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SAVANNAH RIVER LABORATORY
TECHNICAL PROGRESS REPORT

CONVERTER FUEL CYCLE TECHNOLOGY

JULY - SEPTEMBER 1978 (u)

Publication Date: January 1979

APPLIED TECHNOLOGY

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SAVANNAH RIVER LABORATORY
AIKEN, SOUTH CAROLINA 29801

PREPARED FOR THE U.S. DEPARTMENT OF ENERGY UNDER CONTRACT AT(07-2)-1

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E. I. DU PONT DE NEMOURS AND COMPANY
SAVANNAH RIVER LABORATORY
AIKEN, SOUTH CAROLINA 29801

PREPARED FOR THE U. S. DEPARTMENT OF ENERGY UNDER CONTRACT AT(07-2)-1

ABSTRACT

This quarterly report describes applied technology studies directed towards closing the back end of the commercial light water reactor (LWR) fuel cycle, particularly the appropriate disposition of spent fuel elements. Progress is reported in the following major tasks: Studies and Analyses, Fuel Reprocessing, and General Support.

FOREWORD

This quarterly report describes Savannah River Laboratory (SRL) research and development efforts directed toward the development of technology needed to design and estimate the cost of a basic spent fuel disposition facility. These efforts have been structured into a single overall program, the Converter Fuel Cycle Technology (CFCT) program, to optimize disposition of spent fuel from light water reactors (LWR's).

The CFCT program is directed primarily at reprocessing and recycling uranium and plutonium by processes that reduce the risk of nuclear weapons proliferation. Processing steps include head-end treatment of spent fuel, dissolution of fuel, recovery and purification of uranium and plutonium by a solvent extraction process, and treatment of off-gases from various parts of the processing system. The CFCT program includes the earlier LWR fuel recycle program. A preliminary design integration study of a spent fuel reprocessing complex for a U/Pu cycle based on existing technology is expected to be completed in early FY-1979. A second design integration study based on a U/Pu coprocessing flowsheet and using improved technology will be completed in late FY-1979.

The CFCT program will also assess methods for away-from-reactor interim storage of spent light water reactor fuel and will provide a conceptual design of an away-from-reactor spent fuel storage basin. This item was formerly called the International Spent Fuel Storage (ISFS) program. SRL studies will compare the suitability and/or costs of alternatives for storing spent LWR fuel. A draft of the generic environmental statement for the impact of government acceptance of spent nuclear fuel for this item is expected to be completed in the fourth quarter of FY-1978.

The fuel recycle research and development program includes the following tasks:

- Program Management (Task 000)
- Studies and Analyses (Task 100)
- Fuel Handling (Task 200)
- Fuel Reprocessing (Task 300)
- Conversion Processes (Task 400)
- In-Plant Waste Treatment (Task 600)

- General Support - which includes Environmental Effects, Safeguards Criteria, Analytical Methods, and Materials Corrosion - (Task 800)
- Major Facilities (Task 900)

The previous reports in this series are the following:

Document Number	**Period**
DPST-LWR-76-1-1	January-March 1976
DPST-LWR-76-1-2	April-June 1976
DPST-LWR-76-1-3	July-September 1976
DPST-LWR-76-1-4	October-December 1976
DPST-LWR-77-1-1	January-March 1977
DPST-AFCT-77-1-2	April-June 1977
DPST-AFCT-77-1-3	July-September 1977
DP-CFCT-77-1-4	October-December 1977
DP-CFCT-78-1-1	January-March 1978
DP-CFCT-78-1-2	April-June 1978

SRL is also coordinating fuel recycle studies at other sites sponsored by the Department of Energy (DOE). These research and development activities are being summarized quarterly by SRL in a separate report (DP-CFCT-year-2-quarter).

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The preliminary reference fuel cycle for the Thorium Fuel Cycle Technologies Program was modified. (page 7)

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Coprocessing Uranium and Plutonium

Miniature mixer-settler tests at SRL indicated that a modified version of a coprocessing flowsheet developed by General Electric may be feasible. (page 8)

Dissolution of Spent Thorium Oxide Fuel

A process description and technical data summary for dissolving spent thorium oxide fuel was prepared. (page 12)

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Corrosion of High Nickel-Chromium Alloys

Ten high nickel-chromium alloys being evaluated as construction materials for the ThO_2/UO_2 fuel dissolver exhibited corrosion rates ranging from satisfactory to unacceptable within the range of HF concentrations expected in the process. (page 15)

X-ray Diffraction Analysis of Voloxidized LWR Fuels

X-ray diffractometry of 26 samples of voloxidized Robinson, Saxton, and Oconee LWR fuels from seven tests at SRL showed that UO_2 was completely converted to U_3O_8 in all but one test. (page 26)

Determination of Uranium in Fuel Reprocessing Solutions

A method was developed for highly precise and accurate determination of uranium in process solutions. (page 31)

STUDIES AND ANALYSES (TASK 100)

TFCT REFERENCE FUEL CYCLE AND PROGRAM PLAN

The preliminary reference fuel cycle for the Thorium Fuel Cycle Technologies Program was modified as follows:

1) A fabrication technique using vibratory compaction of sol-gel microspheres will be considered as a parallel development rather than as a backup. The preliminary fuel cycle assumed that the fuel would be in the form of pressed pellets.

2) Processing of thorium-based fuels irradiated to 50,000 MWD/MT will be considered. Originally, the maximum reactor-averaged thorium fuel exposure was assumed to be 33,000 MWD/MT; but in the intervening years, until thorium fuel is commercialized, uranium fuel exposures may be extended to 50,000 MWD/MT.

3) About 15 years is estimated to be the minimum time required to implement a modest number of thorium reactor loadings on a commercial basis, and an additional 5 to 10 years will be required to convert power reactors nearly completely to thorium-based fuel.

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1. **Savannah River Laboratory Quarterly Report, Alternate Fuel Cycle Technology, July-September 1977.** USERDA Report DPST-AFCT-77-1-3, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, S. C. (1978).

COPROCESSING URANIUM AND PLUTONIUM

Miniature mixer-settler tests at SRL indicated that a modified version of a coprocessing flowsheet developed by General Electric may be feasible. Four tests of the initial GE flowsheet showed plutonium reflux due to high concentrations of acid in part of the mixer-settler. However, a single test of the modified version showed lower plutonium reflux and good correlation between calculated and experimental U/Pu ratios.

Initial GE Coprocessing Flowsheet

Figure 1 shows the basic flowsheet* developed by GE as part of a subcontract to evaluate coprocessing of uranium and plutonium. The organic stream containing uranium and plutonium (1AP) from the 1A contactor is fed to the B contactor at the stage where the aqueous plutonium-containing stream (1BP) leaves the contactor. To ensure that uranium is present in the aqueous phase, the aqueous strip stream (1BX) contains uranium recycled from the uranium product stream (1CU or 1EU) along with a reductant (hydroxylamine nitrate) for plutonium. A small stream of nitric acid (1BA) is added to the center of the contactor to adjust the nitrate concentration in order to control the concentration of uranium in the plutonium. Calculations at GE showed that the Pu/U ratio goes through a maximum as the uranium concentration in the 1BX is increased (Figure 2).

Tests of Initial Flowsheet at SRL

The initial flowsheet used 0.95M uranium in the 1BX and enough nitric acid from the side stream to yield 3M to 4M HNO_3 in the 1BP. Four tests were run with conditions close to the calculated conditions (Table 1). In the first test, no reductant was added to the 1BX. In the other three tests, 0.02M hydroxylamine nitrate was added to the 1BX. The 1BX flow was varied to simulate the effect of changing the uranium concentration in the 1BX. The 1BA flow was varied to maintain constant acidity in the 1BP.

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* This flowsheet would precede the Coprecal process for coprecipitation and calcination of product from solvent extraction. See the **Savannah River Laboratory Converter Fuel Cycle Technology Technical Progress Report, October-December 1977.** USDOE Report DP-CFCT-77-1-4, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, S. C. (1978).

