Solubility Relationships of Uranyl Fluoride–Hydrofluoric Acid–Boric Acid

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The solubility relationships of uranyl fluoride, boric acid, and hydrofluoric acid were studied in equilibration tests. Upon increasing the concentration of uranyl fluoride, the solubility of boron decreased. This decrease in solubility was related to the increase in acidity of these solutions. By preacidifying the aqueous solutions of uranyl fluoride with hydrofluoric acid, an appreciable increase in the solubility of boron was obtained. An analytical method is described for analyzing the boron and fluoride in the solutions containing uranyl fluoborate ions after removing the uranium with a cation exchange column. The column effluent is reacted with the calcium chloride which precipitates calcium fluoride and releases equivalent amounts of hydrochloric and boric acids. The released amount of H^+ ion, equivalent to the F^- ion, is titrated with a sodium hydroxide solution to a methyl orange end point. After mannitol was added, the boric acid formed in the reaction was determined by continuing the titration with sodium hydroxide solution to a phenolphthalein end point. The fluoride data showed an absolute limit error of ±0.48% (0.95) for a single determination, and the boron data showed an absolute limit of error of ±0.26% (0.95) for a single determination.

To permit economical operation of a nuclear reactor using uranium as a fissionable material, the uranium is usually recovered by chemical processing involving acid dissolution of the spent nuclear fuel elements. For nuclear safety considerations, the recovery processes and equipment must be designed and operated to prevent criticality conditions from occurring. The boron-10 isotope is generally used for neutron absorption (shielding) because of its large thermal-neutron cross section of 3840 barns (*1*).

As part of an experimental criticality program at the Oak Ridge Y-12 Plant (operated by the Union Carbide Corp.—Nuclear Division for the U.S. Atomic Energy Commission), to evaluate aqueous boric acid solutions as reflector and moderator in such an acid dissolution and recovery process, data were needed regarding the stability and compatibility of the solutions at various conditions of pH and levels of uranium, boron, and total fluoride concentrations. Since this information was not available in the literature, solubility values were obtained in laboratory equilibration tests using normal-assay boric acid and U-235-depleted uranyl fluoride. An ion exchange method was developed for the determination of fluoride and boron in the uranium-hydrofluoboric acid solutions.

EXPERIMENTAL

Equilibration Materials and Procedure. The UO_2F_2 used in this study, prepared by treating uranium trioxide (UO_3) with anhydrous hydrogen fluoride, had an analysis of 75.8% uranium and 12.11% fluoride. Emission spectrographic analyses of the UO_2F_2 crystals showed 40 ppm Si, 10 ppm Fe, 8 ppm Al, and 1 ppm Ni as the major impurities present. Reagent-grade boric anhydride (B_2O_3) or boric acid crystals (H_3BO_3), aqueous hydrofluoric acid (48 wt % HF), and demineralized water were used for the equilibration tests conducted in polyethylene bottles. The bottles were agitated periodically with an excess of solute over a period of 48–72 hr at the test temperatures of 23° and 10°C and filtered in a polyethylene funnel through Whatman No. 42 ashless filter paper before analyzing for desired soluble constituents.

Analytical Procedure for Determining Fluorine and Boron. A suitable sample of uranium–hydrofluoroboric acid was pipeted into a beaker (pipet and beaker were of plastic) and diluted to 100 ml with demineralized water, then passed through a cation resin column (Dowex 50-X8, 50–100 mesh). Constructional details of the resin column are shown in Figure 1.

