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ABSTRACT

Consolidated Edison - Sulfex-Thorex Dissolution

Type 304L stainless steel passivates in boiling 6 M H_2SO_4 containing greater than 0.015 M HNO_3 . In 3 M H_2SO_4 -0.1 M HNO_3 , passivation does not occur, but the dissolution rate is lowered. The passivation is easily broken in 3 and 6 M H_2SO_4 containing 0.2 M HNO_3 when dissolving steel wool is in contact with the stainless steel specimen.

Decladding prototype Consolidated Edison fuel pins with boiling 5 M HNO_3 -2 M HCl resulted in uranium losses of 0.3 to 0.4% in decladding periods of 1-2 hr.

Consolidated Edison - Solvent Extraction Flowsheet

Countercurrent batch extractions of synthetic Consolidated Edison fuel solution has demonstrated the following decontamination factors: first cycle, gross γ 3.5×10^5 , Ru γ 2.9×10^4 , Zr-Nb γ 1.8×10^5 , and TRE β 1.2×10^6 ; second cycle, gross γ 7.6×10^4 , Ru γ 3×10^4 , Zr-Nb γ 6.3×10^4 , and TRE β 1.4×10^5 . Passage of the feed through silica gel at 50°C gave a Zr-Nb decontamination factor of 37. The use of cadmium as a neutron poison will not be limited because of extraction by 5% TBP. The maximum distribution coefficient for Cd, E_a^O , found in a wide variety of conditions was less than 0.001.

Dissolution of Borax-IV Fuel

Processing problems which arise from the presence of lead in this fuel are discussed. In dissolving the Al-Ni alloy cladding in mercury-catalyzed nitric acid, rates are very low when lead is present unless the Hg^{++} concentration is about 0.5 M. If not removed during decladding, lead seriously limits the uranium and thorium concentrations which can be attained by dissolution of the core in 13 M HNO_3 --0.04 M NaF --0.04 M $Al(NO_3)_3$ because of the very low solubility of lead nitrate in concentrated nitric acid. Dissolution in 13 M HNO_3 --0.04 M NaF --0.04 M $Al(NO_3)_3$ followed by sufficient dilution to allow both lead and thorium to remain in solution could result in a solution which is about 0.1-0.2 M in Th.

Yankee Atomic Fuel - Sulfex Process

The results of two runs with prototype Yankee Atomic fuel pins irradiated to 500 and 775 Mwd/T using the Sulfex head end flowsheet showed acceptably low uranium and plutonium losses but exhibited unsatisfactory passivation phenomena. Uranium and plutonium losses to the 6 M H_2SO_4 decladding solution were a maximum of 0.02 and 0.08%, respectively.

Passivation of the stainless steel jacket in the decladding solution was overcome by contact with iron wire. Pellet dissolution was performed with 8-10 M HNO_3 at 105°C. However, uranium material balances were poor, i.e., 90.34 and 164%.

APPR-Darex Process

Silica in a Darex solution, immediately after APPR fuel element dissolution, was essentially 100% in a soluble or a colloidal form. The average gravity rate of filtration for 500 ml of this solution through a 4-in. deep sand bed having a filter area of 2.8 cm^2 and with a 6-in.

solution head was 51 ml/min/cm². During chloride removal by the Batch Darex procedure, highly hydrated silica precipitated from solution. After volume adjustment, the average rate of filtration was about 0.09 ml/min/cm².

Low Temperature Chloride Removal

The chloride from a synthetic Darex dissolver solution containing about 60 g SS/l and 1.25 M Cl can be volatilized at room temperatures with nitric oxide and recovered as 3 M hydrochloric acid in an aqueous stripping system. Nitric acid is volatilized and recovered in a similar manner also.

STR Fuel - Recovery of Uranium from Zircex Process Residues

Chlorination at 550-600°C of Zircex residues with carbon tetrachloride resulted in greater than 99.99% recovery of the uranium. Both the hydrochlorination residue and the solids which remain after leaching the hydrochlorination residue with nitric acid were chlorinated with similar results. By this technique, loss of 1-6% of the uranium to the nitric acid insoluble residue, which occurs in simple hydrochlorination and dissolution of STR fuel, is avoided. Other advantages include reduced corrosion and the elimination of possible explosions between U-Zr alloys and nitric acid. A modified flowsheet is proposed.

Radiation Damage to Solvents and Diluents

Radiolysis of 30% W/V TBP in 5 or 10% solutions of isopropyl biphenyl or amyl naphthalene in Amsco 125-82, after contact with 2 M HNO₃, showed that neither of these aromatic compounds had an appreciable effect on the total gas or monobutyl phosphoric acid, MBPA, yields at the 200 or 400 watt-hr/liter level. The MBPA yields of 0.42 to 0.80 support previous conclusions that nitric acid increases the rate of hydrolysis of the predominant radiolysis acid, dibutyl phosphoric acid, to MBPA.

Corrosion Studies

Titanium steam tubes exposed to boiling 2 M HCl--5 M HNO₃ at 135°C for 2000 hours corroded at maximum rates of 1.5-2 mils/mo. Stressed and welded specimens of types 304 ELC and 347 stainless steel exposed in boiling 3 M HNO₃ containing 60 g/liter stainless steel showed severe intergranular attack, though maximum over-all rates were on the order of 5 mils/mo. This attack appears to be independent of chloride concentration at least up to 800 ppm Cl⁻.

Extended contact of Ni-o-nel in boiling 13 M HNO₃--0.04 M HF results in the oxidation of chromium to Cr(VI) and intergranular attack. Over-all rates for 1000 hrs were as high as 6.2 mils/mo vs. 2.1 mils/mo when all chromium was in the (III) state. Ni-o-nel heat-treated at 1950°F appears to be slightly superior to that heat-treated at lower temperatures. The presence of 50 g/l of stainless steel in boiling 3.5 M H₂SO₄ reduced the maximum Ni-o-nel corrosion rate to 1.1 mils/mo.

Welded titanium subjected to boiling 13 M HNO_3 -0.04 M HF corroded at a maximum rate of 11.8 mils/mo for a 24 hour exposure. In the presence of varying amounts of Al(III) and Th(IV) maximum rates as low as 0.5 mils/mo were observed for 240 hr exposures.

The addition of 0.05 M borate and 0.05 M silicate lowered the corrosion rates of Ni-o-nel and Type 309 stainless steel in boiling 6 M NH_4F -1.0 M NH_4NO_3 from 12 to 6 mils/mo and from 7.2 to 4.0 mils/mo respectively.

Waste Treatment and Ion Exchange

Phase compositions have been determined as a function of temperature for the evaporation of TBP-25 ($\text{Al}(\text{NO}_3)_3$ - HNO_3) wastes to 146°C. Little nitrate decomposition occurred below 146°C but the final solution was very viscous. The condensate volume and weights were about 80 and 70%, respectively, of those in the original waste. The condensate contained about 55% of the total nitrate and 100% of the original free nitric acid. The density of the final solid product after calcination at 650°C was 0.5 g/cc as compared to a density of 1.0-2.0 obtained with ferric oxide solids in previous experiments.

Feed Materials Processing

Precipitation of UO_2 from uranyl nitrate solutions in which the reactant mole ratio was 1:2:0.2, $\text{UO}_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O}:\text{HNO}_3$ at 85°C produced high-density hexagonal needles of $1 \times 4 \mu$ average particle size, and at 50°C, 27.5°C and 5°C gave platelets of 1μ average size. All precipitates filtered rapidly and were decontaminated from uranium daughters by a factor of 125.

A method of estimating surface area of UO_2 powders, involving the adsorption of perfluoro-octanoic acid from a CCl_4 -ether solution, correlated fairly well with the B.E.T. method, and is much simpler to apply. Pure UO_2 , when titrated potentiometrically with HCl, gives no inflections other than at pH 7 and 3. This differs from those oxides containing fluoride, which give intermediate inflections. An "iron number," based on the capacity of UO_2 surfaces to reduce ferric ion in acid solution, was studied as an index of UO_2 sinterability. No good correlation was obtained.

In the reduction of $\text{UF}_4 \cdot 2 \text{NaF}$ by sodium, a magnesia crucible did not perform well at 950°C. Sodium vapor reduced part of the MgO to Mg.

