Ruthenium Volatilization in the Distillation of Nitric Acid

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IN NUCLEAR FUEL solvent extraction processes in which nitric acid is used as a salting agent, its recovery is important because of the large savings gained from the re-use of the acid and the reduction in waste storage costs. In addition, it is very desirable to recover nitric acid that is not contaminated by radioactive elements. This uncontaminated nitric acid can then be fractionated and concentrated in equipment placed in contact maintenance zones, which results in additional savings in operating and construction costs. Moreover, the re-use of contaminated nitric acid might result in a build-up of contamination at some stage of the separations process and lead to processing difficulties.

The recovery of uncontaminated nitric acid from nitric acid solutions of fission products, however, is hampered by the volatilization of ruthenium. From experiments done elsewhere (*1*, *3*, *8*), a variety of conclusions have been reached as to the factors that enhance the volatilization of ruthenium from distilling nitric acid solutions. There was no apparent general agreement among experimenters as to the most important causes, but many workers concluded that high acid concentrations and prolonged acid retention times in the concentrator led to high ruthenium volatilization. High wall temperatures in the still were also shown to cause apparent increased volatilization. No general agreement was reached as to ways of suppressing volatilization.

The experiments reported here were designed to examine some chemical factors which enhance ruthenium volatilization and, if possible, to define distillation conditions which would suppress ruthenium volatilization.

EXPERIMENTAL PROCEDURE

The modified Othmer equilibrium still (*10*) used in these experiments is shown in Figure 1. The still was convenient to use because the boiler could be easily shielded, it required only a small amount of hood space, and it was readily decontaminated from radioactive elements.

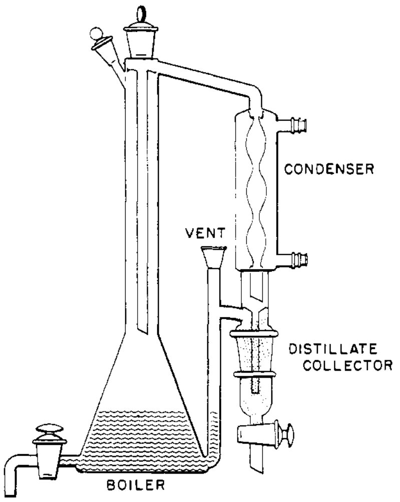

Figure 1. Round-bottomed Othmer still modified for heating with hot plate

Solutions were prepared by adding a small amount of a nitric acid solution of fission product elements to a nitric acid mixture of the constituents of interest. The same solution was used in all experiments. This solution was the source of the radioactive ruthenium which served as a tracer for the volatilized ruthenium. The tetrapotassium ruthenium nitrite salt (*7*) (yellow salt) was used to bring the ruthenium concentrations to levels existing in acid waste solutions, ca. $10^{-3}M$. It was made by addition of commercial ruthenium chloride to a boiling saturated solution of potassium nitrite. The yellow salt precipitated from the solution, and was then washed several times with cold water and dried at 100° C. Other chemicals were of reagent grade, used without further purification.

Analyses were conducted on distillate samples and samples of the boiler solution. Nitric acid was determined by titration with a standardized sodium hydroxide solution, using phenolphthalein as an indicator. Radiochemical determinations of radioactive ruthenium, cesium, and cerium were made in distillate and boiler solution samples by standard procedures (*6*).

In some experiments, distillate samples were taken without replacing the removed acid. In other experiments the removed acid was replaced by a solution identical in nitric acid composition and volume to the distillate sample recovered. The latter procedure was followed when a large fraction of the total acid in the system would have been removed as distillate samples, causing a considerable change in the nitric acid concentration in the boiler solution. In the nitrogen dioxide and nitrite ion experiments, additional modifications in the still were made.