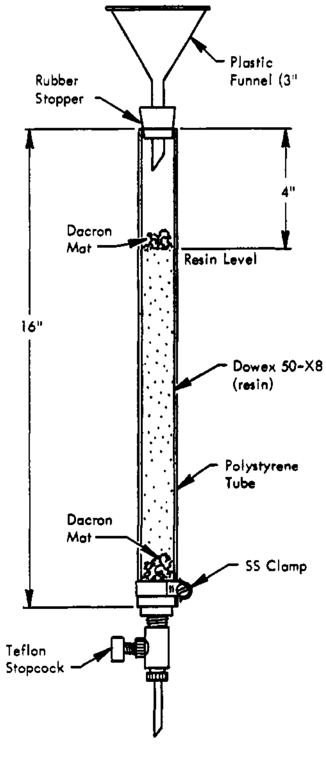

Figure 1. Cation exchange column

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The resin was washed with 300 ml of demineralized water, and the effluent was caught in an 800-ml Teflon beaker. Fifty milliliters of 2*M* calcium chloride were added to the effluent, then the solution was stirred with a Teflon-covered magnetic stirring bar. Three or four drops of methyl orange indicator were added to the solution. The solution was titrated to an end point with standard (0.10*N*) sodium hydroxide solution. This volume was recorded as (V_1). The solution was then transferred to a 1-liter, round-bottom, boiling flask that was connected to a water-cooled condenser. In a heating mantle, the solution was boiled for 1 hr and then cooled to room temperature by means of a water bath. Finally, the solution was transferred to the original beaker and titrated to a methyl orange end point for the second time with the standard (0.10*N*) sodium hydroxide solution. The total volume of sodium hydroxide was recorded as volume (V_2). Mannitol (40 grams) was added to this solution, and the boric acid was determined by continuing the titration with the (0.10*N*) standard sodium hydroxide solution to a phenolphthalein end point. This volume was recorded as (V_3).

Table I. Effect of Uranium Concentration and Temperature on Solubility of Boron in Aqueous Uranyl–Fluoride Solutions

Sample	Equilibration tests Solute[a]	Equilibration tests Temp, °C	pH	Sp gr at 23°C	Concn, g/l. Uranium	Concn, g/l. Fluoride	Concn, g/l. Boron
C-1	H_3BO_3	23	3.86	1.0139	None	None	8.85
C-2	H_3BO_3	23	3.52	1.0859	59.79	9.54	8.64
C-3	H_3BO_3	23	3.31	1.1483	116.64	18.58	8.55
C-4	H_3BO_3	23	3.16	1.2167	177.12	27.89	8.22
C-5	H_3BO_3	23	3.05	1.2852	235.55	37.66	8.13
C-110	H_3BO_3	10	3.75	1.0106[b]	None	None	6.51
C-210	H_3BO_3	10	3.48	1.0810[c]	60.34	9.20	6.17
C-310	H_3BO_3	10	3.25	1.1490[d]	118.48	18.75	5.90
C-410	H_3BO_3	10	3.08	1.2185[e]	178.46	28.65	5.60
B-1	B_2O_3	23	3.85	1.0139	None	None	8.55
B-2	B_2O_3	23	3.50	1.0892	64.95	10.30	8.39
B-3	B_2O_3	23	3.24	1.1631	128.70	20.34	8.32
B-4	B_2O_3	23	3.08	1.2365	192.00	30.55	7.96
B-5	B_2O_3	23	2.96	1.3089	256.20	40.72	7.69

[a] Used 20.0 grams H_3BO_3 or 20.0 grams B_2O_3/200 ml solution for equilibrium tests. [b] Specific gravity at 10°C = 1.0134. [c] Specific gravity at 10°C = 1.0840. [d] Specific gravity at 10°C = 1.1522. [e] Specific gravity at 10°C = 1.2200.

CALCULATIONS

$$\% F = (V_1 + V_2 - \text{blank}) \times \text{NaOH normality} \times \frac{\text{mequiv wt of fluorine}}{\text{wt of sample in grams}}$$

$$\% \text{B} = (V_3 - \text{blank}) \times \text{NaOH normality} \times \frac{\text{mequiv wt of boron}}{\text{wt of sample in grams}}$$

RESULTS AND DISCUSSION

Uranyl Fluoride Solutions. Experimental data on the solubility of boron (added as B_2O_3 and H_3BO_3) in aqueous uranyl fluoride solutions at 23° and 10°C are presented in Table I. For increasing concentrations of uranyl fluoride, it was found that the solubility of boron decreased and that this decrease in solubility was associated with a decrease in pH (i.e., greater acidity) of these solutions.