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1.0 POWER REACTOR FUEL REPROCESSING

1.1 Consolidated Edison Fuel

1.11 Sulfex-Thorex Dissolution (L. M. Ferris, A. H. Kibbey)

Complete dissolution of Consolidated Edison fuel is achieved by removal of the stainless steel cladding with boiling 6 M H_2SO_4 followed by dissolution of the $\text{ThO}_2\text{-UO}_2$ core in 13 M HNO_3 -0.04 M NaF -0.04 M $\text{Al}(\text{NO}_3)_3$.^{1,2} In this process one of the major concerns is cross-contamination of the solutions in successive dissolution cycles. Sulfuric acid, in small amounts, appears to have no deleterious effect on the core dissolution, but, a trace of nitric acid in sulfuric acid can result in passivation of stainless steel. At KAPL, it was found that low carbon stainless steel was completely passivated in 4-6 M H_2SO_4 containing 0.01 M HNO_3 .³ Work in this laboratory has shown that passivation of 304L stainless steel occurs in 6 M H_2SO_4 when the nitric acid concentration is greater than 0.015 M. With 3 M H_2SO_4 , the presence of 0.1 M HNO_3 caused a reduction in the rate of reaction, but did not cause passivation. In either 3 or 6 M H_2SO_4 containing 0.2 M HNO_3 , the passivation was easily broken when dissolving steel wool was in contact with the stainless steel specimen.

Studies concerned with the rate of dissolution of 304L stainless steel in various stoichiometric excesses of boiling 6 M H_2SO_4 have shown that a 100% excess is insufficient to insure a high dissolution rate. The initial rate of dissolution is about 12 mg/min/cm² in either a 100 or 200% excess, but, with a 100% excess of the acid, the rate falls off rapidly after about 50% of the stainless steel is dissolved. Dissolution of 15-30% of the stainless steel in a 100% excess of 6 M H_2SO_4 followed by dilution of the acid to 3 M sulfate caused a reduction in the dissolution rate from about 12 mg/min/cm² to approximately 3 mg/min/cm². In general, dilution of the acid in this manner reduced the rate by a factor of 4 to 8.

So far, two flowsheet demonstration experiments have been performed in which the stainless steel cladding was dissolved in boiling 5 M HNO_3 -2 M HCl . Uranium losses were 0.42 and 0.29% when 1-hr and 2-hr dissolution times were used in decladding. Actually, the 30-mil cladding was dissolved in about 10 min with about another 30 min required for the end caps. The decladding solution contained 50 g SS/liter before addition of wash water.

Complete dissolution of the sintered 95.5% ThO_2 -4.5% UO_2 pellets was achieved in 2 steps with boiling 13 M HNO_3 -0.04 M NaF -0.1 M $\text{Al}(\text{NO}_3)_3$. In the first 5-hr contact, about 96% of the core was dissolved in 200% stoichiometric excess of dissolvent to yield a solution ~ 1 M in Th. A second 3-hr contact with fresh dissolvent completed the dissolution. Combination of these solutions with a small amount of wash water resulted in a solution containing about 10 ppm Cl^- and 0.64 M thorium.

1.12 Solvent Extraction Flowsheet (R. H. Rainey, J. G. Moore)

Conditions for the first solvent extraction cycle for Consolidated Edison fuel using a recycle of the aqueous raffinate from the second cycle to the first cycle are:

Feed: 0.064 M U, 1.0 M Th, 1.2 M Al, zero free acid

Extractant: 2.5% TBP-Amsco

Scrub: 0.9 to 1.0 M Al, zero free acid

Flow Ratio: Feed/Ext/Scrub = 1/2.5/0.5

Stages: 6 extraction, 8 scrub

A countercurrent batch extraction using these conditions, except that the scrub was 0.8 M Al, gave the following decontamination factors: gross γ 3.5×10^5 , Ru γ 2.9×10^4 , Zr-Nb γ 1.8×10^5 and TRE β 1.2×10^6 . Uranium loss was 0.009% but the system had not reached equilibrium at the end of the run.

Distribution coefficients for the uranium with 2.5% TBP-Amsco showed a different dependence on salting agents than those encountered at higher TBP concentrations. The distribution coefficient of uranium to the organic phase increases with increasing aluminum concentration in the absence of acid (Fig. 1)⁴, and increases with increasing acidity in the absence of aluminum (Fig. 2). In the presence of 0.5 M Al varying the acidity between 2-4 M does not appreciably change the extraction of uranium (Fig. 3). Increasing the acidity from 0.5 to 2 M in a solution containing 1 M Th and 1.2 M Al decreases the extraction of uranium (Fig. 4). Increasing the Al from 0.6 to 1.2 M in a solution containing 1.5 M Th and 1.0 M HNO₃ did not appreciably vary the extraction of uranium (Fig. 5).

A countercurrent batch extraction using second cycle flowsheet conditions previously described⁵ demonstrated the following decontamination factors: gross γ of 7.6×10^4 , Ru γ 3×10^4 , Zr-Nb γ 6.2×10^4 and TRE β 1.4×10^5 .

The fission product spike for both these experiments came from Purex aqueous waste concentrate and therefore is probably chemically somewhat different from that to be expected in Consolidated Edison feed solutions. Due to the high activity required, it was not possible to process the same material through two cycles. Consequently, a new feed was prepared for the second cycle. For these reasons, it is not proper to assume that plant decontamination factors would be a product of the two cycles reported, i.e., $(3.5 \times 10^5) \times (7.6 \times 10^4) = 2.7 \times 10^{10}$. However, it seems likely that the proposed flowsheet will give the 5×10^6 gross γ decontamination factor required to reduce the fission product activity of the product activity to less than 10^2 γ c/m/mg U. One day after separation, the daughter activity of the U-232 will be about 320 γ c/m/mg U.⁶

1.13 Head End Decontamination (R. H. Rainey, J. G. Moore)

A synthetic Consolidated Edison feed solution containing 1 M Th, 1.2 M Al, 0.5 M HNO₃ and Zr-Nb tracer was decontaminated by a factor of 37 by passage through untreated silica gel and only 9.2 by passage

Fig. 1. Uranium Extraction Isotherms between 2.5% TBP-Amsco 125-82 and Neutral Aluminum Nitrate

Fig. 2. Uranium Extraction Isotherms between 2.5% TBP-Amsco 128-82 and Nitric Acid

Fig. 3 Uranium Extraction Isotherms between 2.5% TBP-Amsco 128-82 and Nitric Acid in 0.5 M Aluminum Nitrate

Fig. 4. Uranium Extraction Isotherms between 2.5% TBP-Amsco 125-82 and Nitric Acid
in 1.0 M Th(NO₃)₄ - 1.2 M Al(NO₃)₃

Fig. 5. Uranium Extraction Isotherms between 2.5% TBP-Amsco 125-82 and Aluminum Nitrate in 1.0 M Th (NO₃)₄ - 1.0 M HNO₃

through silica gel treated with thorium and phosphate at 50°C. After 50 volume changes the decontamination factor with either adsorbent had decreased to about 5.

A sample of 40-50 mesh silica gel was divided into two parts. One part was treated with thorium and phosphate to convert it to an ion exchange media. Adsorption columns were prepared by loading 15 ml batches of each material in small condensers. Dimensions of the columns were: radius 0.48 cm. length 21 cm, cross sectional area 0.7 cm². The columns were maintained at about 50°C by running hot water through the outside of the condenser. The flow rate of the feed through the column was regulated to about 0.75 ml/min giving a contact time with the silica gel of about 10 minutes.

Since a feed clarification is thought to be necessary, use of silica gel instead of sand in the filter column would give additional decontamination without adding another processing step. Additional experiments will be made to determine the degree of protactinium decontamination achieved with this process.

1.14 Homogeneous Criticality Control (R. H. Rainey, J. G. Moore)

The distribution coefficient for cadmium between 5% TBP-Amsco and a variety of solutions tested was less than 0.001, but increased to 0.6 when 100% TBP was used.