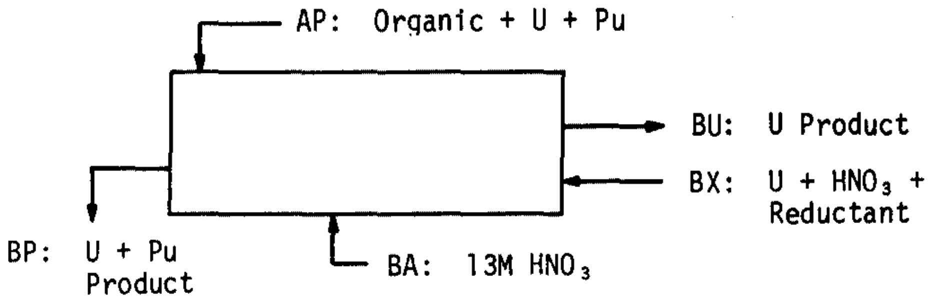

FIGURE 1. General Electric Flowsheet for Coprocessing Uranium and Plutonium

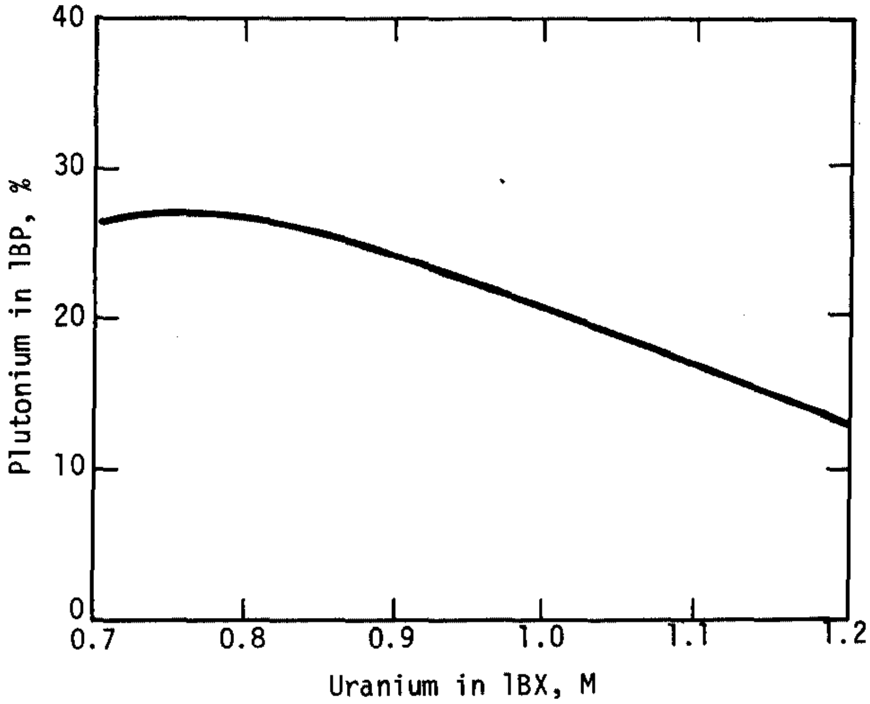

FIGURE 2. Effect of Recycle Uranium Concentration on Plutonium Concentration in Product

In all four tests, plutonium refluxed and uranium concentrations in the 1BP were high. The plutonium refluxed because concentrations of hydroxylamine nitrate were too low and acidities were too high for rapid reduction of Pu^{4+}. Uranium concentrations in the 1BP were too high because high concentrations of uranium in the feed caused excessive uranium concentrations in all stages.

TABLE 1

Calculated and Experimental Conditions for Miniature Mixer-Settler Tests of General Electric's Initial Coprocessing Flowsheet

	Calculated Conditions		Experimental Conditions for First Four Tests	
Stream	Relative Flow[a]	Composition	Relative Flow[a]	Composition
1AP	372	0.322M U 0.00297M Pu 0.077M HNO_3	372	0.344M U 0.0025M Pu 0.056M HNO_3
1BX	80	0.95M U 0.3M HNO_3 Reductant	64 to 96	0.93M U 0.30M HNO_3 0.02M $NH_2OH \cdot HNO_3$[b]
1BA	20	13M HNO_3	16 to 24	13M HNO_3
1BP	93.1	0.0413M U 0.0119M Pu 3.3M HNO_3	74.5 to 112	0.0554 to 0.315M U 0.0015 to 0.0083M Pu 3.14 to 3.35M HNO_3
1BU	391	0.491M U 2.4×10^{-6}M Pu 0.005M HNO_3	381	0.420 to 0.433M U 8.7×10^{-6} to 8.3×10^{-5}M Pu 0.014 to 0.018M HNO_3

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a. Feed = 100.

b. Not used for first test.

Test of Revised Flowsheet

Additional calculations were made at GE to investigate the effect of lower acid concentrations. The computer program was expanded to include the kinetics of plutonium reduction by hydroxylamine nitrate and to determine the minimum effective concentration of hydroxylamine nitrate for the revised flowsheet. The revised flowsheet was tested at SRL as part of a test with irradiated Point Beach reactor fuel. Table 2 shows the calculated and experimental conditions. The results are encouraging. Although the absolute concentrations do not match the predicted concentrations, the calculated percent of plutonium in the 1BP was 11.8% of the total heavy metal and the experimental value was 11.6%. If the concentrations of uranium and plutonium in the feed had been as high as those assumed for the calculations, agreement between predicted and experimental concentrations of uranium and plutonium in the 1BP would have been better.

TABLE 2

Calculated and Experimental Conditions for Miniature Mixer-Settler Tests of General Electric's Revised Coprocessing Flowsheet

	Calculated Conditions		Experimental Conditions for Fifth Test	
Stream	Relative Flow[a]	Composition	Relative Flow[a]	Composition
1AP	372	0.336M U 0.003M Pu 0.14M HNO_3	372	0.304M U 0.00209M Pu 0.11M HNO_3
1BX	65	0.3M U 0.3M HNO_3 0.2M $NH_2OH \cdot HNO_3$	65	0.3M U 0.3M HNO_3 0.2M $NH_2OH \cdot HNO_3$
1BA	3	13M HNO_3	3	13M HNO_3
1BP	69.2	0.120M U 0.016M Pu 1.51M HNO_3	68	0.0782M U 0.0102M Pu 1.47M HNO_3
1BU	370.4	0.359M U 3.6 x 10^{-6}M Pu 0.016M HNO_3	370	0.333M U 8.6 x 10^{-7}M Pu 0.011M HNO_3

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a. Feed = 100.

Continuing Study

Further tests will be made to verify the calculations and to establish the effect of changing uranium concentration in the 1BX on the U/Pu ratio in the 1BP.

DISSOLUTION OF SPENT THORIUM OXIDE FUEL

A process description and technical data summary for dissolving spent thorium oxide fuel was prepared. This process is part of the flowsheet developed for conceptual design and cost studies of a 10-MT/day LWR fuel reprocessing plant.[1] In the flowsheet, spent fuel is sheared into short pieces, separated from the Zircaloy cladding hulls, ground to a small particle size, and heated to remove tritium. The cladding hulls are leached with dissolvent, rinsed with water to remove thorium, passivated with caustic, and transferred to waste treatment for disposal.

The conceptual dissolution process is shown in Figure 3. The dissolvent selected is 12.5M HNO_3-0.05M HF-0.025M $Zr(NO_3)_4$. The ground fuel powder is dissolved semicontinuously in the same solution used previously for leaching the cladding hulls. The dissolver solution is evaporated, steam-stripped, and denitrated with formic acid to reduce the nitric acid concentration of raw metal solution before solvent extraction. Off-gases from the dissolution are treated until they can be safely released.

Selection of a Dissolvent

12.5M HNO_3 was selected as the principal dissolving agent. However, thorium oxide dissolves very slowly in boiling nitric acid, and dissolution is not complete unless the dissolvent contains a small concentration of fluoride. The fluoride acts as a catalyst to significantly increase the rate of dissolution. But nitric acid-fluoride mixture is very corrosive to process equipment and would also dissolve Zircaloy cladding hulls unless a complexing agent for fluoride is present. In previous studies, aluminum nitrate was added to nitric acid-fluoride mixtures as a complexing agent. Zirconium, however, is a much stronger complexing agent for fluoride than aluminum, and was selected because dissolution of the Zircaloy cladding hulls is much less than when aluminum nitrate is used.

Less dissolution of the Zircaloy is desirable because the hulls contain about 40% of the total tritium. This tritium would be released during leaching and would end up in the liquid waste where containment would be very difficult. The addition of 0.5 mole Zr(IV) per mole of fluoride in the dissolvent should greatly reduce the corrosion of the Zircaloy hulls without overly retarding the dissolution of the fuel. The use of zirconium instead of aluminum as a complexing agent for fluoride also

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1. **Savannah River Laboratory Converter Fuel Cycle Technology Technical Progress Report, January-March 1978.** USDOE Report DP-CFCT-78-1-1, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, S. C. (1978).

reduces the solids content of high activity waste by 1076 kg/day. This reduces significantly the amount of waste to be solidified. Thus, the dissolvent selected is 12.5M HNO_3-0.05M HF-0.025M $Zr(NO_3)_4$.