DISCUSSION AND RESULTS

Ruthenium Volatilization. Ruthenium can appear in the distillate through entrainment and volatilization. Entrainment is the carry-over of spray into the distillate from the boiler solution. The entrainment factor can be determined by measuring the ratio of concentrations in the distillate to the boiler solution of a nonvolatile radio element—i.e., cesium or cerium. The distillation factor is measured in the same manner as the entrainment factor. The volatilization factor is the difference between the ruthenium distillation factor and the entrainment factor. A volatilization factor of zero indicates that ruthenium is not volatilizing. Entrainment factors varied from 10^{-4} to 10^{-7}. Because they were low, no attempt was made to maintain a constant entrainment factor among experiments. Ruthenium distillation factors varied from a low of 5×10^{-5} to a high of 0.02, which indicated that the concentration of ruthenium in the vapor phase never exceeded 2% of the concentration of ruthenium in the liquid.

Experimental results are reported in terms of the ruthenium volatilization factor.

Effect of Acid Concentration and Retention Time. Ruthenium build-up in the distillate is slow and usually requires about 5 hours to reach its equilibrium value. This is in general agreement with the work of Flanary and Reilly (3) at the Oak Ridge National Laboratory. Although the kinetics of ruthenium volatilization was not studied in detail, the time for attainment of ruthenium equilibrium does not vary greatly for nitric acid concentrations between 5 and 13*M* (Figure 2). At distillate acid concentrations much below 1*M*, the ruthenium in the distillate is deposited in the initally cool portions of the condenser as a black film, which is probably some form of ruthenium oxide. This retention of volatilized ruthenium in the condenser may have led to ruthenium distillation factors which were lower than expected, and may explain the two low volatilization factors observed in experiment B in Figure 2.

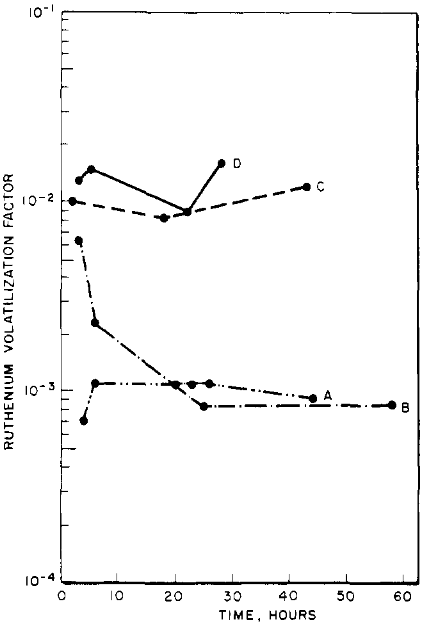

Figure 2. Effect of acid concentration and reaction time

Boiler charged with 250 ml. of HNO_3, 0.5 gram/liter of yellow salt, 2 ml. of fission product–nitric acid solution

A. 5.4 *M* HNO_3 in boiler, 0.22*M* in distillate. Black film deposited in condenser.

B. 6.8*M* HNO_3 in boiler, 0.78*M* in distillate. Black film deposited in condenser.

C. 8.8 to 10.8*M* HNO_3 in boiler, 1.8 to 4.1*M* in distillate. Acid removed by distillate samples not replaced as in other experiments. Distillate drops in condenser colored dark brownish purple.

D. 13.3*M* HNO_3 in boiler, 9.8*M* in distillate. Distillate drops in condenser colorless.

Results of experiments in which the effect of nitric acid concentration on the volatilization of ruthenium was measured as a function of time are given in Figure 2. For all experiments except B, equilibrium was at least reached in about 5 hours. Thus, the volatilization factor at about 5 hours obtained from Figure 2 was plotted *vs.* acid concentration in Figure 3. Volatilization factor increases with increasing acid concentration and approaches a plateau between 8 and 10*M* nitric acid.

