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The Removal of Fluoride from Aqueous Nitric Acid

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ABSTRACT

Several methods for removing fluoride from aqueous nitric acid were investigated and compared with the frequently used aluminum nitrate–calcium nitrate (Ca^{2+}-Al^{3+}) chemical trap–distillation system. Zirconium oxynitrate solutions were found to be superior in preventing volatilization of fluoride during distillation of the nitric acid, producing decontamination factors (DFs) on the order of 2×10^3 (vs ∿500 for the Ca^{2+}-Al^{3+} system). Several other metal nitrate systems were tested, but they were less effective. Alumina and zirconia columns proved highly effective in removing HF from HF-HNO_3 vapors distilled through the columns; fluoride DFs on the order of 10^6 and 10^4, respectively, were obtained. A silica gel column was very effective in adsorbing HF from HF-HNO_3 solutions, producing a fluoride DF of ∿10^4.

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1. INTRODUCTION

Nitric acid used in uranium refining, nuclear fuel reprocessing, and other industrial processes frequently contains significant quantities of fluoride and chloride ions; this leads to rapid corrosion and etching of the process equipment.[1,2] To overcome this problem, methods were developed to remove fluoride during the recovery of the nitric acid solution[3,4] and make it possible to use standard stainless steel or glass process equipment. For example, the Y-12 nitrate recycle facility uses a chemical trap containing 23.8 wt % aluminum nitrate nonahydrate, 52.9 wt % calcium nitrate tetrahydrate, and 23.3 wt % water.[5] Typically, a feed solution of about 10 wt % (1.7 M) nitric acid, contaminated with up to 5000 ppm fluoride, can be distilled from this trap to yield a product that is slightly enriched in nitric acid and contains <10 ppm fluoride.

Under these conditions fluoride decontamination factors, [DF = $(C_{HF}^{feed}/C_{HNO_3}^{feed})/(C_{HF}^{product}/C_{HNO_3}^{product})$], average about 200 for a 1 M HNO_3 feed solution contaminated with 400 ppm fluoride, but they decrease rapidly as the nitric acid concentration in the feed solutions is increased. Decontamination factors for a feed solution of 3 M nitric acid are about 40, while for 6 M nitric acid the DF decreases to <20.[4] When 0.06 M aluminum nitrate is added to the feed solutions, these DFs are improved to ∿1000, 2000, and 200, respectively, for 1, 3, and 6 M nitric acid.

The present work was undertaken to develop alternative methods for removing fluoride from nitric acid, producing improved DFs over a wider range of conditions. Three distinct approaches were taken: (1) metal ions other than aluminum and calcium were tested as complexing agents to decrease fluoride volatilization during nitric acid distillation, (2) HF-HNO_3 mixtures were distilled through columns containing alumina and zirconia to remove fluoride from the vapor phase, and (3) solutions of HF-HNO_3 were passed through a silica gel column at ambient temperature and pressure to adsorb the fluoride.

2. EXPERIMENTAL

2.1 Reagents

2.1.1 Zirconium nitrate

Ninety-five grams of technical-grade zirconium nitrate (A. D. McKay) was added to 170 mL of 90% HNO_3 and stirred at 50 to 60°C for about 3 h. Thirty grams of zirconium nitrate (recrystallized from 85% HNO_3) was dissolved in 100 mL of ∿50% HNO_3 and added to the first solution. The combined solution was heated for 4 h, then stirred overnight at room temperature. The small amount of undissolved residue was filtered off and found to dissolve in water. This dissolved residue was added to the bulk solution, which was then diluted to 410 mL with distilled water. Analysis of this final solution showed 1.0 M Zr and 12.4 M total nitrate.

2.1.2 Zirconium oxynitrate

Zirconium oxynitrate [$ZrO(NO_3)_2 \cdot xH_2O$] (Alfa-Ventron) was used without further purification. However, exposure of the material to moist air caused acidic fumes to evolve and rendered the solid insoluble. Care was taken to weigh and dissolve material from a freshly opened bottle as quickly as possible for each experiment. Unused material was stored under dry nitrogen.

2.1.3 Zirconia

Fused, stabilized, refractory-grade zirconia (Norton) was used as a column packing. The commercial material was crushed slightly and sieved to obtain the 10-20 mesh fraction. The surface area was found to be ~ 0.05 m^2/g.

2.1.4 Alumina

One-eighth-inch-diameter activated alumina pellets (Alcoa), fired for 18 h at 1300°C, were found to be highly resistant to attack by HNO_3-HF vapors. The pellets had a surface area of 2 m^2/g.

2.1.5 Silica gel

Six-to-ten mesh silica gel (Grace Chemical Co.) was degassed under 10 M nitric acid by repeated evacuation and repressurization in a vacuum flask.

2.1.6 Other reagents

All other reagents were analytical grade and were used without further purification.

2.2 Apparatus and Procedure

2.2.1 Equilibrium measurements

The potential of various fluoride complexing agents to decrease HF volatilization was evaluated by the use of an all-Teflon, Othmer equilibrium still. Four-hundred-milliliter aliquots of solutions containing varying amounts of HF and HNO_3 were placed in the distillation pot, along with the fluoride complexing agent to be studied. After allowing the system to reflux for several hours to ensure equilibrium, a 5-mL sample of condensate was withdrawn and analyzed for fluoride and total acid.