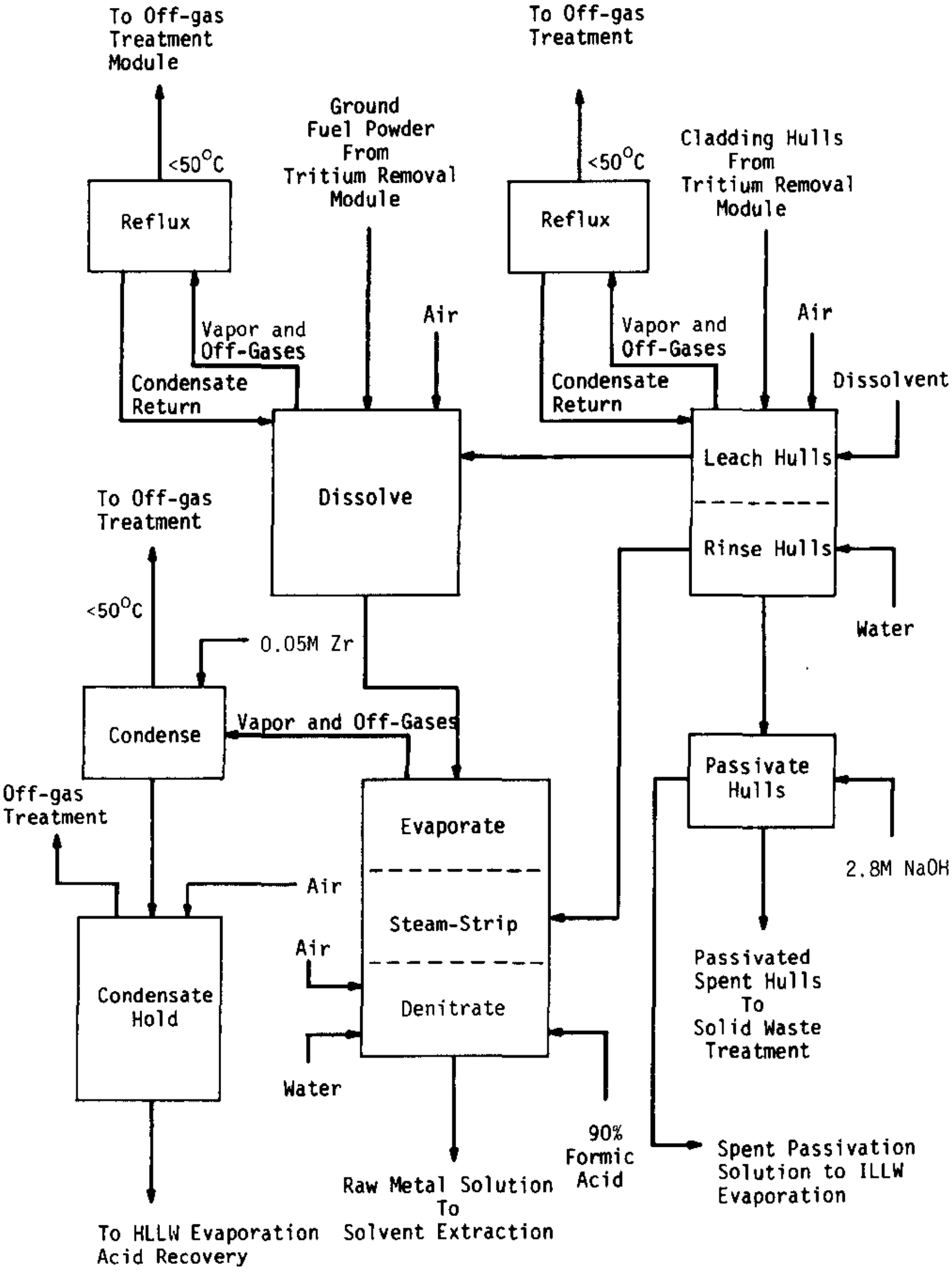

FIGURE 3. Dissolution Process for Thoria

Reuse of Leach and Rinse Solutions

The cladding hulls are leached and rinsed batchwise with fresh dissolvent and rinse water used for each batch of hulls to ensure maximum removal of thorium, uranium, and plutonium from the cladding hulls. The leach and rinse solutions are stored in hold tanks for later use in dissolution of the powdered fuel and then in steam-stripping excess nitric acid from the raw metal solution. This reuse eliminates the need for evaporation of the large volumes of these solutions, which are too dilute in thorium, uranium, and plutonium for economical processing.

Semicontinuous Dissolution

Semicontinuous dissolution of the powdered fuel is recommended. Finely powdered fuel is added slowly into the dissolver solution, with sufficient agitation to suspend the small particles, to provide maximum homogeneity at the minimum concentration of fissile material for criticality control. Sufficient soluble neutron poison is added to the dissolvent to prevent criticality even if the agitation should fail and all of the powdered fuel were allowed to settle to the bottom of an infinitely large vessel.

Radioiodine Removal

The dissolver raw metal solution retains about 85% of the total iodine after air sparging to remove other fission product gases. This iodine, present as iodate because of the high nitric acid concentration, is readily removed by air sparging after denitration with formic acid. The iodate is reduced to iodine by the NO and NO_2 generated during denitration.

Fluoride Volatility

The overall fluoride volatilization to the off-gas was calculated to be 1.5% for 6-hour air sparge times. The volatility of fluoride from boiling solutions increases with nitric acid concentration but is significantly lower when small amounts of complexing agents are present. Although fluoride volatility is reduced by Al(III), Th(IV), Fe(III), and Cr(III), Zr(IV) is the strongest and most efficient complexing agent.

The calculations assumed that equal volumes of air and vapor are equivalent and neglected the effect of Th(IV). The actual fluoride volatilization is probably considerably less because some fluoride is complexed by the Th(IV) present.

CORROSION OF HIGH NICKEL-CHROMIUM ALLOYS

Ten high nickel-chromium alloys being evaluated as construction materials for the ThO_2/UO_2 fuel dissolver exhibited corrosion rates ranging from satisfactory (Inconel® 671, Huntington Alloys, Inc.) to unacceptable (Hastelloy® C-276, Cabot Corporation) within the range of HF concentrations expected in the process. In isothermal corrosion tests with 10M HNO_3-0.01M HF at 95°C, all of the high nickel-chromium alloys, except Hastelloy® C-276, showed adequate corrosion rates (<50 mils/yr) for process equipment. At 0.1M HF, only one alloy (Inconel® 671) had a rate <50 mils/yr under test conditions. At higher temperatures or increased concentrations of either acid, even this alloy would probably not be satisfactory, and F^- would have to be complexed to reduce corrosion rates. Welded specimens corroded about 10% faster than wrought specimens, but intergranular attack in the weld area was not generally observed. However, weld metal attack of Hastelloy® G eliminated it as a potential alloy. These tests generally verified the ranking of the alloys by electrochemical measurements.[1]

Of the common ions, the most effective complexing ions are Zr^{4+} followed in order by Th^{4+} and Al^{3+}. Complex ion stability constants indicate that under comparable conditions, the ratios of free fluoride in solution should be about 1/10/1000 for $Zr^{4+}/Th^{4+}/Al^{3+}$. However, corrosion rates varied by only 1/1/2.5 for $Zr^{4+}/Th^{4+}/Al^{3+}$. The same nine alloys were found to have satisfactory corrosion rates in simulated ThO_2/UO_2 dissolver solution (12M HNO_3-0.05M HF-0.025M Zr^{4+}) at 95°C.

Corrosion Behavior in HNO_3-HF Solutions

The dissolver for ThO_2/UO_2 fuel is expected to contain HNO_3-HF solutions with complexing agents added to minimize corrosion (page 11). However, some of the process equipment, such as the off-gas system, can be exposed to uncomplexed HNO_3-HF. Therefore the corrosion rates of alloys were measured in pure HNO_3-HF

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1. **Savannah River Laboratory Converter Fuel Cycle Technology Technical Progress Report, April-June 1978.** USDOE Report DP-CFCT-78-1-2, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, S. C. (1978).

solutions. These data also serve as a baseline to evaluate the relative effect of complexing agents in controlling corrosion attack.

Corrosion rates of the high nickel-chromium test alloys* were measured in 10M HNO_3 containing either 0.01M or 0.1M HF. The soutions were maintained at a constant 95°C. Coupons (1 x 2 x 1/8 in.) were exposed for 120 hours during which the solution was changed three times. The ratio of liquid volume to sample surface was 30 mL per cm^2. Weight losses ranged from 0.06 to 6.6 g per sample. Corrosion rates are summarized in Table 3.

These data indicate that the F^- must be complexed to reduce corrosion rates when its concentration exceeds about 0.01M. Alloys with corrosion rates <50 mils/yr are considered adequate for the test conditions. Only one alloy, Inconel® 671, meets this criterion in 10M HNO_3-0.1M HF.

Data from Battelle Columbus Laboratories[2] for the alloys in boiling 5M HNO_3-0.1M HF show the same order of corrosion rates as in Table 3 except that Inconel® 690 and 671 are reversed. Battelle obtained corrosion rates of 29 mils/yr for Inconel® 690 and 32 mils/yr for Inconel® 671 after 144 hours in test.

The surface appearance of two alloys representing extremes in corrosion resistance are compared in Figure 4. Hastelloy® C-276 had a very high penetration rate because attack was intergranular and grain dropping occurred. Note the very rough surface of Hastelloy® C-276 compared to that of Inconel® 690.

Instantaneous corrosion rates, measured electrochemically,[3] generally ranked the alloys in the same order as indicated in Table 3. The three best alloys were Inconel® 671, Inconel® 690, and Incoloy® 825; the three poorest were Haynes® 20, Type 304L stainless steel, and Hastelloy® C-276. However, the initial instan-

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* For compositions of these alloys, see **Savannah River Laboratory Converter Fuel Cycle Technology Technical Progress Report, October-December 1977.** USDOE Report DP-CFCT-77-1-4, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, S. C. (1978).

2. J. A. Beavers, et al. **Corrosion Study of Materials for Use in the Thorium Fuel Cycle Technology Nitric Acid System.** USDOE Report BMI-1998, Battelle-Columbus Laboratory, Columbus, Ohio (1978).