Equilibrium of Active and Inactive Ruthenium. Because the yellow salt was used to adjust the ruthenium concentration to levels found in waste solutions, the volatilization behavior of the inactive ruthenium from the yellow salt was compared with radioactive ruthenium from the fission product solution. In the two experiments reported in Table I the nitric acid in the boiler solutions and in the distillate was brought to equilibrium by operating the still overnight with the other constituents absent. After this adjustment period was ended, the yellow salt and the fission product solution were added to the boiler solution and still operation was begun. Distillate samples were taken periodically and the acid and water so removed were replaced. The inactive ruthenium was determined spectrophotometrically after oxidizing the ruthenium in the distillate to ruthenium tetroxide. An aliquot of the distillate was heated at 90° C. for 10 minutes in the presence of an excess of potassium periodate to accomplish this oxidation. The resulting solution was cooled before it was transferred to the spectrophotometer cell. The absorbance of the solution was measured in a 10-cm. Corex cell at 385 mm. on a Beckman Model DU spectrophotometer. Ruthenium concentration was determined by using 930 as the molar absorptivity (2) for ruthenium tetroxide. The results in Table I indicate that the half time for the conversion of the nonvolatile ruthenium species of the yellow salt to the more volatile radioactive ruthenium species was between 3 and 7 hours, determined by a plot of 1−*f* *vs.* time for experiments A and

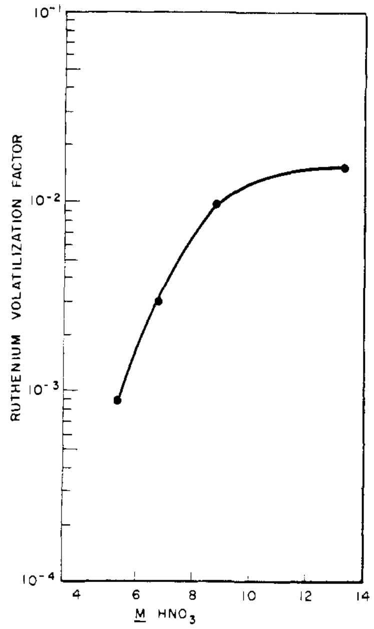

Figure 3. Effect of acid concentration

Data taken from Figure 2 at 5-hour points

Table I. Conversion of Yellow Salt Rutheniun to Volatile Ruthenium Species in Boiling Nitric Acid

Distillate Sample	Time, Hours	Active Ruthenium, C./M./Ml.	Inactive Ruthenium, Mole/Liter	f^a
Experiment A. Boiler solution 9.5*M* HNO_3, 0.71 g./l. yellow salt, 2 ml. fission product-nitric acid solution. Distillate. 2.3*M* HNO_3				
1	2.5	3,770	5.4×10^{-6}	0.08
2	9.8	4,990	6.0×10^{-4}	0.66
3	18.5	4,120	5.4×10^{-4}	0.72
4	24.2	4,934	8.6×10^{-4}	0.98
Boiler	...	725,000	1.32×10^{-2}	...
Experiment B. Boiler solution 10.0*M* HNO_3, 0.78 g./l. yellow salt, 2 ml. fission product-nitric acid solution. Distillate. 3.1*M* HNO_3				
1	5	4,850	0.81×10^{-4}	0.66
2	9	4,120	0.85×10^{-4}	0.83
3	37	5,900	1.6×10^{-4}	1.08
Boiler	...	704,000	1.7×10^{-2}	...

[a] *f* is fraction of yellow salt converted to the volatile ruthenium species. Calculated by taking the ratio of active ruthenium to inactive ruthenium in the boiler solution and dividing by the ratio of active ruthenium to inactive ruthenium in the distillate.

B. A straight line is obtained except for point $f = 0.72$ at 18.5 hours, which is off the curve for experiment A.

Supression of Ruthenium Volatilization. Ruthenium tetroxide has been generally considered the volatile ruthenium species (*5*). It was, therefore, reasonable to predict that a reducing agent such as sodium nitrite would, under the proper conditions, suppress ruthenium volatilization. Evidence existed that nitrite ion or nitrous acid reacted rapidly to reduce ruthenium tetroxide (*9*). Furthermore, nitrous acid under the proper conditions will persist in nitric acid solutions. Therefore, nitrous acid suppression of ruthenium volatilization looked promising. The experiments below described the favorable results obtained. Two other reagents that reduce nitric acid to nitrous acid also suppressed ruthenium volatilization.

Suppression by Nitrous Acid. Previous reports maintained that nitrous acid had no effect on the distillation of ruthenium (*3*). However, these experiments apparently neglected the air oxidation path and other paths by which nitrous acid could be depleted in the nitric acid distillation system.