The use of materials having a high neutron cross section for homogeneous control of criticality depends, among other things, upon the feasibility of separating these materials from the uranium in the solvent extraction step. A series of experiments were made to determine the effect of aluminum, TBP, and nitric acid concentrations on the distribution coefficient of cadmium (Table 1). The extraction of cadmium increases by a factor of about 500 as the TBP concentration increases from 5% to 100%. When the aqueous phase is 1.02 M Al and 0.5 N H⁺, the E_a^O Cd increases from less than 0.0003 at 5% TBP to 0.17 at 100% TBP. Similarly when the aqueous phase is 1.4 M Al and 0.22 M acid deficient, the E_a^O Cd increases from 0.0003 at 5% TBP to 0.58 at 100% TBP. The E_a^O Cd increases rapidly with increasing aluminum concentration but decreases with increasing acidity and with increasing acid deficiency. Using 50% TBP-Amsco as the solvent, E_a^O Cd increased from 0.003 at 0.1 M Al-0.5 N H⁺ to 0.15 at 1.7 M Al-0.5 N H⁺; decreased from 0.006 at 0.1 N H⁺-0.56 M Al to <0.0001 at 2.9 N H⁺-0.56 M Al; and decreased from 0.043 at 0.12 N acid deficient-0.92 M Al to 0.030 at 0.32 N acid deficient-0.95 M Al.

Table 1. Effect of TBP Aluminum and Acid Concentrations on the Distribution Coefficient of Cadmium

Constants	Variables	E_a^0 Cd
1.02 <u>M</u> Al; 0.5 <u>M</u> H^+	5% TBP	< 0.0003
"	15% TBP	0.0006
"	30% TBP	0.003
"	50% TBP	0.015
"	100% TBP	0.17
1.4 <u>M</u> Al; 0.22 <u>N</u> A.D.	5% TBP	0.0003
"	15% TBP	0.007
"	30% TBP	0.05
"	50% TBP	0.14
"	100% TBP	0.58
0.9 <u>M</u> Al; 0.12 <u>N</u> A.D.	5% TBP	.0007
"	50% TBP	.04
"	100% TBP	.2
50% TBP; 0.5 <u>M</u> H^+	0.1 <u>M</u> Al	.003
"	1.02 <u>M</u> Al	.015
"	1.71 <u>M</u> Al	.15
50% TBP; 0.56 <u>M</u> Al	0.1 <u>N</u> H^+	0.006
"	1.0 <u>N</u> H^+	0.003
"	2.9 <u>N</u> H^+	< 0.0001
"	5.0 <u>N</u> H^+	< 0.0001
50% TBP; 0.92 <u>M</u> Al	0.12 <u>N</u> A.D.	0.043
50% TBP; 0.94 <u>M</u> Al	0.24 <u>N</u> A.D.	0.033
50% TBP; 0.95 <u>M</u> Al	0.32 <u>N</u> A.D.	0.030

1.2 Dissolution of Borax-IV Fuel (L. M. Ferris)

In the Borax-IV fuel, lead is used as a bond between the Al-Ni alloy cladding and the ThO_2-UO_2 core. It has been assumed that precipitation of lead during processing is to be avoided. The presence of lead in this fuel will then complicate processing in two ways: (1) Decladding with

mercury-catalyzed nitric acid is markedly inhibited if lead is present.⁷ Preliminary experiments have shown that a mercury concentration of about 0.5 M Hg^{++} will be required in 8 M HNO_3 to provide a satisfactory rate of reaction; (2) Lead is not dissolved³ in NaOH or NaOH- NaNO_3 solutions.⁷ Its presence during core dissolution retards the dissolution rate in HNO_3 - $\text{Th}(\text{NO}_3)_4$ - $\text{Al}(\text{NO}_3)_3$ solutions, and, since it is but slightly soluble, the uranium and thorium concentrations in the product solution are also necessarily low. With lead present only 65% of the core dissolved in 6 hrs whereas 93% dissolved in the same time in the absence of lead. The Th/Pb mole ratio in the fuel is about 1:3.

Work on the decladding of the fuel with HNO_3 - $\text{Hg}(\text{NO}_3)_2$ solutions is progressing. Since the solubility of lead nitrate increases with decreasing acid concentration (Fig. 6), waste volumes can be minimized if 4 M HNO_3 is used.

Only a limited amount of data is available on the solubility of lead nitrate in nitric acid solutions containing thorium and aluminum. It is obvious, however, that the solubility of lead nitrate, at a constant H^+ concentration, decreases with increasing thorium and aluminum concentration (Fig. 6). The use of lower nitric acid concentrations in the dissolution, to permit higher lead concentrations, does not appear feasible since the dissolution rate of ThO_2 decreases rapidly with decreasing nitric acid concentration.⁸

At this time, it appears that this fuel must either undergo a 2-step decladding (one for aluminum and a second for lead), or a high Hg^{++} concentration must be used in decladding with nitric acid. In either case, the use of nitric acid during decladding could result in high uranium losses (see Section 1.11 for uranium losses to 5 M HNO_3 - 2 M HCl).

1.3 Yankee Atomic Fuel - Sulfex Process

1.31 "Hot" Cell Flowsheet Demonstration (J. R. Flanary, J. H. Goode, C. P. Johnston)

The PRFR experimental and flowsheet demonstration program with irradiated fuels was initiated with a series of Sulfex runs in the Mini head end and solvent extraction equipment installed in Cell #2. Ten prototype Yankee Atomic pins with an estimated irradiation level of 500-1000 Mwd/Ton U and "cooled" about 4 months will be processed. The pins were in contact with water at 125°F for 120 days during the irradiation period. The pins, fabricated at ORNL and irradiated at the MTR, are 3-in. lengths of 30 mil, $3/8$ in. OD 304L stainless steel tubing. Each pin contains 40 g of sintered UO_2 pellets. End caps are welded on each end. The total weight of stainless steel per pin is 22 g.

In the Sulfex head end flowsheet, the stainless steel cladding is selectively dissolved in boiling 4 or 6 M sulfuric acid, and the spent decladding solution filtered and discarded to waste. The dissolver and exposed pellets are rinsed with water, which is filtered and discarded to

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Fig. 6. Solubility of $\text{Pb}(\text{NO}_3)_2$ in Nitric Acid and HNO_3 - $\text{Th}(\text{NO}_3)_4$ - $\text{Al}(\text{NO}_3)_3$ Solutions at 25°C

waste. Finally, the UO_2 pellets and any fines caught on the filter are dissolved in 10 M nitric acid. The resultant solution is adjusted to the proper composition for solvent extraction by the standard Purex process. After pellet dissolution, the dissolver must be rinsed to remove traces of nitric acid which can render the stainless steel surface passive in the subsequent sulfuric acid decladding step.

For the first Sulfex run in the Mini equipment, one pin was weighed, inserted into a platinum screen basket attached to a platinum wire, and lowered into the dissolver, which had been previously charged with a 200% excess of boiling 4 M H_2SO_4 . Anticipating passivation, a small wad of steel wool was placed in the basket in contact with the pin. Although the pin was completely covered with the boiling decladding solution, no evidence of reaction was observed. Boiling was continued for 4 hr and hourly samples of the decladding solution were removed. All of these samples were colorless and were non-radioactive. At this point, the pin was removed from the dissolver and examined. It retained its original clean, shiny appearance with no evidence of attack. A second run using another pin under similar conditions with a 6-hr reflux period was also unsuccessful.

A third run using a third pin irradiated to 500 Mwd/T and a 200% excess of boiling 6 M sulfuric acid was also unsuccessful after 4 hrs of reflux. Passivation difficulties with 4 M H_2SO_4 had been experienced in previous studies⁹ with Yankee Atomic prototype pins irradiated to 250 Mwd/T over a period of 42 days in 145°F water. The 250 Mwd/T pin, however, dissolved in 6 M H_2SO_4 . It was concluded that the stainless steel surfaces of these pins were totally passive to boiling 4 and 6 M H_2SO_4 .

In attempts to break the passive film, a small piece of zinc metal was placed in contact with the pin. Following this, the decladding solution was made 0.05 M in sulfamic acid. Neither technique was successful.