2.2.2 Solid adsorbent experiments

Experiments using solid adsorbent columns were carried out in an all-Teflon apparatus similar to the one shown in Fig. 1. Components could be added or removed as needed for individual experiments. The Teflon distillation column measured 24 mm ID by 25 cm long and was packed with either alumina (117 g) or zirconia (120 g). A magnetic stirrer and Teflon turnings were added to the distillation pot to minimize bumping and vortexing of the solution, which interfered with the operation of the liquid-level controller.

Batch experiments were done without the liquid-level controller and feed system by distilling aliquots of HF-HNO_3 mixtures through the column. After exiting the column, the vapors were condensed, sampled, and analyzed.

For long-term experiments (up to 10 d), a platinum liquid-level probe was used to maintain a constant level of solution in the pot. The composition of the feed mixture could be adjusted to maintain a constant composition of material in the distillation pot. A fraction collector was used to collect the distillate.

Temperatures in the various parts of the system were monitored with platinum thermocouples.

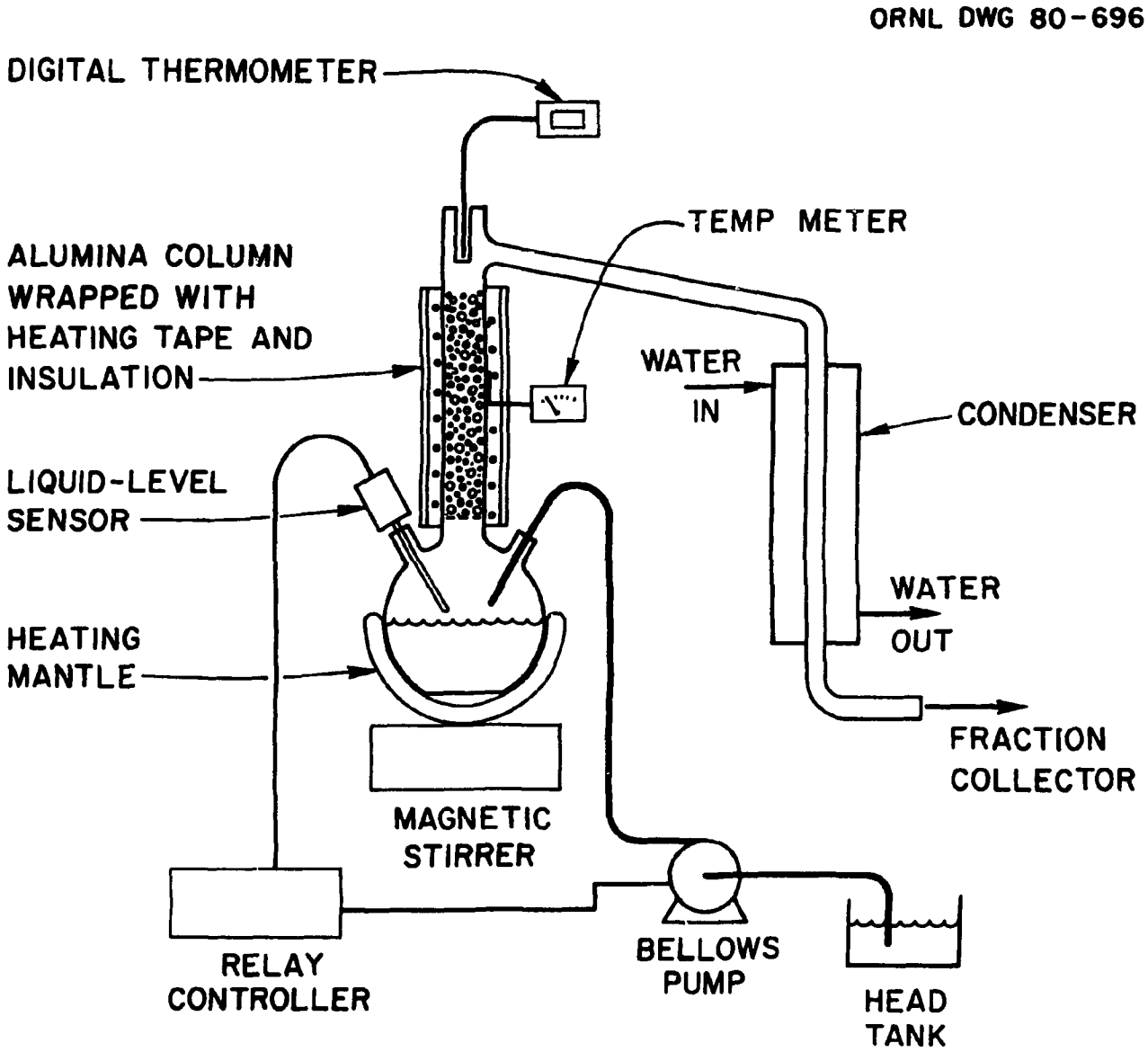

Fig. 1. Teflon continuous-distillation assembly.

2.2.3 Silica gel column

A polystyrene column (9.5 mm ID) was packed to a depth of 50 cm with 27 g of degassed silica gel. The resulting column had a bed volume of 35.4 mL. A feed solution, 10.46 M in nitric acid and containing 106 ppm fluoride, was pumped through the column at the rate of 1.0 mL/min (1.7 bed volumes/h). Samples were collected in an automatic fraction collector and analyzed for fluoride as described below. All components of the system that came in contact with the fluoride solution were polystyrene or Teflon, except for the stainless steel check valves in the bellows pump.