In the experiments reported here, nitrous acid formed from added sodium nitrite was mixed with nitric acid in varying proportions. As long as the added nitrous acid was insufficient to react with the oxygen, which was estimated to be present initally in the air space in the Othmer still, no effect of nitrous acid on ruthenium distillation was noted. However, ruthenium distillation was suppressed with the addition of more sodium nitrite than that needed to react with the oxygen initially present. The excess nitrous acid is referred to as effective nitrous acid in Figure 4.

These experiments were conducted in the modified Othmer still, but vented to a vinyl plastic bag, which was used to exclude air after the sodium nitrite was added and to allow for initial gas expansion in the system. At the beginning of the experiment the plastic bag was collapsed. Samples of the distillate and boiler solution were taken periodically and analyzed for nitric acid and ruthenium. A nonvolatile fission product such as cerium or cesium was also determined in order to calculate the entrainment factor. The increase in the ruthenium volatilization factors for experiments D and E (Figure 4) is probably due to a gradual loss of nitrite from the system in spite of the precautions taken to prevent this.

Suppression by Nitrogen Dioxide Gas. Nitrogen dioxide reacts with nitric acid to produce nitrous acid. Thus, as in the case of sodium nitrite, nitrogen dioxide would be expected to suppress ruthenium volatilization. In this experiment the ruthenium concentration was allowed to reach its maximum in the distillate before nitrogen dioxide was bled into the system. The nitrogen dioxide line was attached to the vent of the still. A constant pressure of nitrogen dioxide was maintained in the still by allowing excess gas to leak to the atmosphere through a tube dipping into 5 cm. of mineral oil. Samples of the distillate and boiler solution were withdrawn periodically. The nitric acid removed frcm the system was replaced after each sampling. The suppressing effect of nitrogen dioxide is shown in Figure 5 by the sudden decrease in the ruthenium volatilization factor of the first sample after the introduction of nitrogen dioxide.

Suppression by 30 Volume % Tributyl Phosphate–Soltrol 170 Mixture. Nitrite had been shown to be effective in suppressing the volatilization of ruthenium from nitric acid, and it seemed probable that any substance which produced nitrous acid through the decomposition of nitric acid should suppress ruthenium distillation. An experiment was conducted in which a mixture of tributyl phosphate and Soltrol 170 (an odorless kerosine, Phillips Petroleum Co.) was added to the equilibrium still (Figure 6). This mixture was chosen because it is similar to those used in the solvent extraction for uranium separation. The waste solutions from these processes would normally be saturated with dissolved or entrained solvent. It seems evident that this organic mixture suppressed ruthenium volatilization. In the solvent addition experiment, the excess solvent collected in the side arm which fed the distillate back to the boiler. The returning distillate was thus saturated with solvent. It was thus shown that a feed solution saturated with this solvent suppressed ruthenium volatilization in the boiler.

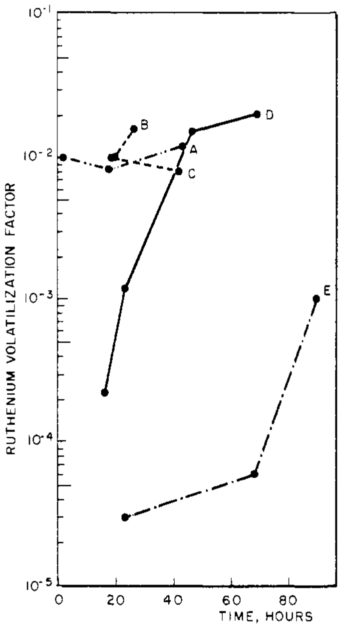

Figure 4. Effect of sodium nitrite in suppressing volatilization

Boiler charged with 200 ml. of 8*M* HNO_3, 1 gram/liter of yellow salt, 2 ml. of fission product–nitric acid solution, and $NaNO_2$.