3. **Savannah River Laboratory Converter Fuel Cycle Technology Technical Progress Report, January-March 1978.** USDOE Report DP-CFCT-78-1-1, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, S. C. (1978).

taneous corrosion rates were higher than the average corrosion rates in 10M HNO_3-0.01M HF and 1/4 to 1/2 as high in 10M HNO_3-0.1M HF. These differences are believed to reflect changes in average rates over the test period.

Effect of Corrosion on Weld Zones

Nickel-chromium alloys often exhibit intergranular corrosion in the heat-affected zone of welds in aggressive solutions; welded corrosion samples typically have corrosion rates higher than wrought samples because weld metal or weld heat-affected zones are generally attacked more rapidly. To check for weld zone effects, corrosion rates of butt-welded samples of all of the alloys were measured in uncomplexed solutions. The test procedures were similar to those for base metal. Samples were 1 in. x 3 in. x 1/8 in. with a 1-in.-long transverse weld. Corrosion was sometimes accelerated slightly in the heat-affected zone or in the weld metal (Table 3).

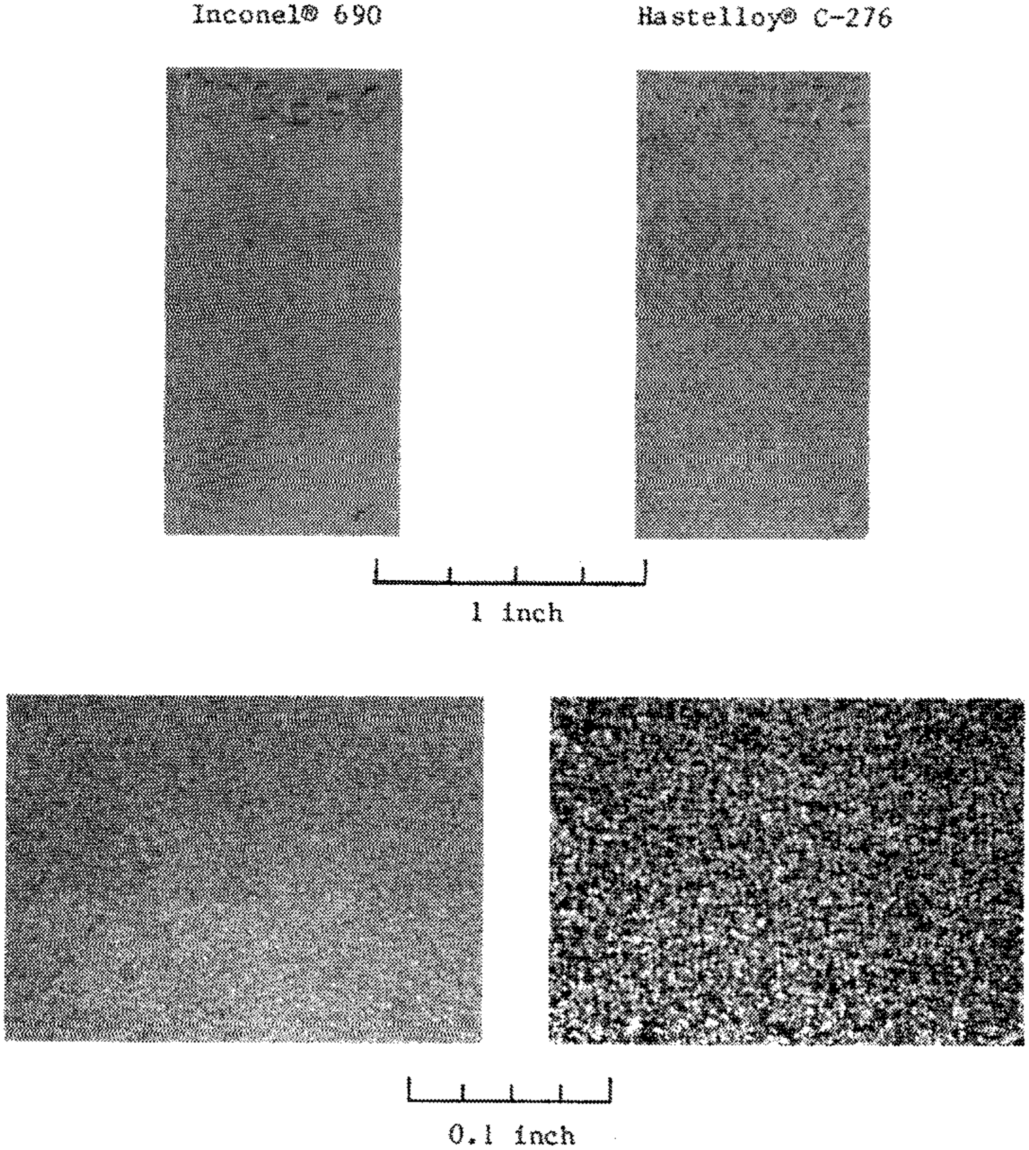
The data show that the corrosion rate for welded alloys is about 10% higher than that for wrought alloys under equivalent conditions. In tests without complexing agents, only Inconel® 671 has an acceptable penetration rate; at higher temperatures, even this alloy would likely be inadequate.

Typical weld zone attack is illustrated for two of the samples in Figure 5. Exposure was for 6 days to 95°C at 10M HNO_3-0.1M HF. Under these same conditions, attack on wrought metal was uniform. Inconel® 690 showed slight intergranular attack along the heat-affected zone and some weld metal attack. The worst preferential attack was for Hastelloy® G, where weld metal was pitted to a depth of about 7 mils, and intergranular attack in the heat-affected zone was 3 to 4 mils deep.

TABLE 3

Isothermal Corrosion Rates at 95°C

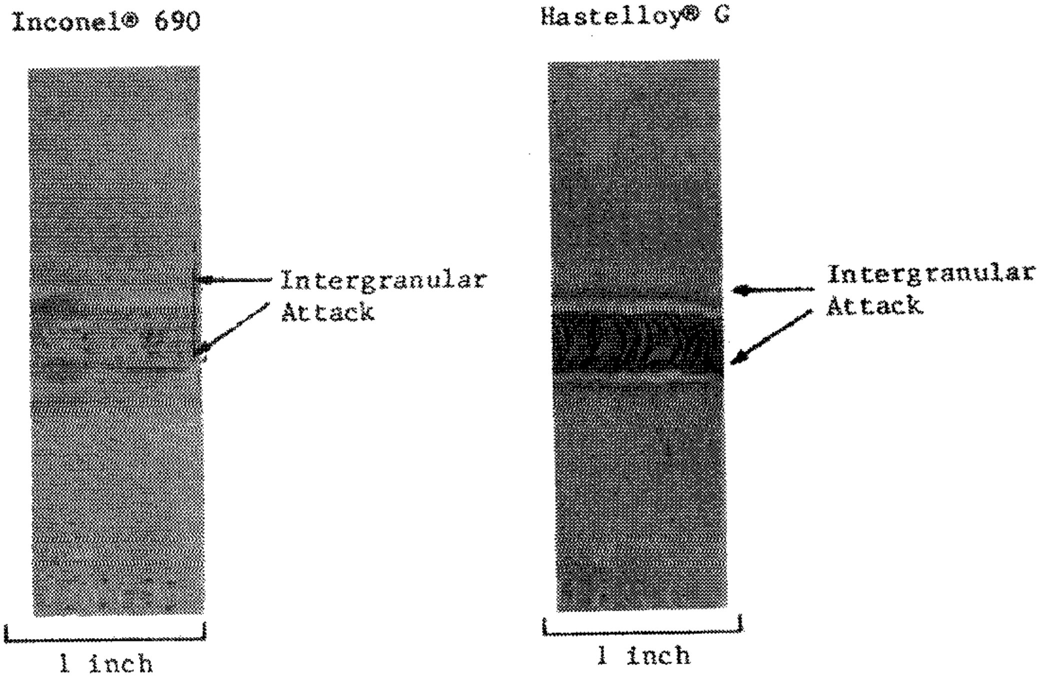
	Penetration Rate, mils/yr			
	Base Metal		Welded Samples	
Alloy	10M HNO_3-0.01M HF	10M HNO_3-0.1M HF	10M HNO_3-0.1M HF	12M HNO_3-0.05M HF
Inconel® 671	8	41	45	31
Inconel® 690	9	63	68	53
Haynes® 25 (Cabot Corporation)	19	92	86	63
Hastelloy® G	18	138	220	140
Inconel® 625	18	147	170	120
Ferralium® (Cabot Corporation)	19	157	140	96
Incoloy® 825 (Huntington Alloys, Inc.)	28	206	230	140
Haynes® 20	46	239	250	200
Type 304L Stainless Steel	21	248	190	100
Hastelloy® C-276	134	841	760	530