2.3 Analyses

2.3.1 Fluoride

Fluoride analyses were done using a fluoride-selective electrode and the method of known addition. It was found that reproducibility and electrode response were best when the sample was buffered to a pH of 5 to 5.5 with a mixture of HCl, sodium acetate, sodium tartrate, and tris(hydroxymethyl)-aminoethane.

2.3.2 Metals

Analyses for the various metal cations were carried out by the Analytical Chemistry Division, Oak Ridge National Laboratory, using atomic absorption and x-ray fluorescence spectroscopy.

3. RESULTS AND DISCUSSIONS

3.1 Equilibrium Measurements

3.1.1 Chemical traps based on aluminum nitrate

Fluoride is presently removed from waste nitric acid generated at the Y-12 Plant (Oak Ridge, Tenn.) by distilling the contaminated acid from the aluminum nitrate–calcium nitrate chemical trap described in the introduction. This method, along with modifications using zinc or

lanthanum nitrate in combination with aluminum nitrate, has been patented.[4] The metal ions in these systems form strong complexes with the fluoride ions, effectively neutralizing the corrosive properties of the anions and decreasing their volatility. These reagents were tested in an Othmer equilibrium still[2] to provide a reference baseline for comparing the effectiveness of other fluoride-removal methods. The equilibrium concentrations of nitric acid and fluoride in the vapor phase above the refluxing mixtures were measured and used to calculate overall fluoride DFs. These results are summarized in Table 1.

The most effective fluoride-removal system will generally maximize the fluoride DF by giving a product with the largest possible nitric acid concentration and the lowest possible fluoride concentration. The data in Table 1 show that aluminum nitrate alone strongly suppresses fluoride volatility but the nitric acid concentration in the vapor is low. Hence, the overall DF is not high. A mixture of aluminum nitrate and calcium nitrate, however, suppresses fluoride volatility even more strongly, while the vapor phase is enriched in nitric acid. Decontamination factors under the conditions used in these studies were typically near 500, but these can be increased to near 2000 if the acid concentration is low ($\sim$1 M), and the Ca/Al ratio is optimized.[4] Substitution of zinc nitrate for calcium nitrate produces a still larger DF by further decreasing fluoride volatility and increasing the concentration of nitric acid in the vapor phase. Lanthanum nitrate in combination with aluminum nitrate is less effective than either calcium nitrate or zinc nitrate, allowing more fluoride to volatilize without increasing the nitric acid concentration in the vapor phase relative to that obtained using calcium nitrate.

It has been postulated that calcium nitrate improves the effectiveness of the aluminum nitrate system by preventing the hydrolysis of the aluminum ions to form insoluble hydrated alumina,[4] but other effects may also be important. In an aqueous nitric acid solution, fluoride will be present almost exclusively as hydrofluoric acid, which will react with aluminum nitrate as follows:

$$Al(NO_3)_3 + 6HF \rightarrow H_3AlF_6 + 3HNO_3 \ . \qquad (1)$$

Table 1. Fluoride removal using aluminum nitrate alone or in combination with calcium nitrate, zinc nitrate, or lanthanum nitrate

Trap solution	$[HNO_3]^a_{pot}$ (M)	$[F^-]^a_{pot}$ (ppm)[b]	$[HNO_3]_{vap}$ (M)	$[F^-]_{vap}$ (ppm)	DF
None[c]	8.0	1,900	2.0	1480	0.32
1 M $Al(NO_3)_3$	4.0	100	0.18	0.43	10
1 M $Al(NO_3)_3$	8.0	100	4.5	0.75	75
1 M $Al(NO_3)_3$	8.0	2,350	4.5	16.4	80
0.93 M $Al(NO_3)_3$ 3.30 M $Ca(NO_3)_2$	4.0	100	7.6	0.41	460
0.93 M $Al(NO_3)_3$ 3.30 M $Ca(NO_3)_2$	4.0	2,350	7.1	8.05	500
0.98 M $Al(NO_3)_3$ 3.24 M $Zn(NO_3)_2$	4.0	100	9.5	0.33	720
0.98 M $Al(NO_3)_3$ 3.24 M $Zn(NO_3)_2$	4.0	1,000	9.3	3.72	625
0.98 M $Al(NO_3)_3$ 3.24 M $Zn(NO_3)_2$	4.0	10,000	9.6	52.6	450
1.00 M $Al(NO_3)_3$ 2.00 M $La(NO_3)_3$	4.0	100	7.3	0.83	220
1.00 M $Al(NO_3)_3$ 2.00 M $La(NO_3)_3$	4.0	1,000	7.5	4.24	440
1.00 M $Al(NO_3)_3$ 2.20 M $La(NO_3)_3$	4.0	10,000	7.2	49.5	360

[a] Initial concentrations.

[b] 100 ppm = 5.26×10^{-3} M F^-.

[c] From ref. 2.

This reaction produces a nonvolatile aluminum fluoride complex and slightly increases the amount of nitric acid in solution. These effects improve the fluoride DF obtained upon distillation of the mixture by reducing the fluoride vapor pressure and increasing the nitric acid vapor pressure above the solution. However, when a second metal nitrate salt is added to the system, more nitric acid can be released by reactions such as:

$$2H_3AlF_6 + 3Ca(NO_3)_2 \rightarrow Ca_3(AlF_6)_2 + 6HNO_3 \ . \qquad (2)$$

This will further increase the vapor pressure of nitric acid. The second metal nitrate may also form a series of fluoride complexes, reducing the fluoride volatility still more. Finally, the increased concentration of nitrate ions will shift the nitric acid dissociation reaction toward molecular nitric acid, thus increasing the vapor pressure of the acid.

