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NITRIC ACID RECOVERY FROM WASTE SOLUTIONS

Archie S. Wilson, Richland, Wash., assignor to the United States of America as represented by the United States Atomic Energy Commission

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This invention deals with the recovery of nitric acid from aqueous solutions and in particular from aqueous waste solutions containing radioactive fission products as they are obtained in processing nitric acid solutions of neutron-irradiated uranium-containing fuel elements.

It is highly desirable to subject waste solutions as were just described to a concentration step by evaporation, because by this the volume is reduced so that less space is required for the disposal and storage of the radioactive waste material and also because the nitric acid is regenerated thereby for reuse. However, there is a problem connected with the concentration of such nitric acid solutions, namely, the radioactive fission product ruthenium also volatilizes during evaporation; this volatilization of ruthenium takes place especially at nitric acid concentrations of between 5 and 13 M. The distillation of radioactive ruthenium involves a hazard and requires complex shielding equipment, and it also causes contamination of the distillate which makes reuse of the nitric acid dangerous or impossible.

It is an object of this invention to provide a process of evaporating nitric acid containing radioactive fission products in which the distillation of radioactive material is reduced to a minimum and a distillate containing a negligible amount of radioactivity is obtained.

It was found that ruthenium normally, in the presence of air, distills not in the form of ruthenium tetroxide, as one would expect, but that ruthenium distills as another unidentified compound. It was also found that by adding nitrous acid, or a substance that forms nitrous acid with nitric acid, the ruthenium volatilization is reduced to a negligible degree, so that the distillate obtained then is practically free from radioactive contaminants.

The process of the invention thus comprises incorporating nitrous acid to a nitric acid solution containing radioactive ruthenium values, heating the solution to above its boiling point whereby a nitric acid-containing distillate and a ruthenium-containing distillation residue are obtained, and heating said distillate for the concentration of the nitric acid.

In addition to nitrous acid, sodium nitrite and nitrogen dioxide were found suitable ruthenium vaporization suppressors. These substances are referred to hereinafter as nitrite-type ruthenium volatilization suppressors. The quantities of these suppressors may vary widely, relatively small amounts being suitable. For instance, in the case of sodium nitrite a quantity of "effective sodium nitrite," which is the excess quantity over that necessary to react with the oxygen in the air space of the still, of about 5 grams per liter of solution containing the ruthenium in concentrations usual for waste solutions was found sufficient; however, about 10 grams per liter was preferred.

The process can be carried out as a batch or as a continuous procedure. If a continuous process is used, the nitric acid solution and ruthenium volatilization suppressor are continuously fed into the evaporator vessel, and the heating rate is then adjusted so that the rate of distillation is about the same as that of feed introduction.

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In the experiments that led to this invention samples of the distillate were analyzed at various intervals for macro-constituents by conventional chemical analyses and for radioactive constituents by counting techniques. Entrainment limited the attainable decontamination to a factor of about 10^5 as was shown by determination of the decontamination factor for the nonvolatile fission product cerium. (The decontamination factor is the ratio of activity in the total charge of the evaporator to the activity in the total distillate obtained.)

The examples given below are illustrative of the improvement accomplished by the process of this invention, but they are not supposed to limit the invention to the details given therein.

EXAMPLE I

An evaporator was charged with 500 ml. of a solution 7.36 M in nitric acid, 0.09 M in sodium nitrate, containing 1 percent of a dissolver solution (neutron-irradiated uranium dissolved in nitric acid) and also containing 0.25 g. of tetrapotassium ruthenium nitrite, $K_4Ru(NO_2)_6 \cdot H_2O$. During distillation a 1.15 M nitric acid was continually fed into the evaporator at an average rate of 85 ml. per hour. The distillation run lasted seven hours, and the distillate was collected in seven fractions of one hour each; no nitrous acid was present in these runs. The γ -distillation factors (=ratio of activity per ml. of boiler solution to that per ml. of distillate) ranged between 5.7×10^2 and 33×10^2 . The distillation factors for ruthenium and cerium, for the fraction of from 434 to 518 ml., were found to be 120 and 3.5×10^5 , respectively.