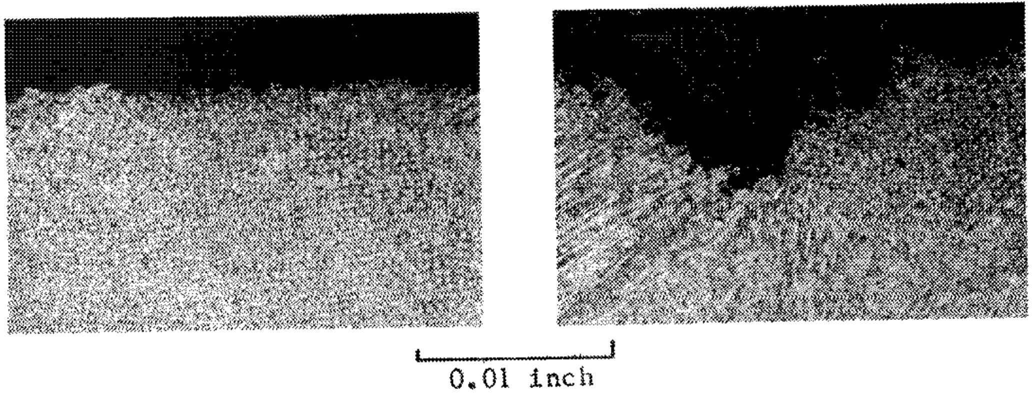
Inconel® 690

Hastelloy® C-276

FIGURE 4. Typical Surface Attack of High Ni-Cr Alloys by 10M HNO_3-0.1M HF at 95°C



Weld Metal Attack



Intergranular Attack

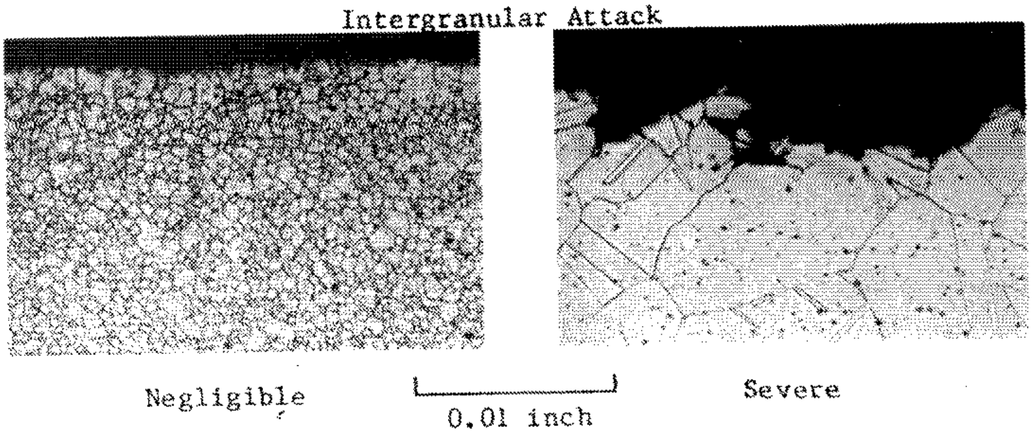


FIGURE 5. Extremes of Weld Area Attack

Effect of Complexing Agents

One method of predicting the relative effectiveness of ions in reducing corrosion is to compare stability constants of the ion-fluoride complexes. A larger constant indicates that a given ion is more effective in reducing corrosion. Selected data are shown in Table 4.

Constants in Table 4 range from about 10^3 for HF to 10^{10} for Zr^{4+}. However, this does not mean that corrosion will be reduced, for example, by a factor of 10^7 in a Zr^{4+}-complexed solution compared to an H^+-complexed solution at the same concentration. The stability constants are calculated specifically for the binary solutions extrapolated to zero ionic strength. In actual corroding systems, many other ions are present that alter the chemical equilibria significantly. However, the constants are a measure of the strength of the respective complexes and are expected to indicate the order of effectiveness of the complexing ions.

To evaluate the effects of complexing agents, the corrosion rates of duplicate samples of the same test alloys were measured first in solutions with no complexing agent, then in solutions with increasing concentrations of complexing agent. Except for Hastelloy® C-276, the corrosion rates were rapidly reduced to acceptable rates (<50 mils/yr).

Table 4

Stability Constants[a] of Fluoride Complexes

Complexing Ion	Log Stability Constant[b]
H^+	3.1
Al^{3+}	7.0
Th^{4+}	8.6
Zr^{4+}	9.8

---

a. Stability Constant = $\frac{[\text{complex}]}{[F^-]\,[\text{complexing ion}]}$

b. At zero ionic strength and 25°C.

Figures 6-8 show the effects of the complexing ions in 10M HNO_3-0.1M HF solutions at 95°C. The reduction in corrosion rate is nonlinear with concentration and slightly different for each alloy. For example, to achieve a corrosion rate of 20 mils/yr for Type 304L, the effectiveness is in the ratio of 1/1/2 for Zr^{4+}/Th^{4+}/Al^{3+}; for Inconel® 671, it is 1/1/4. Generally, the ratio of complexing ions required to get the same corrosion rate is about 1/1/2.5.

In the processing of UO_2/PuO_2 fuels (AFCT program), Zr^{4+} and Al^{3+} were evaluated as complexing agents to reduce corrosion of Type 304L by F^- with similar results. In this process, infrequent HF addition in 3 to 7M HNO_3 may be needed to dissolve accumulated insolubles. Addition of Zr^{4+} at the same concentration as F^- reduced attack on Type 304L to 1 mil/yr; with Al^{3+} at four times the F^-, attack was 10 mils/yr at 95°C.

Complexing agents will be required for dissolution of ThO_2 (TFCT program), HNO_3 recovery, and waste storage. Th^{4+} can be used in the dissolver as a complexing agent, but it will be removed from the solution during extraction and would not follow the F^- into HNO_3 recovery and waste storage. Therefore, Zr^{4+} or Al^{3+} will have to be added even though they increase waste volume.

Corrosion rates of the test alloys were also measured at 95°C in the proposed dissolver solution, 12M HNO_3-0.05M HF-0.025M Zr^{4+}. These data, summarized in Table 5, confirm that except for Hastelloy® C-276, all the alloys have acceptably low penetration rates.

To date, the data show that many of the Ni-Cr, Ni-Cr-Fe, or Co-Cr alloys would be suitable for the ThO_2/UO_2 dissolver if complexing agents were used. Of the ten test alloys, Hastelloy® C-276 is eliminated because of its high corrosion rate and Hastelloy® G because of preferential attack at welds. In addition to the eight alloys that were successfully tested, Inconel® 601 and 617, Hastelloy® X, Haynes® 188, and Types 309 and 310 stainless steels may also be adequate.

Based on corrosion resistance alone, Inconel® 671 would probably be selected as the material for the dissolver and off-gas system; its cost is about $8/lb. If selection is based on corrosion resistance plus cost, probably Inconel® 690 at $6/lb might also be adequate if enough complexing agent is always present and no process upsets occur. If process upsets result with insufficient complexing agent, enough Fe^{3+} and $Cr_2O_7^{2-}$ could be formed to accelerate preferential attack of equipment downstream.