3.1.2 Chemical traps based on zirconium nitrate

The data shown in Table 1 for the aluminum nitrate-based chemical traps are the standard against which other methods may be critically evaluated. The most effective alternatives to these standard methods were found to be the zirconium nitrate and zirconium oxynitrate chemical traps. Decontamination factors for these systems are shown in Table 2. A zirconium nitrate chemical trap produces a fluoride DF on the order of 500, comparable to that obtained for the Al^{3+}-Ca^{2+} trap. However, note that the nitric acid concentration in the zirconium nitrate trap is 9.0 M, well above the optimum range for the standard reagent system. The zirconium oxynitrate trap produces DFs on the order of 1700 — about three times the DF obtained in either the Al^{3+}-Ca^{2+} or the zirconium nitrate system. In addition, a zirconium oxynitrate chemical trap provides excellent fluoride decontamination at nitric acid and fluoride concentrations far higher than can be used in the standard system. When 1 M HF (19,000 ppm F^-) in 9.0 M HNO_3 is distilled from 1.0 M zirconium oxynitrate, a DF of 870 is obtained, and the product nitric acid has a fluoride concentration low enough (10 ppm) to meet specifications for most applications.

Table 2. Fluoride removal using zirconium nitrate and zirconium oxynitrate

Trap solution	$[HNO_3]_{pot}$[a] (M)	$[F^-]_{pot}$[a] (ppm)[b]	$[HNO_3]_{vap}$ (M)	$[F^-]_{vap}$ (ppm)[b]	DF
1.00 M ZN[c]	9.0	100	7.9	0.29	300
1.00 M ZN	9.0	2,350	7.6	4.01	500
1.00 M ZON[d]	9.0	100	4.7	0.13	400
1.00 M ZON	9.0	1,000	4.8	0.30	1800
1.00 M ZON	9.0	10,000	4.6	3.07	1700
1.00 M ZON	9.0	19,000	4.3	10.4	870
1.00 M ZON 1.33 M $Al(NO_3)_3$	5.0	100	4.9	0.20	490
1.00 M ZON 1.33 M $Al(NO_3)_3$	5.0	1,000	4.1	0.34	2400

[a] Initial concentrations.

[b] 100 ppm = 5.26×10^{-3} M F^-.

[c] ZN = zirconium nitrate.

[d] ZNO = zirconium oxynitrate.

The DFs obtained for the zirconium oxynitrate trap can be improved slightly by adding aluminum nitrate to the system, which might also be expected to increase the fluoride-removing capacity of the trap. This possibility was not tested experimentally, however. Adding calcium nitrate to the zirconium nitrate caused the formation of large amounts of undesirable precipitates in the distillation pot.

Careful inspection of the data in Table 2 shows that, while the fluoride concentration in the distillate from the zirconium oxynitrate trap was lower than that from the zirconium nitrate trap, the nitric acid concentration was also substantially lower. This decrease in the vapor pressure of nitric acid may be partially due to the decrease in total nitrate concentration that occurred when zirconium nitrate was replaced with zirconium oxynitrate (13 M vs 11 M total nitrate).

However, it does not seem likely that this effect alone could decrease the vapor pressure of the acid by almost 40%. There is clearly a fundamental difference between the zirconium species present in zirconium nitrate and those in zirconium oxynitrate solutions, and these species interact differently with fluoride and nitrate ions.

3.1.3 Miscellaneous chemical traps

Table 3 shows the results of experimental testing of a number of other reagents as chemical traps for fluoride. None was very effective, although the potential for the formation of strong, nonvolatile fluoride complexes existed in each case.

Table 3. Fluoride removal using various chemical trap solutions

Trap solution	$[HNO_3]^a_{pot}$ (M)	$[F^-]^a_{pot}$ (ppm)[b]	$[HNO_3]_{vap}$ (M)	$[F^-]_{vap}$ (ppm)[b]	DF
1.00 M $Th(NO_3)_3$	9.5	100	6.4	3.38	20
1.00 M $Th(NO_3)_3$ 1.00 M $Al(NO_3)_3$	4.0	100	1.4	0.51	69
1.00 M $Th(NO_3)_3$ 1.00 M $Al(NO_3)_3$	4.0	1,000	1.4	2.51	140
1.00 M $Th(NO_3)_4$ 1.00 M $Al(NO_3)_3$	4.0	10,000	1.8	26.8	170
1.75 M $La(NO_3)_3$ 0.875 M $Mg(NO_3)_2$	4.0	100	1.7	24.9	1.7
1.75 M $La(NO_3)_3$ 1.75 M KNO_3	4.0	100	0.76	18.4	1
1.00 M H_3BO_3 2.00 M $LiNO_3$	9.0	100	2.83	43.9	0.7

[a] Initial concentration.

[b] 100 ppm = 5.26×10^{-3} M F^-.