	$NaNO_2$, G./L.	HNO_3, *M*	
		In distillate	In boiler
A	0	4.11	10.8
B	1.25	1.78	8.7
C	3.14	2.51	9.58
D	5.85[a]	2.34	10.1
E	6.90[b]	2.79	10.1

[a] 0.2 g./l. effective $NaNO_2$.

[b] 2.4 g./l. effective $NaNO_2$.

Acid concentrations are those found in final samples.

Volatile Ruthenium Compound. Other workers have concluded that the volatilizing ruthenium compound was ruthenium tetroxide. In the experiments in this laboratory ruthenium tetroxide was observed only when nitric acid distillation was carried out in the absence of oxygen or in purified nitrogen. In the presence of air the spectrum of ruthenium tetroxide was not observed in the distillate but the spectrum of a different and unknown species was observed, which changed with time. The initial brown color became purple and then slowly faded to brown again. Similar observations have been made by Fletcher and others (*4*).

CONCLUSIONS

Mild reducing agents such as sodium nitrite, nitrogen dioxide, and a mixture of tributyl phosphate and a hydrocarbon diluent, Soltrol 170, suppressed ruthenium volatilization.

In the presence of reducing agents nitric acid could be distilled from fission product wastes with ruthenium volatilization factors as low as 10^{-6} and in the absence of reducing agents with factors as high as 10^{-2}.

Ruthenium volatilization is enhanced by increased acid concentration and long distillation times.

Volatilization of ruthenium occurs over a range of nitric acid concentration from 5 to 13*M*.

Spectrophotometric evidence indicates that the distilling

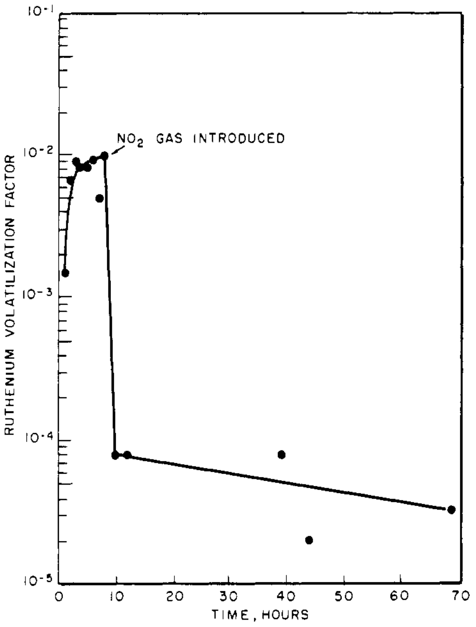

Figure 5. Effect of nitrogen dioxide

Boiler charged with 250 ml. of 8*M* HNO_3, 1.5*M* $NaNO_3$, product–nitric acid solution

1 gram/liter of yellow salt, 2 ml. of fission product–nitric acid solution. 2.4 ± 0.1*M* HNO_3 in distillate NO_2 introduced into system after 8-hour sample

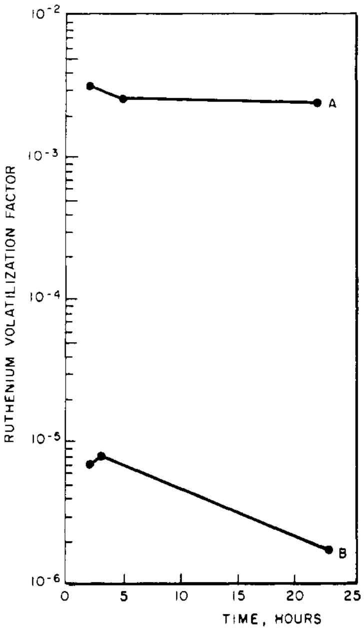

Figure 6. Effect of tributyl phosphate in Soltrol 170

Boiler charged with 300 ml. of 7.4*M* HNO_3, 0.09*M* $NaNO_3$, 0.5 gram of yellow salt, 3 ml. of fission product–nitric solution

A. Control, no additive

B. 50 ml. of 30 wt. % TBP–Soltrol 170 added

ruthenium species is ruthenium tetroxide when air is excluded, and in the presence of air another species is collected.

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