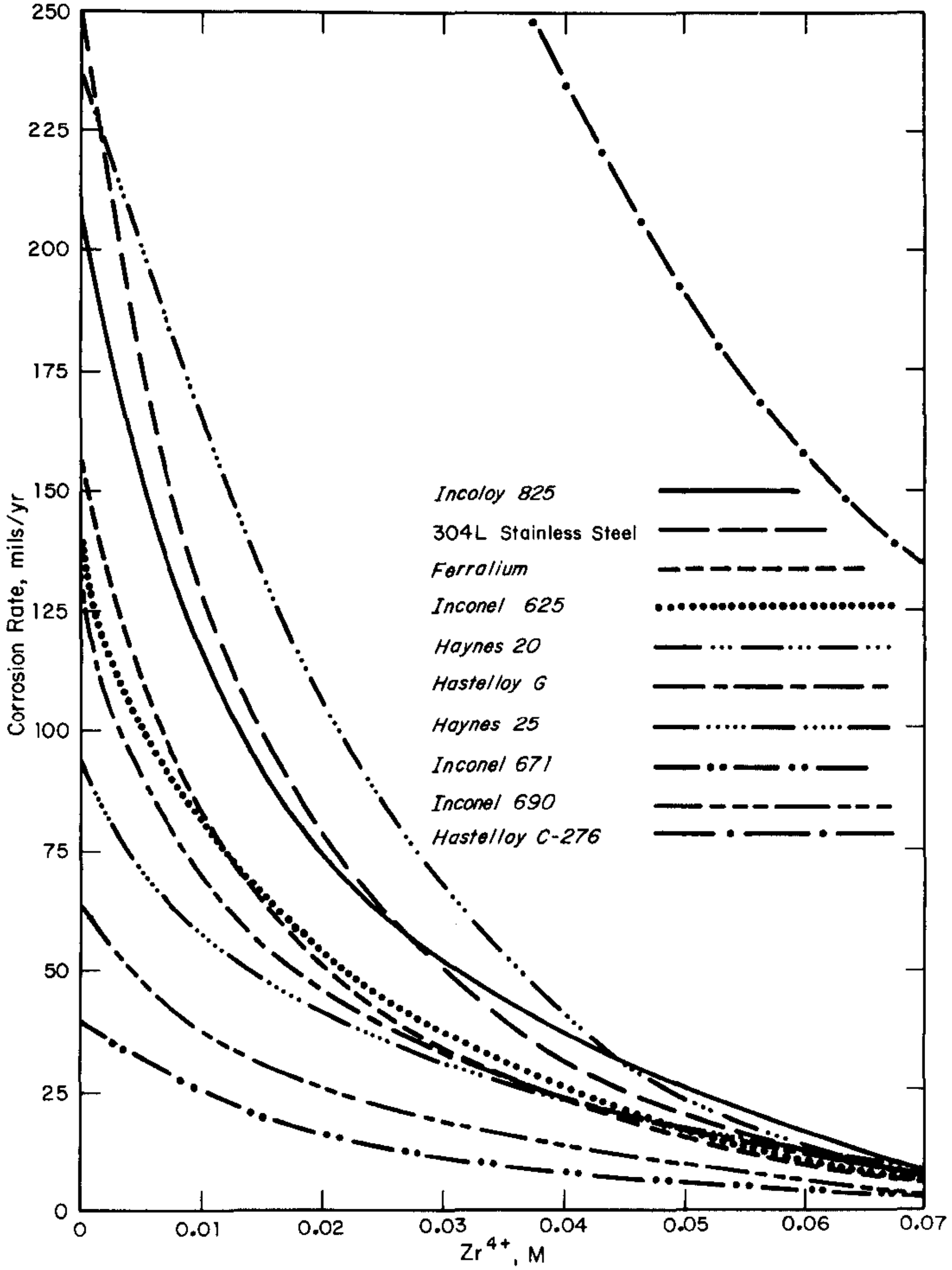


FIGURE 6. Corrosion of High Ni-Cr Alloys in
$10M\ HNO_3-0.1M\ HF - Zr^{4+}$ at 95°C

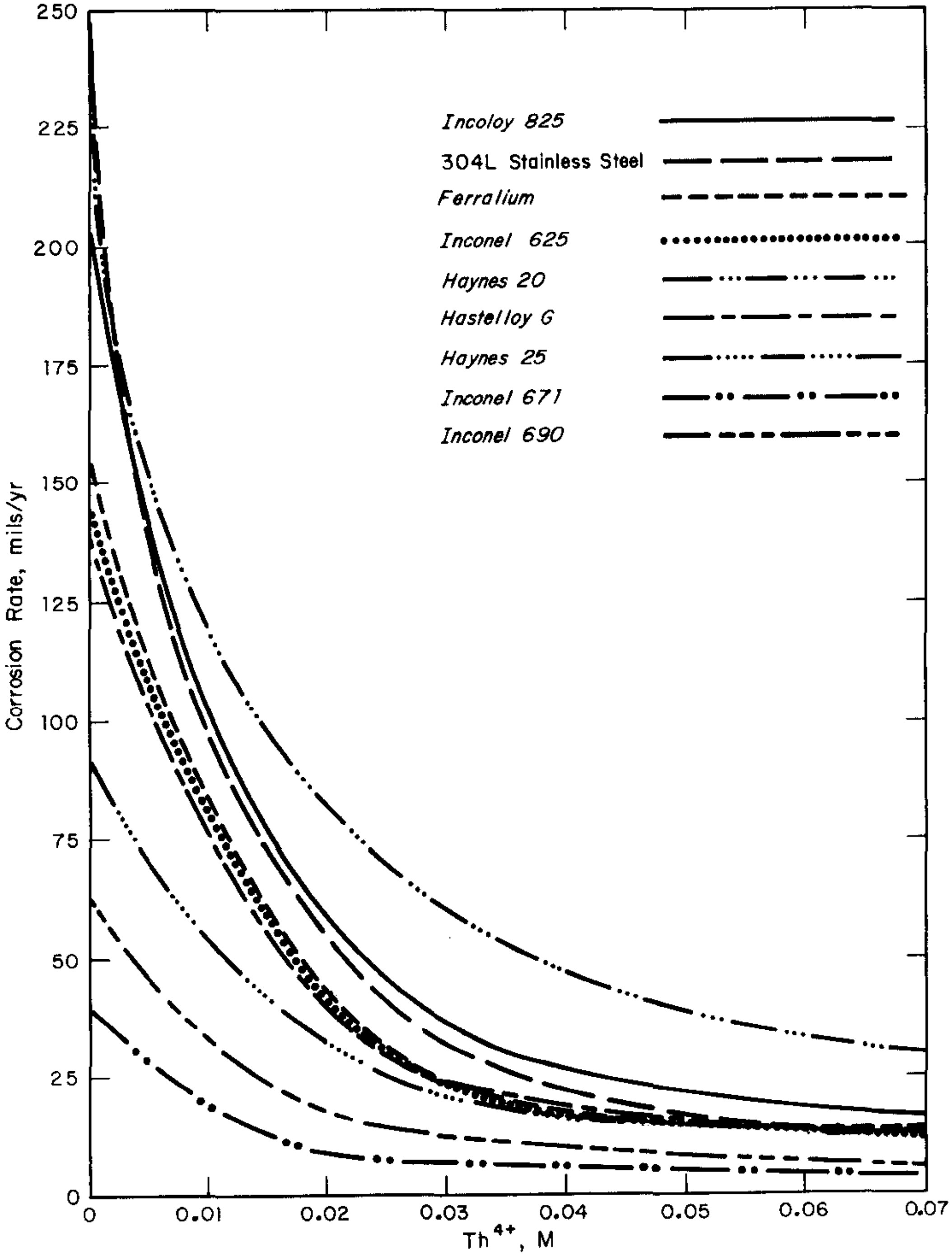


FIGURE 7. Corrosion of High Ni-Cr Alloys in 10 M HNO_3-0.1M HF + Th^{4+} at 95°C

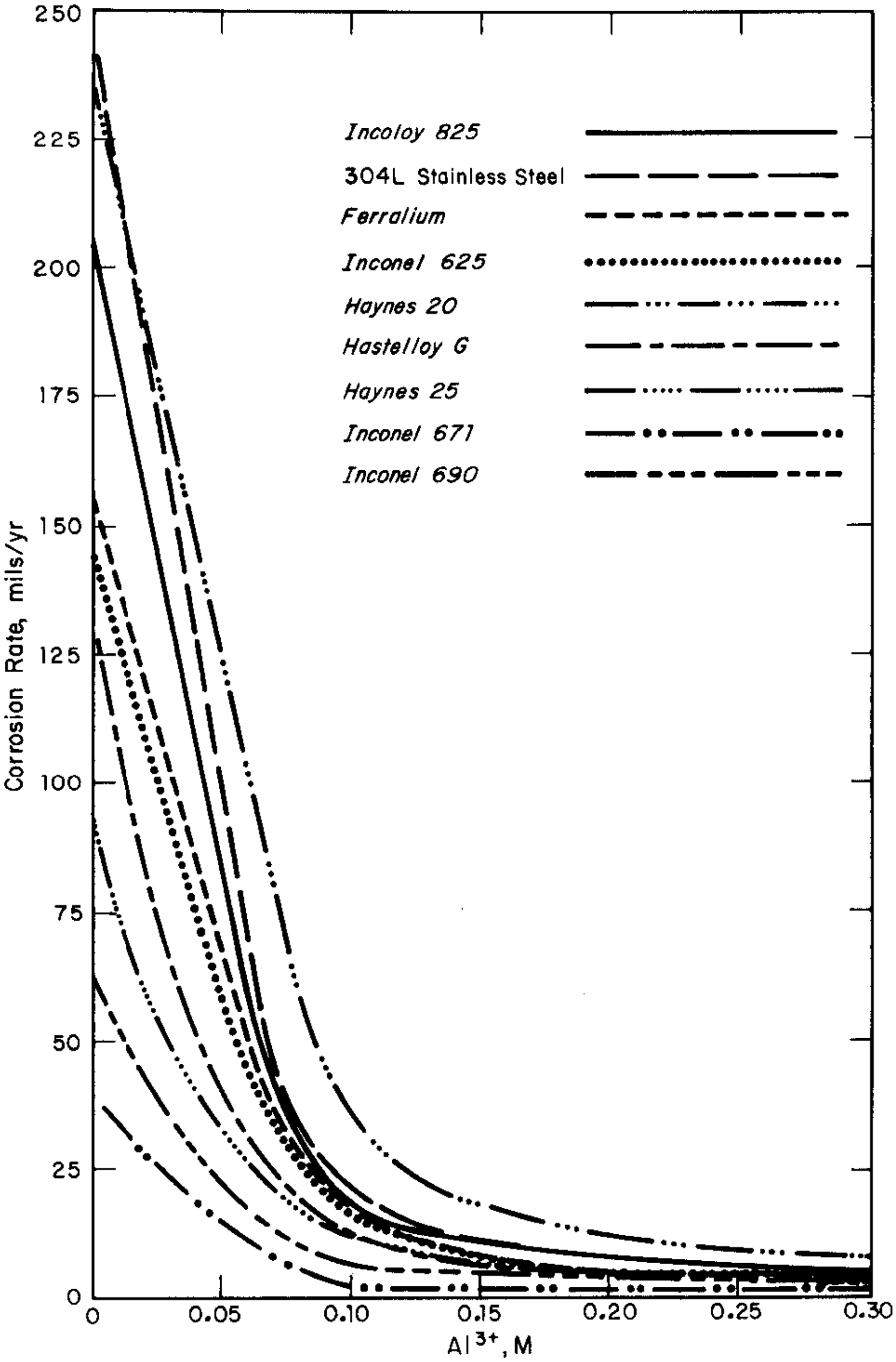


FIGURE 8. Corrosion of High Ni-Cr Alloys in 10M HNO_3 - 0.1M HF + Al^{3+} at 75°C

TABLE 5

Corrosion Rates at 95°C in Proposed ThO_2/UO_2 Dissolver Solution[a]

Alloy	Penetration Rate, mils/yr
Inconel® 671	2
Inconel® 690	4
Haynes® 25	10
Hastelloy® G	10
Ferralium®	11
Inconel® 625	12
Type 304L	13
Incoloy® 825	15
Haynes® 20	19
Hastelloy® C-276	190

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a. 12M HNO_3-0.05M HF-0.025M Zr^{4+}.