In a third attempt, the pin was placed in a loosely woven iron, wire basket which was drawn tight by wrapping with additional iron wire. The assembly was placed in the platinum basket and lowered into the dissolver containing a 200% excess of fresh boiling 6 M H_2SO_4 . Dissolution started almost immediately and proceeded vigorously. After 1 hr, the pin was dissolving preferentially at the mid section; after 1.75 hr, the cladding had broken into pieces. The boiling decladding solution was allowed to reflux in contact with the exposed UO_2 pellets for 4 hr to obtain data on the solubility of UO_2 in the partially spent decladding solution as a function of pellet exposure time. Observations showed that jacket dissolution was complete after the 2 hrs. Thus, reducing conditions provided by dissolving metal were present throughout the 4 hr reflux; a stainless steel end plug was found in the basket after pellet dissolution.

Table 2 summarizes the pertinent results available from this run. Uranium loss to the decladding solution is low, ~0.01%, when the cladding is first penetrated and remains about the same during the 4 hr reflux period. It appears that, upon initial contact of the declad solution

with the UO_2 pellets, a small amount of the oxide surface dissolved with no further dissolution during the reflux period. This behavior is also emphasized by the plutonium losses which follow the same pattern. The plutonium loss, however, is ten-fold higher than that of uranium; owing, it is believed, to a buildup of plutonium at the oxide surface during irradiation. The gross gamma activity of the decladding solution reflects the presence of activated stainless steel components. The concentration of this activity does not increase during reflux.

Analyses of the caustic scrubbers indicated that about 0.1% of the total activity associated with the decladding solution was released to the off-gas and trapped.

Two hours were allowed for pellet dissolution in 125 ml of 8 M HNO_3 at 105°C. Inspection after the first hour indicated that the pellets had dissolved. Uranium analysis of the first-hour sample indicated that 90% of the UO_2 had dissolved. Analysis at the second hour showed no increase in uranium concentration. The dissolver product was dropped to the FAT tank and 200 ml of 10 M HNO_3 was charged to the dissolver to dissolve any remaining heel of UO_2 . After one hour, an additional 0.34% of the uranium was found in this solution. The material balance for uranium and plutonium was therefore only 90.3%.

From the Pu/U ratio obtained from analyses of the dissolver product solution, burnup calculations showed that the first pin had been irradiated to only 500 Mwd/T instead of an anticipated 4200 Mwd/T. Only $1.1 \times 10^{-4}\%$ of total fission product activity associated with the UO_2 was trapped in the off gas scrubbers during pellet dissolution.

A second pin was wrapped in iron wire and immersed in boiling 6 M H_2SO_4 to initiate a second Sulfex run designed to duplicate the first. Brown fumes were observed momentarily and dissolution of the pin did not start. Analysis of this decladding solution revealed 0.2 M NO_3^- , indicating that sufficient residual HNO_3 had remained in the dissolver, presumably from pellet dissolution, to dissolve the iron wire and more important, to maintain passivation.

After carefully rinsing the dissolver with water, the run was repeated with success. The results generally agree with those obtained with the first pin. Uranium and plutonium losses to the decladding solution were 0.003 and 0.08% shortly after the clad was penetrated, with no significant increase during the reflux period. Material balance on uranium and plutonium from pellet dissolution was 164%. The reason for poor uranium and plutonium material balances is unknown. Some dark colored solids were trapped by filtration of the spent decladding solution. This material failed to dissolve in 10 M HNO_3 or 5 M HNO_3 -2 M HCl and is thought to be a silica impurity from the stainless steel. Burnup calculations from the uranium and plutonium analyses of the dissolver product showed that the second pin had been irradiated to 775 Mwd/Ton U.

Table 2. Sulfex Process Applied to Prototype Yankee Atomic Fuel Pins

Fuel: One prototype Yankee Atomic Pin

Jacket: 30 mil thick 304L SS; 3/8" OD; SS end caps; total SS, 22 g

Core: Sintered UO_2 pellets, 37 g U

Irradiation: 500 Mwd/Ton U^* ; 125°F water for 130 days

Cooling Period: 120 days

Decladding Solution: 200% excess of boiling 6 M H_2SO_4 , 570 ml.

UO_2 Dissolvent: 8 M HNO_3 , 125 ml

Heel Dissolvent: 10 M HNO_3 , 200 ml

Off-gas Scrubbers: 3 M NaOH, 1000 ml each (two gas bubblers in sequence)

Decladding

Time, hr	Fe, mg/ml	% SS in Sol'n	U mg/ml	% Loss	Pu γ c/m/ml	% Loss	Scin. Gamma c/m/ml
1	6.56	25					3.72×10^7
1.75	Cladding observed to break up.						
2	20.68	80	0.0068	0.01	800	0.04	1.87×10^8
	Four hour reflux begun						
3	24.02	93	0.003	0.004	860	0.044	2.17×10^8
4	24.18	93	0.0038	0.006	680	0.035	2.20×10^8
5	24.02	93	0.0124	0.02	780	0.040	2.19×10^8
6	20.88 ?		0.0032	0.005	940	0.048	2.17×10^8

2	Off-gas scrubber #1						2.88×10^3
	#2						302
6	Off-gas scrubber #1						1.12×10^5
	#2						2.58×10^4

Time, hr	U mg/ml	% in Sol'n	Pu γ c/m/ml	% in Sol'n	Scin. Gamma c/m/ml
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Dissolver and UO_2 pellets rinsed three times with 600 ml aliquots of water; UO_2 dissolvent charged to dissolver.

1	266	90	8.12×10^6	90	5.63×10^9
2	268	90	8.09×10^6	90	5.78×10^9

Dissolver product solution dropped to FAT** tank; heel dissolvent charged to dissolver.

3	0.63	0.34	2.31×10^4	0.34	2.87×10^9
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3	Off-gas scrubber #1				4.40×10^3
	#2				6.30×10^3

* Calculated from U and Pu analyses of dissolved pellets

** FAT, i.e. Feed Adjustment Tank

1.4 APPR-Darex Process

1.41 Feed Clarification (O. C. Dean, A. F. Messing)

The removal of silica from Darex solution is being studied. Means of removal immediately following the dissolution step is being emphasized.¹⁰ For reference, 30 g of a prototype APPR fuel element was dissolved in 520 ml of 5 M HNO_3 -2 M HCl by the current Darex procedure.¹¹ Immediately after dissolution, the resulting 500 ml of solution was filtered by gravity through a 4-in. deep sand bed having a filter area of 2.8 cm^2 . A solution head of 6 in. was maintained throughout the filtration. Approximately 3.5 min (an average rate of 51 ml/min/cm^2) was required and essentially no silica was removed from solution. This experiment showed that the silica is in solution or is in a colloidal form, during and immediately following fuel element dissolution. Fine, crystalline silica approximately 50% SiO_2 , was observed to slowly separate from this solution.

The filtrate was treated for chloride removal by the Batch Darex procedure¹¹ during which time hydrated silica precipitated. With no further treatment, the solution volume was adjusted to 500 ml and filtered. About 3 hr was required to filter 150 ml. By extrapolation to 500 ml, 35 hr would have been required for the complete filtration, giving an average rate of filtration of 0.09 ml/min/cm^2 .

1.5 STR Fuel - Recovery of Uranium from Zircex Process Residues (L. M. Ferris, T. A. Gens)

Several problems have prevented the immediate use of the Zircex Process¹³ as a means of reprocessing spent nuclear fuel alloys. Chlorination with carbon tetrachloride at 550-600°C of residues produced by Zircex hydrochlorination has been investigated as a promising solution to the problems of uranium loss to the residue in the case of STR fuel, of corrosion in the hydrochlorinator caused by cyclic use of hydrogen chloride gas at 350-800°C and boiling nitric acid, and to the possibility of explosive reactions resulting from the contact of nitric acid with U-Zr alloy, should hydrochlorination be incomplete.