It is interesting that distillation of contaminated nitric acid from a thorium nitrate–aluminum nitrate trap produced DFs that are only slightly greater than those for aluminum alone. Even though thorium forms a stronger fluoride complex than does aluminum (log K_1 = 7.65 for Th, 6.10 for Al, at 25°C), it does not strongly suppress fluoride volatility either when used alone or in combination with aluminum nitrate. There seems to be no simple correlation between the suppression of fluoride volatility by a particular metal ion and any other readily discernible physical property. However, since little information is available on the properties of these systems at elevated temperatures, conclusions based on stability constants or other parameters measured at 25°C may not be valid for temperatures of 100°C or more. Without relevant thermodynamic data on these systems at or near reflux temperatures, it is not obvious why one metal nitrate or combination of metal nitrates is more effective at suppressing fluoride volatility than another, or why the nitric acid vapor pressure varies, even when the nitric acid and total nitrate concentrations are held constant.

3.2 Solid Adsorbents

3.2.1 Alumina and zirconia

A second approach to fluoride decontamination involved distillation of HF–HNO_3 vapors from a Teflon pot through a column packed with a fluoride-adsorbing material, such as alumina or zirconia, and condensation of the purified nitric acid that passed through the column. The distillation system used is described in Sect. 2.2 and is illustrated in Fig. 1.

In one experiment, the distillation pot was charged with 500 mL of 9.84 M HNO_3–0.526 M HF (9990 ppm F^-). The solution was distilled through 117 g of alumina, and nine 50-mL samples, equivalent to 0.44 volume of the adsorption column, were collected. As shown in Table 4, fluoride removal from the vapor was essentially quantitative. The combined distillate samples were 9.19 M in nitric acid concentration and contained 0.08 ppm fluoride. The overall DF for the combined distillate, compared

Table 4. Fluoride removal by batch distillation of HNO_3 from 9.84 M HNO_3–0.526 M HF through alumina

Sample	Total distillate volume (mL)	$[HNO_3]$ (M)	$[F^-]$ (ppm)	DF[a]
Head		9.84	9990	
1	50	1.32	0.14	0.01×10^6
2	100	3.74	0.26	0.01×10^6
3	150	5.60	0.20	0.03×10^6
4	200	8.03	<0.01	$>0.82 \times 10^6$
5	250	9.25	0.07	0.13×10^6
6	300	12.01	0.01	1.2×10^6
7	350	13.53	<0.01	$>1.4 \times 10^6$
8	400	14.14	<0.01	$>1.4 \times 10^6$
9	450	15.05	<0.01	$>1.5 \times 10^6$
Heel		15.4	315.4	

$$\alpha_{DF} = \frac{[F^-]_{head}[HNO_3]_{sample}}{[F^-]_{sample}[HNO_3]_{head}} .$$

to the initial feed solution, was 1.2×10^5. Comparing individual fractions to the feed solution, DFs ranging from 10^4 to $>10^6$ were obtained. In this experiment, 4.99 g of fluoride was loaded on the alumina column (42.6 mg F^-/g alumina) with no significant breakthrough.

In an attempt to determine the capacity of alumina for fluoride, a fresh 117-g column was prepared, and the distillation pot was charged with 500 mL of 14.1 M HNO_3–0.0377 M HF (717 ppm F^-). Purified nitric acid was distilled through the column at the rate of 1.6 mL/min. The addition of a feed solution containing 717 ppm fluoride in 10.5 M HNO_3 was controlled by a liquid-level controller and platinum probe to maintain a nearly constant nitric acid concentration in the distillation pot. A fraction collector removed a 22.4-mL sample every 14 min. Every tenth sample was analyzed for fluoride and total acid, and some typical results are summarized in Fig. 2 and Table 5. The fluoride DF reached a maximum value of $\sim 6 \times 10^4$ near the beginning of the distillation and slowly declined until, after 60 h, 5.7 L (50 column bed volumes) of solution had been processed and the instantaneous fluoride concentration in the