Preacidification of aqueous uranyl fluoride solutions (250 g U/l.) with hydrofluoric acid produces appreciable increases in the solubility of boron. The effect of hydrofluoric acid on the solubility of boron in aqueous uranyl fluoride solutions at 23°C is summarized in Table II. The variation of pH (from hydrofluoric acid additions) and boron solubility in uranyl fluoride solutions is shown in Figure 2.

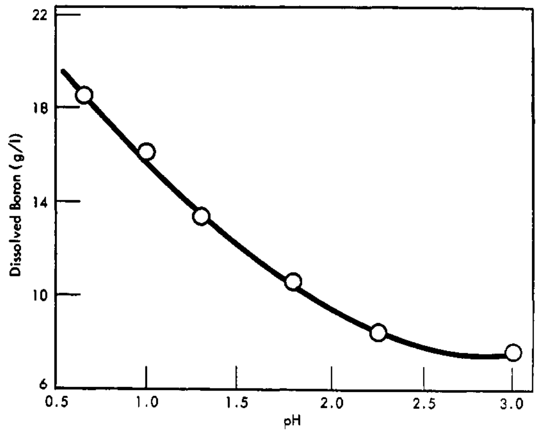

Figure 2. Variations of pH from hydrofluoric acid additions and boron solubility in uranyl fluoride solutions (250 g U/l.)

Boric Acid–Hydrofluoric Acid Solutions. Solubility of uranium added as uranyl fluoride in aqueous solutions of boric and hydrofluoric acids was studied in laboratory equilibration tests at 25°C. Chemical analyses of the initial and final compositions of solutions used for the boric acid–hydrofluoric acid and uranyl fluoride equlibration tests are given in Table III. For solutions of varying acidity over the pH range from 1.2–2.1, Table III shows that the total dissolved fluoride remained fairly constant despite the wide variations observed in the dissolved boron and uranium concentrations. The effect of boric acid pretreatment of hydrofluoric acid solutions on the solubility of uranyl fluoride is shown in Figure 3.

Table II. Effect of Hydrofluoric Acid on Solubility of Boron in Aqueous Uranyl–Fluoride Solutions of 23°C

Sample	UO_2F_2 content,[a] ml	48% HF content, ml	Solute	pH	Sp gr	Concn, g/l Uranium[b]	Concn, g/l Fluoride	Concn, g/l Boron
A-0[c]		None	UO_2F_2	2.50	1.275	243.9[d]	38.53	None
A-1	198.0	2.0	B_2O_3	2.28	...	295.4[e]	50.54	8.54
A-2	195.0	5.0	B_2O_3	1.76	...	285.1	60.57	10.70
A-3	190.0	10.0	B_2O_3	1.31	...	274.0	73.49	13.61
A-4	185.0	15.0	B_2O_3	1.04	...	261.0	88.73	16.26
A-5	180.0	20.0	B_2O_3	0.68	...	259.7	103.93	18.64

[a] As the aqueous solution (244 g U/l.). [b] By potentiometric titration. [c] Solution used to equilibrate samples A-1 through A-5 with B_2O_3. [d] Solution analyzed 245.2 g U/l. by X-ray absorption. [e] Solution analyzed 298.0 g U/l. by X-ray absorption.

Table III. Analyses of Aqueous Boric Acid–Hydrofluoric Acid–Uranyl Fluoride Solutions