Thereafter another set of runs was carried out in which the evaporator was charged with 500 ml. of a 9 M nitric acid, 1.5 M in sodium nitrate, containing 1 percent of the same dissolver solution used in the above-described runs and also containing 0.25 g. of the same tetrapotassium ruthenium nitrite. The nitric acid removed from the evaporator was continually replaced by feeding a mixture of nitric and nitrous acids at a speed of 43 ml. per hour to the evaporator. The acid mixture had a total acidity of 3.74 M and a nitrous acid concentration of 0.51 M. The γ -distillation factors ranged between 3×10^3 and 20×10^5 . The distillation factor for either, the ruthenium and cerium, for the fraction of from 651 to 695 ml. was 1.5×10^5 .

EXAMPLE II

A boiler vessel was charged with 200 ml. of an 8-M nitric acid containing 1 g./l. of tetrapotassium ruthenium nitrite, one percent of the same dissolver solution used in Example I and sodium nitrite in the quantities shown below in Table I. The solution was brought to boiling, and samples of the distillate were taken periodically and analyzed for nitric acid and ruthenium contents. The boiler solution was also analyzed. Furthermore, the cesium content (derived from the added dissolver solution) was determined in order to calculate the entrainment distillation factor. From the analytical results the ruthenium and cesium distillation factors were calculated. They are shown in Table I.

Table I

NaNO ₂ gm./l.	Time in hours	Distillate M HNO ₃	Boiler M HNO ₃	Ruthenium Distillation Factor	Cesium Distillation Factor
0	18	3.06	10.46	120	2.0×10^4
5.85	16	1.49	8.16	3,100	1.1×10^4
	23	1.99	9.1	760	1×10^4
6.90	23	1.49	7.95	30,000	1.2×10^4

This table shows the favorable effect of the addition

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of sodium nitrite, namely, the radical increase of the distillation factors.

The next example will illustrate the sudden increase of the ruthenium distillation factor when nitrogen dioxide gas was introduced into the boiler solution.

EXAMPLE III

The boiler vessel was charged with 250 ml. of an 8-M nitric acid containing sodium nitrate in a concentration of 1.5 M, 1 g./l. of tetrapotassium ruthenium nitrite, and one percent of the same dissolver solution used in the previous examples. The distillation was carried out without the addition of nitrogen dioxide for the first 8 hours, and then distillation was continued while nitrogen dioxide was introduced and maintained in the vessel at a constant pressure.

The ruthenium and cesium distillation factors are summarized in Table II.

Table II

Time in Hours	Distillate, M HNO ₃	Ruthenium Distillation Factor	Cesium Distillation Factor
1	2.2	6.5×10 ²	1.3×10 ⁵
2	2.4	1.5×10 ²	
3	2.4	1.1×10 ²	
4	2.4	1.2×10 ²	5.7×10 ⁴
5	2.4	1.2×10 ²	
6	2.4	1.1×10 ²	5.9×10 ⁴
7	2.4	2.0×10 ²	4.9×10 ⁴
8	2.1	1.0×10 ²	5.5×10 ⁴
NO ₂ gas introduced after 8 hours			
10	2.7	1.2×10 ⁴	3.1×10 ⁶
12	2.6	1.2×10 ⁴	
39	2.4	1.2×10 ⁴	1.4×10 ⁶
41	2.4		4.1×10 ⁶
44	2.4	4.7×10 ⁴	1.4×10 ⁶
69	2.2	3 ×10 ⁴	4.3×10 ⁶

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It is obvious that the nitrogen dioxide had a radical effect on the retention of the ruthenium in the boiler solution.

It will be understood that this invention is not to be limited to the details given herein, but that it may be modified within the scope of the appended claims.

What is claimed is:

1. A process of recovering nitric acid from a solution containing said nitric acid together with ruthenium values comprising incorporating nitrous acid in said solution, heating the solution to above its boiling point so that nitric acid distills away from a ruthenium-containing distillation residue, condensing the nitric acid vapors to form a distillate, and heating said distillate for concentration of the nitric acid.

2. The process of claim 1 wherein nitrous acid is incorporated by the addition of nitrous acid.

3. The process of claim 1 wherein the nitrous acid is incorporated by the addition of sodium nitrite to the nitric acid solution.

4. The process of claim 1 wherein the nitrous acid is incorporated by the addition of nitrogen dioxide to the nitric acid solution.

No references cited.