The carbon tetrachloride is used to convert all residues left after hydrochlorination to volatile chlorides from which all uranium is recoverable (Fig. 8). The first operation is hydrochlorination at 350-800°C as in previous flowsheets. Hydrochlorination removes about 98% of the zirconium from the reactor in the case of STR fuel. Essentially all of the uranium remains in the reactor or in a filter chamber at the exit. The zirconium tetrachloride is removed from the off-gas stream and discarded as waste. After hydrochlorination, a stream of nitrogen is passed through a liquid carbon tetrachloride bubbler at room temperature and then into the reactor which is held at temperatures between 550 and 600°C. All of the hydrochlorination residue is converted to volatile chlorides which are removed from the nitrogen gas stream by desublimation. The desublimation can be performed at room temperature. No nitric acid or water is introduced into the reactor, thereby simplifying the corrosion problem and eliminating all possibility of explosive reactions between U-Zr alloys and nitric acid. The uranium-containing chlorides dissolve readily in nitric acid to yield a $\text{HNO}_3\text{-HCl}$ solution from which the uranium might be recovered by the same techniques used in the Darex Process.¹⁴

The chlorinations with carbon tetrachloride were performed with samples of hydrochlorination residue which had previously been leached with nitric acid (runs 1-4, Table 3) and on samples as obtained after hydrochlorination. Chlorinations could be performed three times as rapidly with the samples that were not leached with nitric acid. Nearly 100% of the starting material was converted to volatile and water-soluble chlorides in all runs. The residue left after chlorination from run ZrI was found to be mostly silicon by spectrographic analyses. No uranium was found. In all chlorinations, except runs Zr5 and Zr8, carbon was observed collecting on the reaction surface. This carbon burned off immediately when oxygen was admitted. Very little reaction occurred with pure hydrogen chloride gas (run Zr2) or when air was used as a carrier gas for the CCl_4 (run Zr3).

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Conditions: Temp 25°C., atmos. press. Countercurrent absorption into water of hydrochloric and nitric acids from nitric oxide gas equilibrated with 1.25 M Cl⁻ and 9.99 M NO₃⁻.

Fig. 7. Chloride Recovery Column Profile

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Fig. 8. Modified Zircex Process: Gas-Phase Hydrochlorination Followed by Chlorination with Carbon Tetrachloride

Table 3. Recovery of Uranium from Zircex Residues by Chlorination with Carbon TetrachlorideVapor pressure of CCl_4 : 116 mm Hg

Total pressure with carrier gas: 760 mm Hg

Maximum amount of uranium not recovered by chlorination is $10^{-3}\%$ of that in the residue sample

Run No.	T, °C	Residue Sample Size, g	Carrier Gas	Sample Leached in 7 M HNO_3 Before Chlorination	Total Time hr	Sample Remaining in Boat, %	No. of Times Carbon Burned Off During Run	Quantity of CCl_4 , Multiple of Stoichio-metric	Source of Hydrochlorination* Residue, Zircex Run No.
ZR1	550	2.9422 (13.4% U)	HCl	Yes	3.0	1.1	2	-	HC76
ZR2	550	2.9422 (13.4% U)	HCl (no CCl_4)	Yes	0.2	100	0	0	HC76
ZR3	550	2.9422 (13.4% U)	Air	Yes	0.2	100	0	-	HC76
ZR4	550	1.0067 (13.4% U)	N_2	Yes	4.0	0.3	1	49	HC76
ZR5	600	1.0948 (13.4% U)	N_2	No	0.8	0.03	0	20	HC76
ZR6	600	1.9446 (13.4% U)	HCl	No	1.0	0.02	1	11	HC76
ZR7	600	1.2904 (2.77% U)	N_2	No	1.0	0.2	1	48	HC79
ZR8	600	4.4183 (57.8% U)	N_2	No	1.1	0.0	0	7.4	HC82

* STR fuel (1% U, 97% Zr, 2% Sn) was used in Zircex runs HC76 and HC79. Before treatment with CCl_4 , 7.5% and 19.59%, respectively of the uranium in the residue samples was insoluble in nitric acid.

EBWR fuel (93.5% U, 5% Zr, 1.5% Nb) was used in Zircex run HC82. Before treatment with CCl_4 , 0.02% of the uranium in the residue sample was insoluble in nitric acid. All uranium was soluble in all runs after treatment with CCl_4 .

By assuming all solids present after hydrochlorination of STR alloy to be ZrO_2 , an approximate calculation was made of the excess carbon tetrachloride that was used above that required by the reaction $ZrO_2 + CCl_4 \longrightarrow ZrCl_4 + CO_2$ (see Table 3). A similar calculation was made for EBWR alloy (Table 3, run Zr8) by assuming that the minimum amount of carbon tetrachloride required was one mole per mole of uranium in the residue. Considering that the vapor pressure of carbon tetrachloride is 116 mm at 25°C, and assuming that a single STR charge to the hydrochlorinator will produce 4 kg of residue, the volume of nitrogen carrier gas (STP) required under the conditions of run Zr6 would be 5000 liters.

1.6 Radiation Damage to Solvents and Diluents (W. Davis, Jr.)
(Work Performed at Stanford Research Institute on Subcontract 1081)

Radiolysis of Tributyl Phosphate. Tributyl phosphate, TBP, as a 30% W/V solution in a diluent, was irradiated to the 200 and 400 watt/hr-liter levels after contact with 2 M HNO_3 . The diluents were Amsco 125-82, 5 or 10 vol % isopropyl biphenyl in Amsco, 5 or 10 vol % amyl naphthalene in Amsco, and 50 or 100 vol % diethyl carbonate, DEC, in Amsco. Excepting solutions containing DEC, gas yields, G_{gas} , from all solutions were 1.55 to 2.20 molecules/100 ev, and monobutyl phosphoric acid yields, G_{MBPA} , were 0.42 to 0.80; corresponding values for solution containing DEC or DEC-Amsco diluent were 2.72 to 4.52 for G_{gas} and 0.75 to 0.77 for G_{MBPA} . These results show that isopropyl biphenyl and amyl naphthalene, as 5 or 10% solutions in Amsco 125-82, do not have an appreciable effect on either total gas yields or monobutyl phosphoric-acid, MBPA, yield in the radiolysis of TBP. The aromatic structure of these two additives had been expected to show some protective effect on TBP radiolysis. In all cases the yield of MBPA was 5 to 10 times greater than the corresponding yield from TBP-Amsco solutions not previously contacted with nitric acid. This increase was previously shown¹⁵ to be primarily due to hydrolysis of dibutyl phosphoric acid by the nitric acid to MBPA rather than to a corresponding increase in the radiolysis of TBP.

1.7 Corrosion Studies (W. E. Clark)
(Work done by Battelle Memorial Institute under Subcontract No. 988)

1.71 Darex Process

Titanium steam tubes, exposed for 2000 hours to various Darex solutions with metal surface temperatures of approximately 135°C, have been examined metallographically and corrosion rates estimated by measuring the decrease in wall thickness. After 2010 hours in 2 M HCl -5 M HNO_3 , the average rate was in the range of 1.5 to 2 mils/mo. Hairline cracks observed near the interface on this tube at the 1000-hr inspection did not reappear during the second 1000-hr exposure on new replaced sections of the tube inserted at the interface zone. It is thought that imperfections were present but unnoticed in the original tubing as received. A lower range of corrosion rates, 0.5 to 1 mil per month after 2049 hr, was found for the tube exposed to the Beginning solution, i.e., 2 M HCl , 5 M HNO_3 , ~0.01 M SS, 0.004 M U^{+6} . There were crevices in the weldment

of this tube after 2049 hr similar to those observed on the same tube after 1000 hr, but sectioning showed these to be reasonably shallow and apparently no cause for concern. Finally, little, if any, loss in thickness could be measured on the tube exposed to the Middle Darex solution. It is, therefore, concluded that titanium can be expected to withstand all the normal operating conditions of the Darex dissolver without undergoing excessive attack provided that care is exercised during welding.

The exposure of welded coupon and stress-type specimens of Types 304 ELC and 347 stainless steel to boiling Darex Fission Product Recovery solutions, 3 M HNO_3 , 60 g/l SS, has been completed. No stress-corrosion cracking was observed. However, heavy attack occurred on the surfaces of all specimens independent of the chloride content of the solutions. A knife-line type of attack was so pronounced in one of the stressed Type 347 specimens after 1250 hr that the longitudinal weldment was excised completely from the parent metal. General intergranular attack was abundant on both Types 347 and 304 ELC but was more localized in the heat-affected areas of Type 347.