	Initial compn			Final compn				
Sample	H_2O, ml	48% HF, ml	H_3BO_3, g[a]	pH	Sp gr	g F/l.	g B/l.	g U/l.
			Boric Acid-Hydrofluoric Acid Equilibration					
D-1	200	None	15	2.09	1.0177	None	8.77	...
D-2	198	2.0	15	1.36	1.0185	4.83	9.57	...
D-3	195	5.0	15	1.27	1.0208	11.48	10.45	...
D-4	190	10.0	15	1.24	1.0351	23.18	12.05	...
D-5	180	15.0	15	1.28	1.0388	34.69	13.72	...
			Uranyl-Fluoride Equilibration					
D-1-UF	D-1 filtrate + UO_2F_2 powder[a]			2.13	2.1184	155.8	5.14	993.7
D-2-UF	D-2 filtrate + UO_2F_2 powder[a]			1.92	2.1178	156.4	5.28	984.6
D-3-UF	D-3 filtrate + UO_2F_2 powder[a]			1.67	2.0848	157.9	6.02	958.9
D-4-UF	D-4 filtrate + UO_2F_2 powder[a]			1.40	2.0430	157.5	8.08	909.7
D-5-UF	D-5 filtrate + UO_2F_2 powder[a]			1.21	1.9871	159.2	10.76	849.7

[a] Added as an excess of powder.

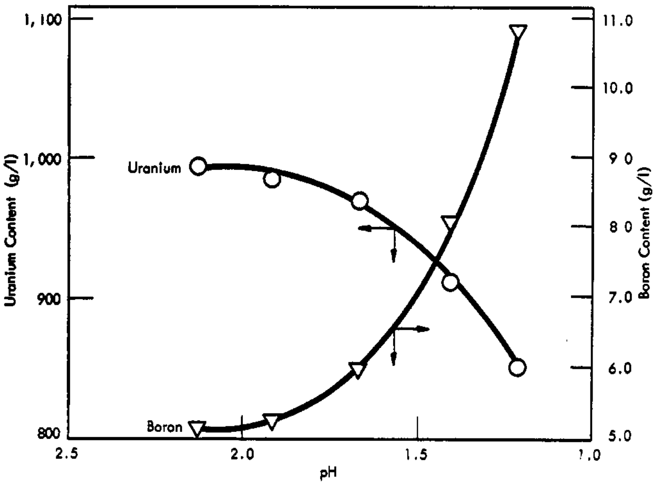

Figure 3. Variation in solubility of uranium and boron with pH in UO_2F_2–H_3BO_3–HF–H_2O solutions

Solubility relationships in the system UO_2F_2–HF–H_2O by Kunin (*2*) had also shown that the solubility of uranyl fluoride decreased very markedly with increasing concentrations of hydrofluoric acid at constant temperature. By preacidifying aqueous solutions of uranyl fluoride with hydrofluoric acid, an appreciable increase in the solubility of boron was obtained (Figure 3). This would be desirable from the standpoint of neutron absorption. Ths increase in boron solubility was greater for those solutions having the highest acidity (free fluoride content) and lowest pH.

Analytical data for dissolved boron in the presence of dissolved uranium and free fluoride, which resulted from the preacidification of the solution with hydrofluoric acid, posed a difficult problem by standard analytical procedures. Consequently, the cation exchange method, described previously, was developed for these solutions. By passing the solution through the resin column, uranium was adsorbed. The effluent from the column containing three acids (H_3BO_3, HF, and HBF_4) was reacted with calcium chloride. Calcium fluoride was precipitated releasing equivalent amounts of hydrochloric and boric acids as shown in the reaction HBF_4 + $2CaCl_2 + 3H_2O \rightarrow 2CaF_2 + H_3BO_3 + 4HCl$. The released amount H^+ ion, equivalent to the F^- ion, was titrated with a standard sodium hydroxide solution (*3*). The precision of this method is shown by 10 determinations made on a synthetic uranyl-hydrofluoboric acid solution as given in Table IV. A statistical evaluation of these accumulated data for fluorine showed an absolute limit of error of ±0.16% (0.95) for the mean and ±0.48% (0.95) for a single determination. The boron data yielded an absolute limit of error of ±0.20% (0.95) for the mean and ±0.26% (0.95) for a single determination.

Table IV. Determination of Fluorine and Boron Contents

Sample	F, %	B, %	Sample no.	F, %	B, %
1	11.33	17.37	6	11.42	17.50
2	11.06	17.41	7	11.47	17.24
3	11.02	17.37	8	11.17	17.31
4	11.34	17.51	9	11.12	17.21
5	11.28	17.35	10	11.16	17.32

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