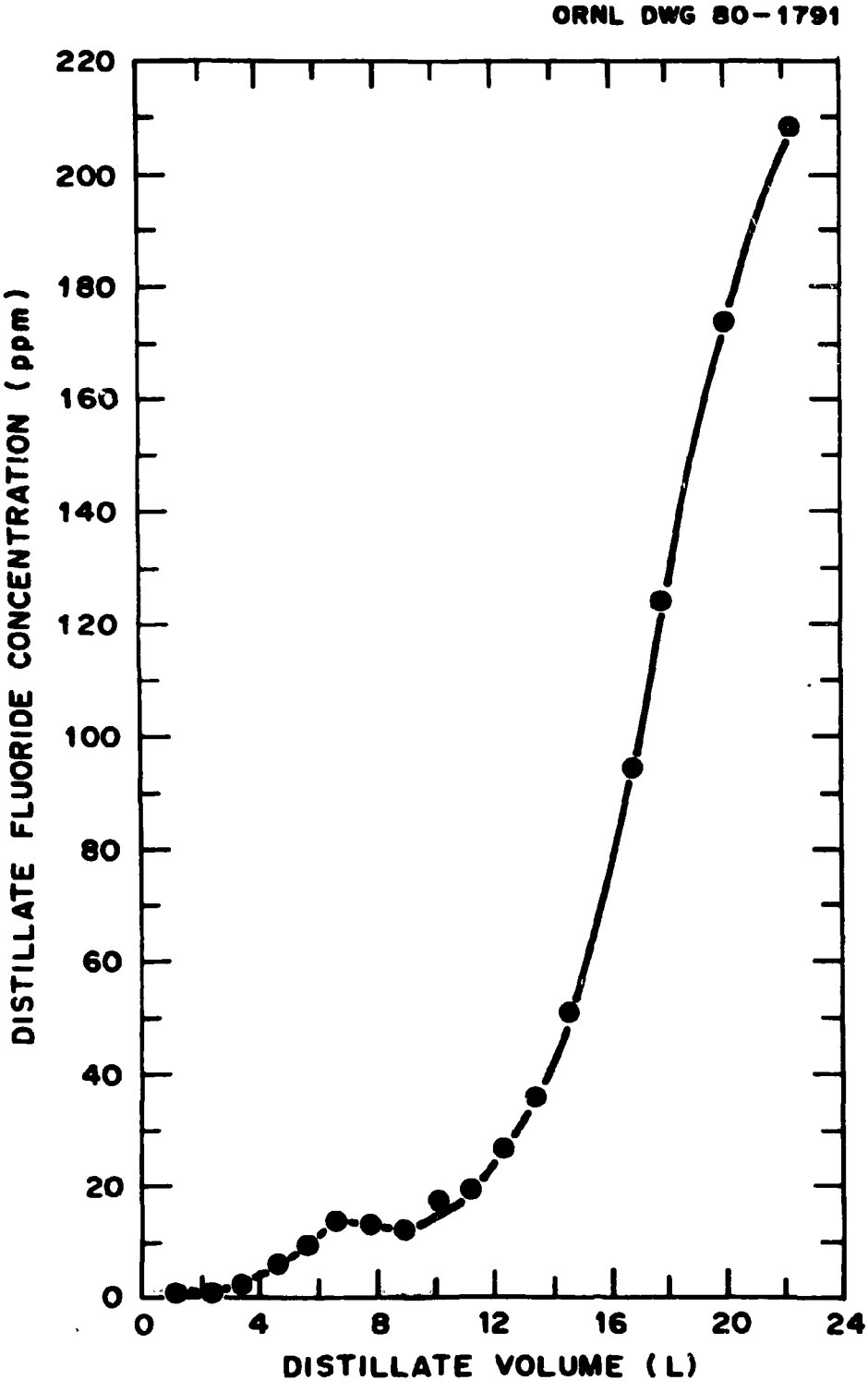

Fig. 2. Breakthrough curve for alumina-packed distillation column.

Table 5. Fluoride removal by continuous distillation of HNO_3 from 14.1 M HNO_3–0.377 M HF through alumina

Sample	Total distillate volume (L)	$[HNO_3]$ (M)	$[F^-]_{sample}$ (ppm)	DF^a_{feed}
Feed		10.5	717	
10	0.224	10.13	0.36	1921
50	1.12	10.45	0.70	1019
100	2.24	10.36	1.10	643
150	3.36	10.52	2.56	280
200	4.48	10.48	6.01	119
250	5.60	10.58	9.37	77
300	6.72	10.26	13.4	52
350	7.84	10.64	13.6	53
400	8.96	11.10	12.0	63
450	10.08	10.55	17.5	41
500	11.20	10.92	19.1	39
550	12.32	10.80	26.5	28
600	13.44	10.47	35.8	20
650	14.56	10.74	50.7	14
700	15.68	9.34	76.2	8.4
750	16.80	9.93	94.3	7.2
800	17.92	10.75	124	5.9
900	20.16	10.70	173	4.2
1000	22.40	10.04	208	3.3

$$\alpha_{DF_{feed}} = \frac{[F^-]_{feed}[HNO_3]_{sample}}{[F^-]_{sample}[HNO_3]_{feed}} .$$

distillate exceeded 10 ppm. At this point, the fluoride DF had decreased to 72 (98.6% of F^- removed) and 4.08 g fluoride had loaded on the column (34.9 mg F^-/g alumina; 1.84 meq F^-/g alumina). While the nitric acid concentration in the distillate remained nearly constant (~10.5 M), the fluoride concentration continued to increase causing a steady decline in the fluoride DF. After 120 h, 11.4 L (100 bed volumes) of distillate had been collected and the fluoride concentration in the condensate had increased to 20 ppm (DF = 36). The column loading at this point had reached 69.9 mg F^-/g alumina (3.66 meq/g alumina). After 10 d and 23.0 L (204 bed volumes) of solution, the column was still loading fluoride, although the DF had decreased to ~3. A total of 14.2 g of fluoride (121 mg F^-/g alumina; 6.37 meq F^-/g alumina) was loaded onto the column during the experiment.

Zirconia was also tested as a solid adsorbent for fluoride in nitric acid vapors. Zirconia (201 g) was loaded in the same apparatus that had been used for alumina, and the distillation pot was charged with 400 mL of 10.0 M HNO_3–0.0526 M HF (1000 ppm fluoride). The solution was distilled through the column and the condensate collected in 25-mL fractions. The samples were analyzed for total acid and fluoride, and the results are shown in Table 6. The zirconium column was quite effective in trapping HF vapors, although the DFs obtained were not quite as high as for alumina. When the 14 distillate samples were combined, the resulting solution was 8.62 M in nitric acid and contained 0.18 ppm fluoride, for an overall DF of 4800. Comparing individual fractions to the initial solutions, DFs on the order of 10^4 were obtained. However, the surface area of the zirconia was much less than that of the alumina column (2.0 m^2/g vs 0.05 m^2/g), and a zirconia column was almost totally ineffective when a solution containing 10,000 ppm fluoride was distilled through it. While zirconia could be used to remove HF from HF-HNO_3 vapors, alumina is cheaper and more readily available in a form suitable for packing columns with a high specific surface area.