Since both these austenitic grades are reasonably resistant to localized attack by boiling nitric acid, it was thought that the presence of hexavalent chromium in the solution might be responsible for the observed corrosion. Such effects have been established by investigators at ORNL. However, analyses showed that, following exposure, all of the solutions contained less than 5 mg per liter of Cr^{+6} . Apparently, this is not the causative factor. It is possible that the high concentration of Fe(III) was largely responsible for the accelerated local attack though this is by no means certain.

It is possible that boiling temperatures need not be employed in the Darex Fission Product Recovery System. Lower temperatures would be expected to result in less attack. Even though stress-corrosion cracking does not seem to be a problem, neither of these stainless steels can be recommended for use with these boiling solutions because of the highly localized attack. Study of this system has been terminated for the time being.

Over-all corrosion rates are listed in Table 4.

1.72 Sulfex-Thorex Process

The investigation of the effects of various heat treatments on the corrosion of Ni-o-nel in Thorex dissolver solution has continued. For 1000 hour exposures, rates for specimens heat-treated to 1850°C and 1950°C after welding with filler strip were in all cases no greater than 2.1 mils/mo. When the corrosion-product chromium was allowed to become oxidized to the +6 state, rates rose to as high as 6.2 mils/mo. Intergranular attack was observed in the presence of Cr(VI) but none in its absence. It is believed that rates of 1.5-2.0 represent the maximum rates to be expected in this process since Cr(VI) should not be stable under process conditions (Table 5). While there is little difference in the rates or

appearance of the specimens subjected to the listed heat-treatments, the specimens heat-treated at 1950°F appear to be slightly superior to other unquenched specimens. Consequently, this treatment will be given the Ni-o-nel dissolver to be used for cyclic Sulfex-Thorex dissolution tests.

Stabilized, welded Ni-o-nel exposed to boiling 3.5 M H_2SO_4 containing 50 g/l of dissolved stainless steel continues to show maximum rates of 1.1 mils/mo or less for exposures of 72 hours or longer (Table 6).

1.73 Darex-Thorex Process

A possible alternative method of processing Consolidated Edison fuel elements would be to remove the stainless steel cladding from the core with $\text{HNO}_3\text{-HCl}$ prior to dissolving the core with Thorex dissolver solution. To determine the feasibility of using titanium for this process, corrosion tests were run in which welded 75A titanium was exposed to boiling Thorex dissolver solutions containing various amounts of Al(III) and Th(IV). The results (Tables 7 and 8) indicate the strong probability that titanium will give satisfactory service since the maximum rate observed over a 240 hr exposure to solution containing 0.04 M Al^{+3} was 1.3 mils/mo. In the absence of both Al(III) and Th(IV) in solution, 24 hour exposure gave a rate less than 12 mils/mo (Table 9) which is better by a factor of three than the next best material tested. However, these tests should be considered only preliminary until at least 1000 hours of exposure have been obtained and until a reasonable number of cyclic Darex-Thorex dissolutions have been made in a titanium dissolver.

In these titanium tests two types of weldments were exposed. These were coupons containing butt welds and coupons overlapped, with a weld bead at each end of the lap, so that a crevice was formed. Since the irregular shape of the latter type precluded accurate area measurements, corrosion is reported as weight losses for these specimens. After a few periods of exposure, cracking was noted on several of the specimens, especially on those with lap welds. All of these specimens had been sheared from welded strips and some tearing had been observed along the sheared edges prior to exposure. Further examination of the welds showed that they had been contaminated due to insufficient shielding during welding. This had produced embrittlement. Shearing across the weldments, especially those of the irregularly shaped lap-weld specimens, had caused cracking of the metal. These cracks had then been opened and revealed by corrosion. More substance has been added to this explanation by a scouting study in which sheared specimens were exposed along with sawed specimens. Cracking was observed on the sheared but not on the sawed titanium. A second series of tests (Table 9) on specimens with carefully prepared welds shows no very significant differences in over-all rates from those obtained on poor welds, but no cracking of weld areas has been observed.

1.74 Zirflex Process

Experiments carried out to determine the effect of adding 0.05 M each of $\text{Na}_2\text{B}_4\text{O}_7$ and Na_2SiO_3 to the initial Zirflex dissolver solution indicate that maximum corrosion rates decreased roughly 50% from 12 to 6 mils/mo for Ni-o-nel and from 7.2 to 4.0 mils/mo for Type 309 stainless

Table 4. Corrosion Rates for Welded Specimens of Types 304 ELC and 347 Stainless Steel Exposed to Boiling Darex Fission Product Recovery Solutions(a)

Specimen	Specimen Type	Specimen Position	Cl ⁻ , ppm	Over-all Corrosion Rate, (b) mils per month	
				<u>1250 hr</u>	
Type 304 ELC	Coupon	Vapor	800	0.07	
	Coupon	Interface	800	3.7	
	Coupon	Liquid	800	5.0	
Type 304 ELC	Stressed	Vapor	800	0.52	
	Stressed	Interface	800	2.7	
	Stressed	Liquid	800	3.9	
Type 347	Coupon	Vapor	800	0.10	
	Coupon	Interface	800	2.2	
	Coupon	Liquid	800	3.7	
Type 347	Stressed	Vapor	800	0.18	
	Stressed	Interface	800	2.8	
	Stressed	Liquid	800	4.0	
				<u>576 hr</u>	<u>914 hr</u>
Type 347	Coupon	Vapor	400	0.11	0.12
	Coupon	Interface	400	1.9	2.9
	Coupon	Liquid	400	3.5	4.4
Type 347	Stressed	Vapor	400	0.06	0.08
	Stressed	Interface	400	2.5	3.3
	Stressed	Liquid	400	4.0	4.4
Type 347	Coupon	Vapor	-	0.12	0.11
	Coupon	Interface	-	2.0	3.1
	Coupon	Liquid	-	4.3	5.2
Type 347	Stressed	Vapor	-	0.10	0.11
	Stressed	Interface	-	2.5	3.3
	Stressed	Liquid	-	4.9	5.2

(a) Solution composition: 3 M HNO₃, 60 g per liter dissolved stainless steel.

(b) All specimens showed intergranular attack.

Table 5. Corrosion Rates for Welded, Stabilized Ni-o-nel
in Boiling Initial Thorex Solutions^(a)

(0.20 M Al⁺³, Liquid-Phase Exposure)

Heat Treatment	Exposure, hr	Corrosion Rate, mils per month			
		Air Quenched		Water Quenched	
		A (b) (White)	B (b) (Black)	A	B
1850°F, 0.5 hr, after welding with filler strip.	24	1.6	1.7	1.6	1.8
	96	1.2	1.4	1.2	1.3
	192	1.1	1.7	1.1	1.4
	288	1.1	1.7	1.1	1.3
	500	1.4	1.9	1.2	1.5
	755	4.0	1.7	2.7	1.4
	1000	6.6	2.1	4.6	1.6
1850°F, 2.25 hr, after welding with filler strip.	24	1.6	1.8	1.5	1.7
	96	1.2	1.4	1.2	1.3
	192	1.1	1.7	1.1	1.3
	288	1.1	1.6	1.1	1.3
	500	1.4	1.8	1.2	1.4
	755	3.8	1.7	2.6	1.3
	1000	6.2	2.0	4.4	1.5
1850°F, 10.0 hr, after welding with filler strip.	24	1.6	1.7	-	-
	96	1.2	1.3	-	-
	192	1.1	1.5	-	-
	288	1.0	1.5	-	-
	500	1.3	1.6	-	-
	755	3.4	1.5	-	-
	1000	6.0	1.8	-	-
1950°F, 2.0 hr, after welding with filler strip.	24	1.7	1.9	-	-
	96	1.2	1.3	-	-
	192	1.1	1.5	-	-
	288	1.0	1.5	-	-
	500	1.2	1.6	-	-
	755	3.3	1.5	-	-
	1000	5.7	1.8	-	-

(a) Solution composition: 13.0 M HNO₃, 0.05 M F⁻.

(b) A and B represent duplicate specimens exposed in different reflux units. Those listed under A were exposed in white Teflon and Cr(VI) was present in solution after 1000 hrs; those under B were exposed in Teflon containing a carbon filler and all corrosion-product Cr was in the (III) state.