Continuing Study

Tests will continue on welded specimens. Attack by solutions containing complexing agents will be measured at about 130°C, the temperature anticipated for heat transfer surfaces in the dissolver. Because chemical reaction rates generally increase rapidly with increased temperature, more complexing agents may be needed than at 95°C. A Teflon®-lined (E. I. du Pont de Nemours and Co., Inc.) autoclave will be used for the tests at 130°C.

X-RAY DIFFRACTION ANALYSIS OF VOLOXIDIZED LWR FUELS

X-ray diffractometry of 26 samples of voloxidized Robinson, Saxton, and Oconee LWR fuels from seven tests at SRL[1] showed that UO_2 was completely converted to U_3O_8 in all but one test. The product from Test 4 with Oconee fuel[2] contained U_4O_9, which is structurally similar to UO_2. Plutonium and fission products introduced into these fuels during irradiation caused changes in the a and b lattice parameters of the orthorhombic $-U_3O_8$ voloxidation product. For the Robinson fuel, with an exposure of 28,000 MWD/MTU, the lattice parameter changes were sufficient to produce a transformation to hexagonal $\alpha'-U_3O_8$.[3]

Experimental Methods

Twenty-six samples from seven voloxidation tests with irradiated fuels were analyzed by x-ray diffractometry. Each sample consisted of about 50 mg of material sieved to a given particle size range. Radiation levels of 22 samples were too high for handling in the contained x-ray diffraction facilities at SRL. These samples were therefore analyzed at the ORNL High Level Radiation Examination Laboratory, and the data were sent to SRL for interpretation.

At ORNL, the particles were mixed with a dilute glue and dispersed in a depression in an epoxy sample holder. When dry, individual samples were remotely loaded into an adjacent shielded x-ray diffractometer, which has a horizontal design that allows the sample to remain stationary while the x-ray tube and detector are positioned to maintain the Bragg diffraction condition. ORNL data were recorded at 1°/min and 0.1°/min with a copper x-ray tube operated at 40 kV and 18 mA.

Figure 9a shows a portion of an ORNL diffraction record for a standard mixture of 50% UO_2 - 50% $-U_3O_8$. Figure 9b is SRL data for the same mixture recorded with a high intensity copper x-ray tube operating at 50 kV and 40 mA. The signal-to-noise ratio for the SRL data is about forty times higher than for the

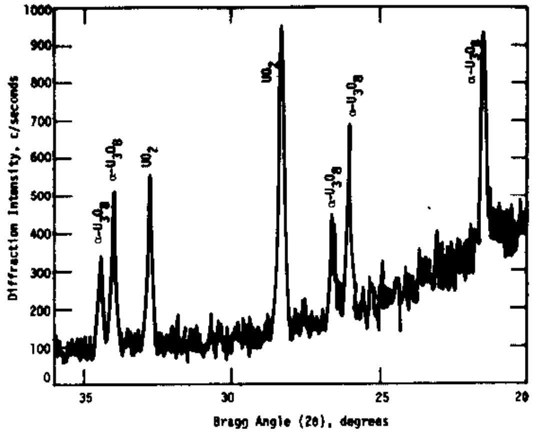
---

1. **Savannah River Laboratory Converter Fuel Cycle Technology Technical Progress Report, April-June 1978.** USDOE Report DP-CFCT-78-1-2, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, S. C. (1978).

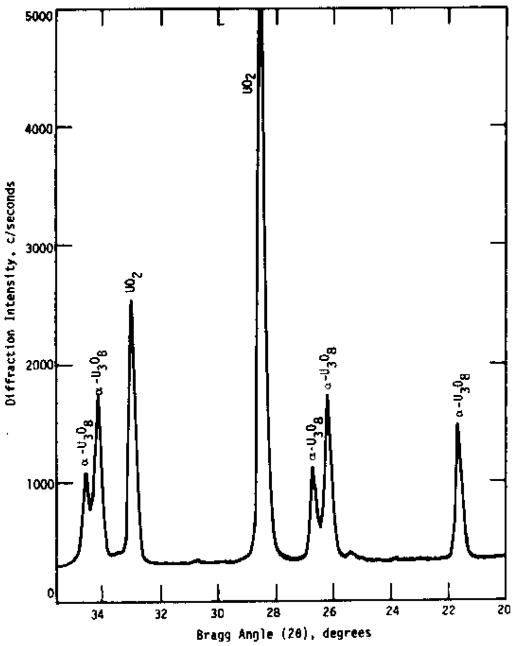
2. **Savannah River Laboratory Converter Fuel Cycle Technology Technical Progress Report, October-December 1977.** USDOE Report DP-CFCT-77-1-4, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, S. C. (1978).

3. **Savannah River Laboratory Quarterly Report, Light Water Reactor Fuel Cycle, July-September 1976.** USERDA Report DPST-LWR-76-1-3, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, S. C. (1976).

a. 50% UO_2 - 50% U_3O_8 (ORNL)



b. 50% UO_2 - 50% U_3O_8 (SRL)



c. Oconee Run 4 (ORNL)

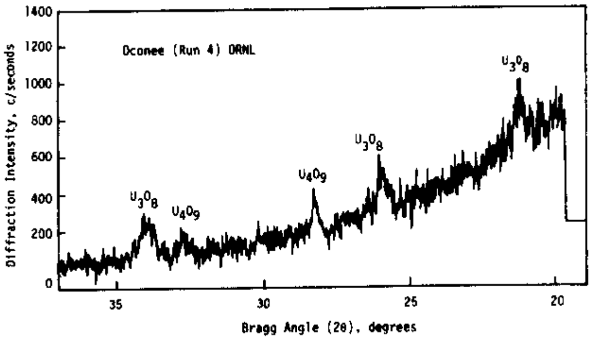


FIGURE 9. X-Ray Diffration Analysis

ORNL data. The ORNL diffractometer had slightly better resolution than the SRL unit. The ratio of intensities of UO_2 peaks to α-U_3O_8 peaks in ORNL data was slightly less than for SRL data, probably because of slight inhomogeneity in the powder mixing. Figure 9 shows ORNL data for the 44- to 75-μm fraction from voloxidation Test 4 with Oconee fuel.

Phases Observed

Analyses are summarized in Table 6. Diffraction records were best with the fine (<44μm) fractions. Two samples of the 150 m fractions contained insufficient material for analysis. U_3O_8, the expected voloxidation product, was identified in all the other samples. The orthorhombic U_3O_8 (002) peak was used as an internal standard for measurement of interplanar spacings because its d-value (2.073 A) is relatively insensitive to compositional changes. Also, for irradiated fuels the broadening of the (001) and (002) peaks was less than for other peaks.

Samples from Test 4 all contained an fcc phase with a = 5.44 A. Both U_4O_9 and UO_2 have fcc structure. This value corresponds to U_4O_9 (a = 5.443 A) rather than UO_2 (a = 5.468 A). The voloxidation process did not oxidize the sample enough to cause the necessary complete structural change. The smaller size fractions contained less U_4O_9, which showed that pulverization is an indication of the completeness of voloxidation.

Traces of α-$UO_2(OH)_2$ were detected in products from Test 1 with Robinson fuel, Tests 5 and 6 with Saxton fuel, and the test with unirradiated fuel. This U^{6+} phase indicates that oxidation proceeded further than expected. Such oxidation is not expected to affect head-end processing.

Effect of Exposure on Structure

The lattice constants of the U_3O_8 phase in the voloxidation products varied with exposure as shown in Figure 10. The structure of the Robinson fuel was similar to that of hexagonal α-U_3O_8 (b/a = 1.732), which is stable above 300°C. However, the unit cell volume did not change with exposure. These structural changes are attributed to plutonium and fission products introduced into the UO_2 fuel during irradiation. Table 7 gives the estimated conversion of ^{235}U and ^{238}U for the reported exposures.

