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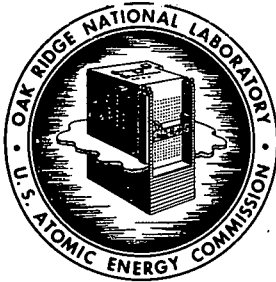
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DATE: August 6, 1959  
SUBJECT: The Use of Boron for Fluoride Complexing  
in Thorex Dissolver Solutions  
TO: F. L. Culler, Jr.  
FROM: F. G. Kitts

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ABSTRACT

Preliminary measurements of the corrosion of titanium were made in 13 M  $\text{HNO}_3$ -0.05 M fluoride using 0.1 M  $\text{H}_3\text{BO}_3$  as a liquid and vapor phase complexing agent. Titanium Ax-55 was attacked at average rates of 0.58 and 0.33 mils/month in the liquid and vapor. In dissolver solutions containing 0.5 and 1.0 M titanium, all rates were less than 0.1 mils/month.

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## 1.0 INTRODUCTION

The dissolution of irradiated power reactor fuels consisting of stainless steel clad  $\text{UO}_2\text{-ThO}_2$  pellets (such as Consolidated Edison) must be accomplished in two steps because there is no reagent which will dissolve both the stainless steel clad and the ceramic core at acceptable rates. The clad is to be removed either by boiling 4-6 M  $\text{H}_2\text{SO}_4$  (Sulfex) or 5 M  $\text{HNO}_3$  - 2 M  $\text{HCl}$  (Darex). The core material is then dissolved in 13 M  $\text{HNO}_3$  - 0.05 M fluoride with a fluoride complexing agent added as a corrosion inhibitor. If Sulfex is used, a thorough washing of the de-clad solution from the core material ( $\text{UO}_2\text{-ThO}_2$  pellets) is necessary to avoid sulfate contamination of the core solution and care must be taken to keep fine particles of core material from being lost with the de-clad and wash solutions. If Darex is used for de-jacketing, cross-contamination is not an important factor, and a greater "loss" of core material in the de-cladding solution can be tolerated since it can be recovered by conventional solvent extraction from the nitrate system.

With Sulfex, both clad and core dissolutions can be carried out in the same vessel made of Ni-o-nel. The Darex de-cladding requires containment in titanium, which does not possess satisfactory resistance to uncomplexed fluoride. Since it is desirable to carry out both dissolutions in a single vessel to avoid pellet transfer, a complexing agent for fluoride was desired which would allow the Thorex core dissolution to proceed in titanium equipment with tolerable corrosion rates. Aluminum was evaluated as a complexing agent<sup>1</sup> and although it did afford considerable protection, corrosion rates remained higher than desirable. Boron (added as  $\text{H}_3\text{BO}_3$ ) was tested in the hope that it would afford a higher degree of protection, especially in the vapor phase, than did aluminum. Corrosion rates, solution compositions, and dissolution rates were determined.

## 2.0 EQUIPMENT AND PROCEDURE

The boiling flasks used were spherical, pyrex flasks of 1 liter capacity equipped with pyrex reflux condensers operating updraft. In all three flasks the two liquid phase specimens (0.79-in. x 0.50-in. x 0.0905-in. weighing ~2.4 g) rested on the bottom of each flask while the duplicate vapor phase specimens were suspended on titanium wire.

The specimens were positioned in the flasks and the measurement of the exposure period began when boiling started. When dissolutions were made, the specimens were not inserted until the dissolution had been completed. At the end of each aging period the specimens were removed from the hot solution, washed, boiled in ~3 M  $\text{NaOH}$ , washed, dried and weighed. Solutions were not changed during the rather brief exposure period.

## 3.0 CORROSION RESULTS

The average corrosion rates of titanium A55 in boiling 13 M  $\text{HNO}_3$  - 0.05 M fluoride containing 0.1 M  $\text{H}_3\text{BO}_3$  (initial solution) were 0.58 and 0.33 mils/mo in the liquid and vapor phases, respectively, for an exposure

<sup>1</sup> Under subcontract to BMI.

period of 253 hours. Although the rates were somewhat erratic in the three periods comprising the 253 hour total, (see Table 1) the highest rate observed was less than 1.4 mil/mo, occurring in the liquid phase. No pitting or intergranular corrosion could be detected visually. Attack in the middle and final solutions (initial solution with  $UO_2 - ThO_2$  pellets dissolved to 0.5 M and 1.0 M Th, respectively) was less than 0.1 mil/mo in both liquid and vapor over a 229 hour exposure. Four of the eight specimens showed a weight gain for the 229 hour period.