Table 6. Corrosion Rate of Welded, Stabilized Ni-o-nel in Boiling 3.5 M H₂SO₄
Containing 50 g/l of Dissolved Stainless Steel

Specimen Type	Solution Type	Specimen Position	Corrosion Rate, mils/mo				
			24 hr	48 hr	72 hr	144 hr	480 hr
As received, sheared coupon	Synthetic, from reagents	Vapor	g ^(a)	0.02	0.01	0.00	0.01
		Interface	0.14	.24	.27	.31	0.31
		Liquid	.20	.28	.31	.36	0.35 ^(b)
Welded, heat-treated coupon	Synthetic from reagents	Vapor	g	g	g	g	0.01
		Interface	0.10	0.28	0.23	0.30	.36
		Liquid	.10	0.24	0.30	0.33	.43 ^(b)
As received, sheared coupon	From dissolution of 304 Stainless Steel	Vapor	0.59	0.59	0.62		
		Interface	2.0	1.3	1.1		
		Liquid	1.1	.80	.77		
Welded, heat-treated coupon	From dissolution of 304 Stainless Steel	Vapor	0.43	0.43	0.45		
		Interface	1.4	.98	.87		
		Liquid	1.0	.69	.65		

(a) g represents a small gain in weight

(b) Some intergranular corrosion observed. Chromium in synthetic solution was as Cr(VI).

Thorex Solutions with Al³⁺ Addition

(Poor Weldments)

Solution ^(a)	Al ⁺³ , molar	Specimen Position	Butt Welds				Original Weight, mg	Lap Welds			
			Corrosion Rate, mils per month					Weight Loss, mg			
			24 hr	48 hr	72 hr	240 hr		24 hr	48 hr	72 hr	240 hr
Initial	0.04	Vapor	4.5	3.1	2.9	1.3	2671.	g ^(b)	g	2.2	93.2
		Interface	0.41	0.26	0.79	0.69	2920.	1.5	2.0	11.2	38.0
		Liquid	0.38	0.22	0.93	0.86	2926.	1.8	1.2	11.2	31.1
Initial	0.09	Vapor	0.95	1.1	0.84	1.1	2839.	2.9	2.8	4.8	34.9
		Interface	0.32	0.17	0.16	0.13	2812.	2.6	2.1	3.4	4.9
		Liquid	0.09	0.02	0.05	0.01	2786.	2.3	1.1	3.1	3.0
Initial	0.15	Vapor	0.35	0.51	0.38	0.45	2932.	4.0	5.9	8.0	73.8
		Interface	0.13	0.13	0.13	0.06	2765.	1.1	0.8	2.5	4.1
		Liquid	0.16	0.07	0.08	g	2994.	1.7	0.9	2.9	0.7
Initial	0.20	Vapor	2.3	1.1	0.98	0.28	2958.	g	2.5	3.5	71.1
		Interface	0.20	0.06	0.09	0.01	2815.	0.4	g	1.5	3.1
		Liquid	0.00	g	g	g	3101.	0.1	g	g	g
Middle	0.04	Vapor	2.7	1.4	0.95	1.4	3193.	1.3	8.2	18.6	132.9
		Interface	0.40	0.15	0.10	0.13	2827.	3.4	2.8	3.3	10.0
		Liquid	0.07	g	0.01	0.00	3053.	3.4	2.4	3.1	5.8
Final	0.04	Vapor	0.20	0.15	0.59	1.6	2940.	2.5	4.2	5.0	7.1
		Interface	0.10	0.05	0.07	0.22	3023.	2.2	1.0	2.8	4.8
		Liquid	0.27	0.12	0.09	g	2913.	2.8	0.9	3.4	5.3

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(a) Thorex solution compositions: Initial - 13.0 M HNO_3 , 0.04 M F^- .
 Middle - 10.8 M HNO_3 , 0.04 M F^- , 0.5 M Th^{+4} .
 Final - 8.5 M HNO_3 , 0.04 M F^- , 1.0 M Th^{+4} .

(b) g indicates small gain in weight

Table 8. Corrosion Rates for Welded Titanium 75A in Boiling Thorex Solutions with Th^{+4} Additions

(Butt-welded specimens, poor weldments)

Solution (1)	Th^{+4} , Molar	Specimen Position	Corrosion Rate, mils per month		
			24 hr	48 hr	72 hr
Initial	0.04	Vapor	8.1	7.1	7.0
		Interface	2.4	3.2	3.2
		Liquid	1.7	3.0	2.9
Initial	0.09	Vapor	0.32	0.54	0.56
		Interface	0.44	0.30	0.36
		Liquid	0.96	0.40	0.24
Initial	0.15	Vapor	g ⁽²⁾	0.07	0.28
		Interface	0.50	0.27	0.22
		Liquid	1.1	0.51	0.31
Initial	0.20	Vapor	g	0.32	0.04
		Interface	0.67	0.39	0.29
		Liquid	1.2	0.50	0.31

(1) Initial Thorex composition: 13.0 M HNO_3 , 0.04 M F^- .

(2) g indicates small gain in weight.

Table 9. Corrosion Rates and Weight Losses for Welded Titanium
75A in Boiling Thorex Solutions

(Good weldments)

Solution (1)	Addition	Specimen Position	Butt Welds		Lap Welds		
			Corrosion Rate, mils per mo		Original wt, mg	Weight Loss, mg	
			24 hr	96 hr		24 hr	96 hr
Initial	-	Vapor	g(2)	6.7	2789.	23.1	125.0
		Interface	7.5	8.1	2713.	31.5	116.5
		Liquid	11.8	9.0	2620.	34.5	123.5
Initial	0.04 M Al ⁺³	Vapor	1.4	1.9	2415.	0.2	15.5
		Interface	0.60	0.51	2499.	1.9	8.6
		Liquid	1.2	0.59	2986.	2.3	11.7
Initial	0.09 M Al ⁺³	Vapor	g	1.6	2514.	0.1	4.4
		Interface	0.39	0.02	2874.	1.5	0.6
		Liquid	0.37	0.02	2526.	1.7	0.7
Initial	0.15 M Al ⁺³	Vapor	0.00	0.02	2649.	0.5	2.6
		Interface	0.26	0.45	2689.	1.0	0.8
		Liquid	0.31	0.05	2406.	1.1	0.9
Initial	0.20 M Al ⁺³	Vapor	0.45	0.64	2761.	0.1	0.4
		Interface	0.31	0.03	2424.	0.6	0.2
		Liquid	0.21	g	2834.	0.9	0.2
Initial	0.04 M Th ⁺⁴	Vapor	0.33	6.0	-	-	-
		Interface	3.5	3.1	-	-	-
		Liquid	1.7	2.5	-	-	-
Middle	0.04 M Al ⁺³	Vapor	0.03	0.03	2674.	5.4	5.5
		Interface	0.25	0.04	2369.	0.6	1.5
		Liquid	0.26	0.06	2516.	0.8	0.8
Final	0.04 M Al ⁺³	Vapor	0.03	0.54	-	-	-
		Interface	0.22	0.09	-	-	-
		Liquid	0.41	0.14	-	-	-

1) Thorex solution compositions: Initial - 13.0 M HNO₃, 0.04 M F⁻
Middle - 10.8 M HNO₃, 0.04 M F⁻, 0.5 M Th⁺⁴
Final - 8.5 M HNO₃, 0.04 M F⁻, 1.0 M Th⁺⁴

2) g indicates a small gain in weight.

steel over 72 hour exposures. It will be observed (Table 10) that there was relatively little change in rate with time for either alloy and that addition of the inhibiting substances caused an increase in the vapor phase corrosion from a few hundredths of a mil/mo to as high as 0.7 mils/mo.