Table 6. Fluoride removal by batch distillation of HNO_3 from 10.0 M HNO_3–0.0526 M HF through zirconia

Sample	Total distillate volume (L)	$[HNO_3]$ (M)	$[F^-]$ (ppm)	DF[a]
Head		10.0	1000	
1	25	1.59	0.51	312
2	50	3.12	0.15	0.21×10^4
3	75	3.82	0.03	1.3×10^4
4	100	4.77	0.04	1.2×10^4
5	125	5.98	0.03	2.0×10^4
6	150	6.98	0.04	1.7×10^4
7	175	8.32	0.29	0.29×10^4
8	200	9.55	0.26	0.37×10^4
9	225	10.61	0.23	0.46×10^4
10	250	11.55	0.28	0.41×10^4
11	275	12.53	0.17	0.74×10^4
12	300	13.27	0.19	0.70×10^4
13	325	14.11	0.14	1.0×10^4
14	350	14.43	0.20	0.72×10^4
Heel		14.93	79.8	

$$\alpha_{DF} = \frac{[F^-]_{head}[HNO_3]_{sample}}{[F^-]_{sample}[HNO_3]_{head}} .$$

3.2.2 Silica gel

The final method investigated for removal of fluoride from nitric acid was simple column chromatography at room temperature and pressure using silica gel as the adsorbent. A solution of 10.46 M HNO_3–0.00558 M HF (106 ppm F^-) was passed through a 3.54-mL bed (27.0 g) of silica gel at the rate of 1.0 mL/min (1.69 bed volumes/h), for a retention time of about 20 min. The effluent was collected in 24.5-mL fractions, and every tenth fraction was analyzed for fluoride. The results of these analyses, summarized in Table 7, were used to construct the breakthrough curve shown in Fig. 3. The first 140 samples (3.43 L or 96.9 bed volumes of effluent) each contained 0.2 ppm fluoride or less. The variation in the fluoride concentrations for these samples, shown in Table 7, is probably due more to analytical uncertainties at these low concentrations than to real changes in the fluoride concentrations. On the average,

Table 7. Removal of fluoride from 10.46 M HNO_3—0.00558 M HF using silica gel

Sample	Eluent volume (L)	Eluent volume (bed volumes)	$[F^-]$ (ppm)	DF [a]
10	0.245	6.92	0.11	964
20	0.490	13.8	0.10	1060
30	0.735	20.8	0.19	558
40	0.980	27.7	0.09	1180
50	1.22	34.5	0.11	964
60	1.47	41.5	0.09	1180
70	1.72	48.6	0.05	2120
80	1.96	55.4	0.09	1180
90	2.20	62.1	0.17	623
100	2.42	68.4	0.20	530
109	2.67	75.4	0.10	1060
120	2.94	83.1	0.18	589
130	3.19	90.1	0.16	662
140	3.43	96.9	0.18	589
150	3.68	104	0.35	303
160	3.92	111	0.46	230
170	4.16	118	0.96	110
180	4.41	125	1.61	66
190	4.66	132	2.54	42
200	4.90	138	4.20	25
210	5.14	145	6.57	16
220	5.39	152	9.63	11
230	5.64	159	13.4	8
240	5.88	166	17.6	6

[a] Composition of head solution = 10.46 M HNO_3, 106 ppm F^-.