TABLE 6

X-ray Diffraction Analyses of Voloxidized Fuels

					Orthorhombic Lattice Constants			
Test	Reactor	Exposure, MWD/MTU	Particle Size, μm	Phases Detected[a]	a, Å	b, Å	c, Å	b/a
1	Robinson	28,000	<44	B,C	6.81	11.81	(4.15)	1.73
			>44	B,C,E	-	11.81	4.15	-
2	Saxton	3000 to 6000	<44	A	6.74	11.94	(4.15)	1.77
			44 to 75	A	6.74	11.90	(4.15)	1.78
			>150	A	6.74	11.94	(4.15)	1.77
3	Saxton	3000 to 6000	<44	A	-	11.96	(4.15)	-
			44 to 75	A	6.76	11.95	(4.15)	1.77
			>150	A	6.76	11.93	(4.15)	1.77
4	Oconee	10,000	<44	D(5%),A	-	11.88	(4.15)	-
			44 to 75	D(20%),A	-	-	(4.15)	-
			75 to 150	D(40%),A	-	-	(4.15)	-
			>150	Insufficient Sample		-		
5	Saxton	3000 to 6000	<44	A,C	6.74	11.94	(4.15)	1.77
			44 to 75	A,C	6.74	11.94	(4.15)	1.77
			>150	A,C	6.74	11.94	(4.15)	1.77
6	Saxton	3000 to 6000	<44	A,C	6.74	11.93	(4.15)	1.77
			44 to 75	A,C	6.74	11.93	(4.15)	1.77
			>150	A,C	-	11.94	(4.15)	-
7	Oconee	12,000	<44	A	6.75	11.88	(4.15)	1.76
			44 to 75	A	6.74	11.87	(4.15)	1.76
			75 to 150	A	Weak Lines			-
			>150	Insufficient Sample				
Unirradiated		0	<44	A,C	6.724	11.958	(4.146)	1.778
			44 to 75	A,C	6.720	11.958	(4.146)	1.779
			75 to 150	A,C	6.728	11.958	(4.146)	1.777
			>150	A,C	6.730	11.970	(4.146)	1.777

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a. A = αU_3O_8

B = $\alpha' U_3O_8$

C = $UO_2(OH)_2$

D = U_4O_9

E = Al

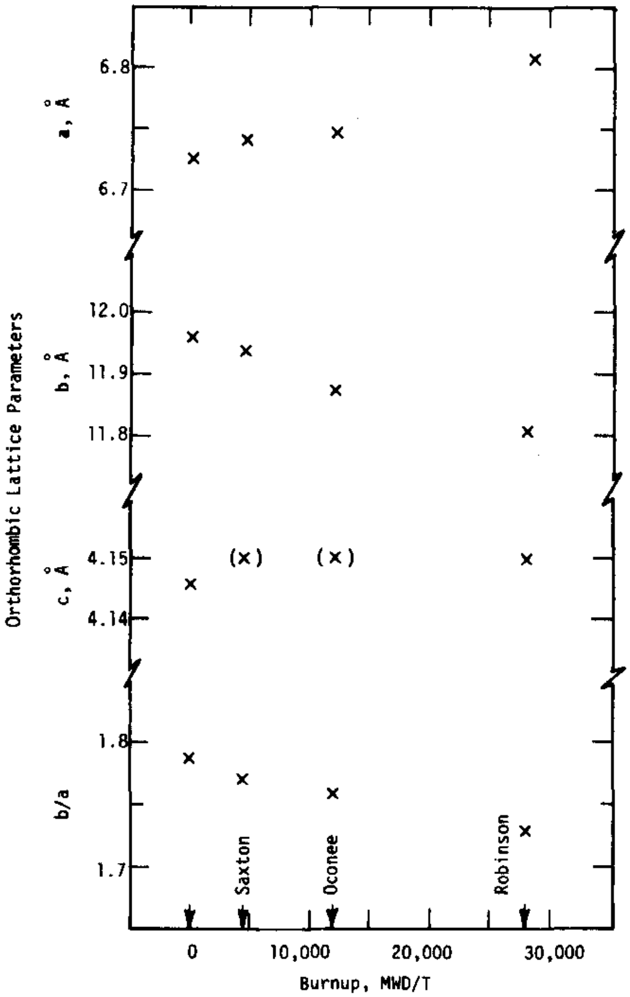

FIGURE 10. **Effect of Exposure on Orthorhombic Lattice Parameters of Voloxidized LWR Fuels**

TABLE 7

Conversion of U to Pu and Fission Products

Reactor	Exposure, MWD/MTU	Uranium Converted, % Plutonium	Fission Products	Total
Saxton	3,000 to 6,000	0.1	0.4	0.5
Oconee	10,000 to 12,000	0.4	0.9	1.3
Robinson	28,000	0.6	1.9	2.5

DETERMINATION OF URANIUM IN FUEL REPROCESSING SOLUTIONS

A method was developed for highly precise and accurate determinations of uranium in process solutions. Accuracy and precision (relative standard deviation) are about 0.1%. The method is based on a modified Davies-Gray titration.[1] Uranium is selectively reduced from U(VI) to U(IV) and quantitatively reoxidized by titration with potassium dichromate to a potentiometric end point. Plutonium, thorium, iron, nitric acid, and tributyl phosphate (TBP), all of which could be present in process streams, do not interfere with the analysis.

The method will be used in the joint Los Alamos Scientific Laboratory (LASL)-SRL evaluation of a new on-line nondestructive assay instrument, the x-ray absorption-edge densitometer (XRAED). The much greater precision of the titrimetric method allows realistic evaluation of the XRAED, which must have a precision of 0.5%.

Improvements to the Published Method

Several methods of sample measurement and titrant delivery were investigated to obtain maximum precision. Aliquots are weighed on an analytical balance and titrated with a precision digital buret. 50 mL of concentrated phosphoric acid was found to be more effective than the 40 mL in the published method. Also, 100 mL of 3.2M sulfuric acid is used instead of water, and 10 mL of a 7.5-g/L vanadyl sulfate solution is used instead of crystals. The potassium dichromate concentration was 0.1700N. Temperature corrections were applied to titrant volumes.

Concentrated phosphoric acid, sulfamic acid, ferrosulfate, nitric-sulfamic-molybdate, vanadyl sulfate, and sulfuric acid solutions are used in this procedure. Some of these are unstable. The ferrous ion in ferrosulfate solutions can be air-oxidized. To ensure an accurate ferrous content, the solution is checked daily by direct titration with potassium dichromate in a strong sulfuric acid medium with diphenylamine as a visual redox indicator. The vanadyl sulfate solution also air-oxidizes with time, and fresh solutions are prepared daily.

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1. **1977 Annual Book of ASTM Standards.** pp. 184-186, Sections 5-13. American Society for Testing and Materials, Part 45 - Nuclear Standard, C696.

The phosphoric acid solution is treated as described in Reference 1. A blank titration in the absence of uranium determines the overall condition of the reagents. If the dichromate titer of the blank is equivalent to 0.1% or more of the uranium content, all reagents are replaced.

Several electrodes were tested to minimize the effect of tributyl phosphate, which can accumulate on the electrode surfaces and severely decrease sensitivity and increase response time.

Tests With Solutions Containing Uranium Only

With the recommended electrode system, fifteen titrations of a uranium standard solution [prepared from National Bureau of Standards (NBS) uranium metal] with NBS potassium dichromate gave a precision of 0.14% RSD (relative standard deviation) and an accuracy of 0.05%. However, with small amounts of organic material added, sensitivity gradually decreased and response time increased. The design of the combination reference and platinum electrode precluded effective cleaning.

A calomel reference electrode and a separate platinum wire spiral counter-electrode performed satisfactorily (0.15% RSD) if the platinum wire was meticulously cleaned daily. However, a gradual irreversible poisoning of the platinum was observed, and the potential between the electrodes began to drift.

A partially isolated electrode (platinum spiral in a glass tube with an unfired Vycor® tip, Corning Glass Works) and a platinum counter-electrode circumvented the need for a reference electrode. Response was excellent, but titration potentials shifted with each sample. In sixty determinations, precision was 0.15% RSD.

A tin oxide-treated glass electrode was tested as the counter-electrode with a commercial calomel reference electrode. The titration potentials remained constant over several weeks without loss of response or sensitivity, and without the need to clean electrodes. Because the endpoint potential was stable, the titrant could be weighed to increase precision. In seven determinations a 60-g/L uranium solution, precison was 0.06% RSD.

Analytical results were converted from a weight basis to a volume basis by measurement of the solution density. A titration of a volumetrically measured uranium solution was tested with the tin oxide electrode system. Five replicate analyses on 29-, 70-, and 90-g/L uranium standard solutions gave precisions of 0.04%, 0.07%, and 0.09% RSD, respectively. The pipets used in these measurements are being standardized, which could make the solution density measurements unnecessary.

Tests With Solutions Containing Uranium and Plutonium

The method was tested in process solutions that contain uranium, plutonium, and hydroxylamine nitrate (HAN). HAN interferes and must be removed before sample titration. Concentrated nitric acid is added with heating until the blue Pu^{3+} changes to the amber Pu^{4+}. With the standard titration procedure, uranium determinations for ten replicates of individually treated samples yielded 0.16% RSD. Sample concentration was 12.40 g U/kg, and the platinum pair electrode system was used. Precision can probably be improved further by using the tin oxide electrode and weighing the titrant.

Continuing Study

High accuracy uranium analyses will continue on various process solutions. A high accuracy coulometric determination of plutonium is also being developed.

Methods will be studied to automate the Davies-Gray procedure with commercially available equipment.

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