the tetroxide, better decontamination might be expected.

5.0 REFERENCES

(1) F. L. Hahn, Anal. Chem., 19: 811 (1947).

(2) R. M. Rieder and A. R. Thompson, Ind. Eng. Chem., 41: 2905 (1949).

(3) D. T. C. Gillespie, Ind. Eng. Chem., Anal. Ed., 18: 575 (1946).

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