#### 4.0 EFFECT OF REFLUXING ON SOLUTION COMPOSITION

As refluxing was continued, the  $HNO_3$  and boric acid concentrations of all three solutions remained essentially constant while the fluoride concentrations dropped sharply at first and then continued a gradual decline (see Figure 1)\*. The slight increase in boron was probably caused by a slight reduction in volume produced by the loss of water vapor through the updraft condenser. The reduction in fluoride concentration might be attributed to the gradual loss of volatile HF or to the reaction of fluoride with the exposed glass walls in the vapor phase. At the end of the tests samples of condensate from the middle and final solutions contained 8 ppm boron and 36 ppm fluoride, and 7 ppm boron and 38 ppm fluoride, respectively. A solid appeared only in the initial solution; the white precipitate was checked qualitatively by X-ray diffraction with  $TiO_2$  being the only recognizable pattern. The solid contained only 0.89% boron.

#### 5.0 DISSOLUTION OF $UO_2-ThO_2$ PELLETS

The middle and final solutions were prepared by dissolving sintered  $UO_2-ThO_2$  pellets in 200 cc portions of refluxing initial solution in 1 liter flasks. To prepare middle solution 27 g of  $UO_2-ThO_2$  (11 pellets 0.264-in. dia) were completely dissolved in 6-1/2 hours; for final solution 54 g (17 pellets) were dissolved in 8 hours. The resulting solutions contained 112.2 g Th, 5.28 g U/liter and 11.4 M  $HNO_3$ , and 225.9 g Th, 10.47 g U/liter and 9.3 M  $HNO_3$ , respectively. Average pseudo reaction rates of 2.54 and 2.2 mg/sq cm-min were calculated from the expression:

$$R = \frac{W}{A_0 T}$$

where:

- R = reaction rate (mg/sq cm-min)
- W = weight of pellets (mg)
- $A_0$  = original area of pellets (sq cm)
- T = time for total dissolution (min)

These rates are obviously conservative since the original area was used while the actual area approached zero as dissolution neared completion. Dissolution rates for the boron complexed solutions were no slower than those for Thorex solutions containing 0.1 M aluminum.

\*A single curve would have adequately represented the boron and fluoride data for all three solutions but separate lines were drawn to show the reproducibility of the trend regardless of Th concentrations.

Table 1. Weight Loss Data for Boron Complexed 13 M HNO<sub>3</sub> - 0.05 M Fluoride