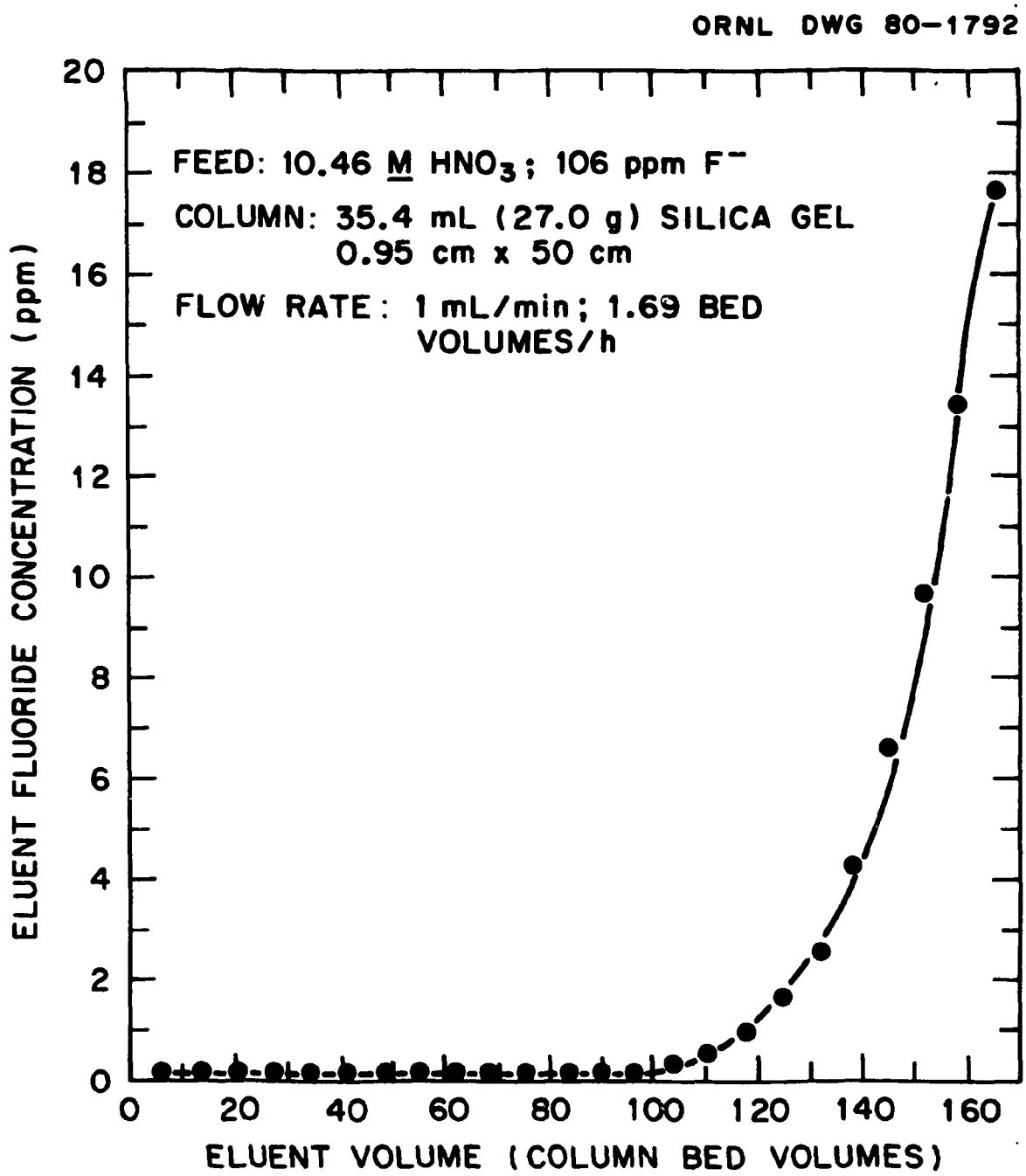

Fig. 3. Breakthrough curve for silica gel column.

these samples contained 0.11 ppm fluoride, for an overall DF of 947 (99.9% fluoride removal). At this point, 363 mg (19.1 meq) of fluoride had loaded on the column (13.4 mg F^-/g silica gel).

Fluoride breakthrough occurred at about 4.16 L (118 bed volumes), where the fluoride concentration approached 1 ppm (DF = 106) and the column was loaded with 440 mg (23.2 meq) of fluoride (16.3 mg F^-/g silica gel). After this point, the efficiency of the column decreased rapidly. The fluoride concentration in the eluent reached 10 ppm after ∿5.4 L (153 bed volumes) of solution had passed through the column (DF = 11). At the end of the experiment, 5.00 L (166 bed volumes) had passed through the column, 620 mg (32.6 meq) of fluoride had loaded (23.0 mg F^-/g silica gel), and the DF had decreased to 6.

From these results, it is clear that untreated silica gel can reduce fluoride concentrations in nitric acid to very low levels. Moreover, the adsorption characteristics of silica gel can often be greatly improved by various physical and chemical modifications of its surface; possibly such modifications could be found to increase the capacity of silica gel for fluoride, but no modified silica gels were examined in this study.

4. CONCLUSIONS

Three methods for removing fluoride from contaminated nitric acid have been described. Each may have advantages over the conventional aluminum nitrate–calcium nitrate chemical trap in some applications. For example, a zirconium nitrate or zirconium oxynitrate chemical trap can be used over a much wider range of nitric acid and fluoride concentrations and can produce higher DFs. Distilling $HF-HNO_3$ mixtures *through* an alumina (or zirconia) column instead of *from* a chemical trap produces even higher DFs, is effective over a wider concentration range, and traps the fluoride in a compact solid, allowing greater ease in handling and disposal than the slurries from chemical trap mixtures. Finally, a silica gel column traps the fluoride in a solid matrix without the use of distillation. When the nitric acid to be purified is concentrated relative to the final concentration needed, it can simply be passed through the column

and diluted for use. If other impurities not removed by the silica gel are present, or if a more concentrated nitric acid solution is required, the eluent can be distilled in conventional glass or stainless steel equipment.

5. REFERENCES

1. D. S. Arnold, A. Whitman, and F. J. Podlipec, "Nitric Acid Recovery from Raffinate by Evaporation and Fractional Distillation," *Chem. Eng. Prog.* 52: 362 (1956).

2. R. L. Moore, *Liquid-Vapor Equilibrium in the System Nitric Acid-Water-Trace Fluoride*, Hanford Atomic Products Operations Report HW-47813 (Jan. 14, 1957).

3. E. R. Johnson and E. O. Rutenkroger, *Fluoride Volatilization During Nitric Acid Recovery from Solvent Extraction Raffinates — Laboratory Investigation*, AEC Research and Development Report NLCO-576 (May 1, 1955).

4. W. D. Dietrich, "Chemical Trap," U.S. Patent 3,846,256 (Nov. 5, 1974).

5. E. G. Laggis, *An Operational Guide to the Y-12 Nitrate Recycle Facility*, Y-12 Plant Report Y-DA-6094, Oak Ridge, Tenn. (1974).