Specimens: 0.090 in. thick Ti Ax-55

Solutions: Initial: 13 M HNO<sub>3</sub> - 0.05 M fluoride - 0.10 M boron

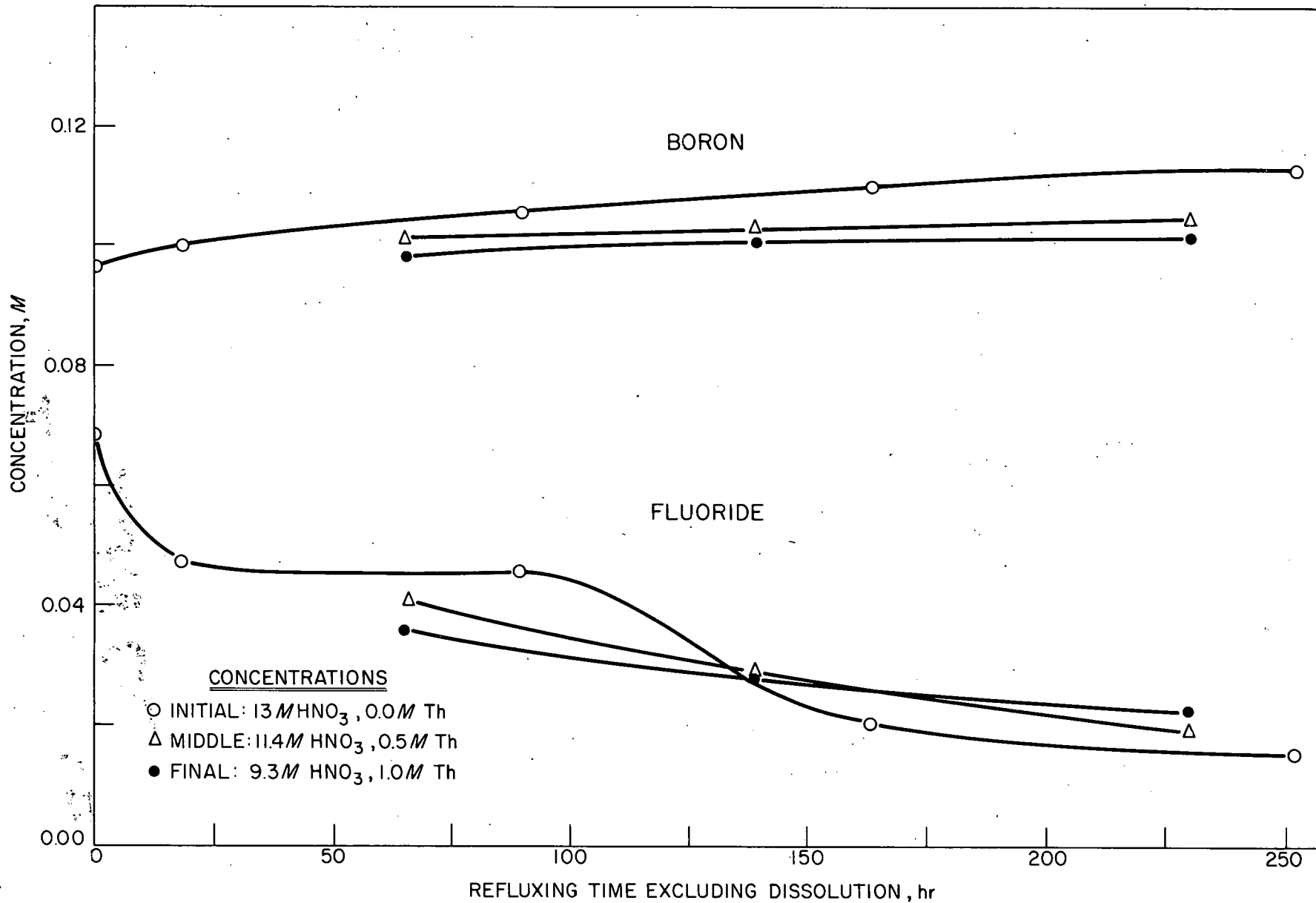
Middle: Initial solution with UO<sub>2</sub> - ThO<sub>2</sub> pellets dissolved to 0.5 M Th

Final: Initial solution with UO<sub>2</sub> - ThO<sub>2</sub> pellets dissolved to 1.0 M Th

Periods of Exposure

Sam- ple No.	Area (sq in)	Solution	Location	Orig. wt (g)	Wt (g)	Corrosion Rate mils/mo	Wt (g)	Corrosion Rate mils/mo	Wt (g)	Corrosion Rate mils/mo	Average Rate mils/mo
				(0-89 1/4 Hours)			(89 1/4 to 163 1/4 Hours)			(163 1/4 to 253 1/2 Hours)	
T-2	1.073	Initial	Liquid	2.5580	2.5546	0.35	2.5544	0.025	2.5427	1.18	0.55
T-5	1.023	Initial	Liquid	2.4370	2.4336	0.36	2.4340	g*	2.4209	1.38	0.60
T-7	1.025	Initial	Vapor	2.4186	2.4193	g	2.4116	0.99	2.4105	0.12	0.30
T-8	1.014	Initial	Vapor	2.4571	2.4567	0.04	2.4499	0.88	2.4476	0.25	0.36
				(0-65 Hours)			(65-139 Hours)			(139-229-1/4 Hrs)	
T-9	1.014	Middle	Liquid	2.4270	2.4276	g	2.4277	g	2.4274	0.032	g
T-11	1.014	Middle	Liquid	2.4269	2.4269	0.00	2.4269	0.00	2.4266	0.032	0.013
T-12	1.022	Middle	Vapor	2.4391	2.4381	0.15	2.4383	g	2.4377	0.063	0.058
T-13	1.031	Middle	Vapor	2.4766	2.4758	0.12	2.4760	g	2.4759	0.010	0.029
T-14	1.030	Final	Liquid	2.4539	2.4549	g	2.4548	0.013	2.4552	g	g
T-16	1.022	Final	Liquid	2.4598	2.4596	0.03	2.4595	0.013	2.4594	0.011	0.017
T-17	1.027	Final	Vapor	2.3714	2.3725	g	2.3723	0.026	2.3723	0.00	g
T-18	1.014	Final	Vapor	2.4145	2.4153	g	2.4154	g	2.4153	0.011	g

\* g denotes weight gain



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Fig. 1. Effect of refluxing time on reagent concentration.

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