Table 10. Scouting Experiments in Inhibited Zirflex Dejacketing Solutions^(a)

Specimen	Inhibitor Added ^(b)	Specimen Position	Corrosion Rate, mils per month			
			24 hr	48 hr	72 hr	144 hr
Ni-o-nel ^(c)	No	Vapor	0.04	0.03	0.02	--
		Interface	9.9	9.9	9.6	--
		Liquid	12	12	12	--
Ni-o-nel ^(c)	Yes	Vapor	0.24	0.14	0.15	0.09
		Interface	3.6	2.9	3.2	3.5
		Liquid	6.6	5.7	6.0	6.4
Type 309 ^(d)	No	Vapor	0.02	0.01	0.00	--
		Interface	6.8	5.9	5.5	--
		Liquid	7.8	7.1	7.2	--
Type 309S Cb ^(d)	Yes	Vapor	0.78	0.64	0.73	0.46
		Interface	3.6	2.6	2.3	1.8
		Liquid	5.3	4.3	4.0	4.3

- (a) Zirflex dejacketing solution composition: 6.0 M NH_4F , 1.0 M NH_4NO_3 .
- (b) Inhibitors added were: 0.05 M $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$, 0.05 M $\text{Na}_2\text{SiO}_3 \cdot 9 \text{H}_2\text{O}$.
- (c) Stabilized Ni-o-nel specimens were welded, heat treated for 0.5 hr at 1850°F and air quenched after welding, and surface ground prior to exposure.
- (d) Specimens of Types 309 and 309 (Cb) were exposed in the as-received condition.

2.0 WASTE TREATMENT AND ION EXCHANGE STUDIES (J. T. Roberts)

2.1 Characterization of High Level Wastes (H. W. Godbee, J. E. Davidson)

Batch evaporation of synthetic acidic TBP-25¹⁶ ($\text{Al}(\text{NO}_3)_3\text{-HNO}_3$) waste was carried out in a glass flask with gentle heating and continuous stirring to 146.2°C. The residue was a thick, sticky, white liquid with a tinge of yellow at 146.2°C and a crystalline white solid with a slight yellow cast (density 1.74 g/ml) at 24°C. The volume reduction factor was about 5.1. The total volumes, weights, and g-moles of NO_3^- contained in the residue and condensate are given in Table 11. Volume of condensate,

weight of condensate, and moles of NO_3^- in condensate as a function of liquid temperature in the still are shown in Fig. 9. The weight per cent nitrate in the condensate as a function of temperature is given in Fig. 10. The per cent of original free nitric acid in the condensate as a function of weight of original charge distilled over is shown in Fig. 11. The weight per cent nitrate in the condensate versus weight per cent nitrate in the still pot is shown in Fig. 12.

Table 11. Batch Evaporation of Acidic TBP-25 Waste to 146.2°C

TBP-25 Waste Composition: 1.6 M $\text{Al}(\text{NO}_3)_3$, 0.002 M $\text{Fe}_2(\text{SO}_4)_3$,
0.02 M $(\text{NH}_4)_2\text{SO}_4$, 0.01 M $\text{Hg}(\text{NO}_3)_2$,
0.03 M NH_4NO_3 , 0.5 M HNO_3

	Volume (at 24°C)	Weight (grams)	g-mole NO_3^-
Initial TBP-25 Waste	4000	5160	21.4
Condensate	3405	3752	11.9
Residue	788	1400	

Calcination of 258 grams of the residue to 650°C yielded a porous, crumbly, off-white solid weighing 86 grams. The density of the calcined waste was about 0.5 g/cc. The volume reduction factor on evaporation and calcination is about 4.

2.2 Ion Exchange Studies (R. R. Holcomb, J. T. Roberts)

The proposed flowsheet for recovery of uranium and plutonium from Sulfex decladding solutions by ion exchange¹⁷ required an undesirably large dilution. This large dilution is necessary to achieve reasonable distribution coefficients for uranium and plutonium on quaternary amine resins and Dowex-50, respectively. Primary amines, e.g., the solvent Primine JMT and 1-nonyldecylamine, offer high distribution coefficients without the need for dilution. However, primary amine ion exchange resins are not available. Polyamine resins, which contain some primary amine resin, showed the following distribution coefficients when contacted with synthetic Sulfex decladding solutions:

U-IV in 3 M H_2SO_4 : Dowex 3 Resin	4.2
Pu-IV in 3 M H_2SO_4 : Dowex 3 Resin	8.2
U-IV in 3 M H_2SO_4 : Amberlite IR-45	4.8
Pu-IV in 3 M H_2SO_4 : Amberlite IR-45	8.7

These distribution coefficients are probably not high enough to be competitive with the liquid primary amines. Attempts were made to solidify Primine JMT and 1-nonyldecylamine by sorbing them on oven dried silica gel, with little success. Activated alumina, glass wool and charcoal are now being considered as alternates to silica gel.

Fig. 9. Batch Evaporation of Acidic TBP-25 Waste to 146.2°C

Fig. 10. Batch Evaporation of Acidic TBP-25 Waste to 146.2°C

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Fig. 11. Batch Evaporation of Acidic TBP-25 Waste to 146.2°C

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Fig. 12. Batch Evaporation of Acidic TBP-25 to 146.2°C

2.3 Maritime Reactor Waste Disposal Studies (R. R. Holcomb, J. T. Roberts)

Test operation of the 304SS pressure loop was continued. Pressure fluctuation, particularly above 1500 psi, is the most noticeable defect. The following changes have been made in the loop in order to reduce these fluctuations: (1) a new Lapp LS-20 "Microflo" pump, designed to operate under low flow and 2000 psi pressure conditions, has been ordered; (2) a new head with mated check valves was installed in the Lapp CPS-1 pump now in service; (3) an additional Hoke ball type check valve was placed in the line in front of the pump; (4) two Hoke vernier type needle valves were installed in series for use as fine control throttling or pressure let-down valves; and (5) a tank of argon was incorporated into the system to furnish a gas over-pressure. These changes have greatly improved the operation of the loop, but not to the level desired. The new pump, instrumented for automatic on-off control, should produce the desired operating conditions.

3.0 FEED MATERIALS PROCESSING (O. C. Dean)

3.1 Production of UO_2 for Reactor Fuels

The production of UO_2 pellets for reactor fuels is being studied according to several approaches:

1. Pure UO_2 is being prepared by using crystalline $UO_4 \cdot H_2O$ (to be referred to as UO_4) as the starting material.
2. Pure UO_2 and doped UO_2 will be tested for sinterability.
3. The surface area, particle size, and certain chemical properties of UO_2 will be studied in order to provide indices to sinterability.
4. Development of a simple test to predict the sinterability of UO_2 powder.

3.11 Preparation of Crystalline UO_4 (H. B. Whetsel)

Precipitation of UO_4 from acidic solutions, ¹⁸ i.e., pH 0.2 or less, is being evaluated as a method for producing a superior grade of UO_2 . Common practice is to precipitate UO_4 at a pH > 2.0.

In two experiments, $UO_4 \cdot 2 H_2O$ was precipitated from 100 ml of 0.015 M uranyl nitrate by the addition of 16 ml of a solution 0.19 M in HNO_3 and 2.0 M in H_2O_2 . The molar ratios of the reactants was 1:2:0.2, $UNH:H_2O_2:HNO_3$, and the precipitation temperature was 85°C. Precipitation was begun by adding the H_2O_2 reagent dropwise to the agitated uranyl nitrate solution until a haze developed. The nuclei thus formed were aged at 85°C for 5 min, then the remainder of the reagent was added dropwise during 1/2 hr. The product consisted of hexagonal needles, ~1 x 4, in dia, and had a settled density of ~8. The ppt had rejected about 80% of the UX_1 and UX_2 according to an estimate based on a portable G-M counter. Uranium peroxide was also precipitated at 50, 27.5 and 5°C according to the above procedure with only the temperature being varied. The precipitations were nearly quantitative

at 27.5 and 5°C. Platelets were produced at 5°C but the particle size of the other products were below the limit of resolution of the optical microscope ($< 1\mu$). The settled densities of these precipitates were below that of the 85°C product but all settled and filtered rapidly.

In a fifth experiment, 134 ml of reagent 2.46 M in H_2O_2 and 2.38 M in HNO_3 was added rapidly to 100 ml of 0.1 M $UO_2(NO_3)_2$ at 50°C. The precipitate settled slowly, and therefore was aged at ~45°C for 21 hr and then was filtered at 35°C. The $UO_4 \cdot 2 H_2O$ product occurred as hexagonal needles ~15 μ long and 1 μ in dia. The decontamination factor from uranium daughters was ~125 and the filtration rate was fast but uranium recovery was only ~50%. It was concluded that the HNO_3 concentration (2.4 M) was too high for good recovery, and the procedure would have value only if the precipitate particles were to have special merit in UO_2 preparation.

3.12 Surface Area and Particle Size (H. B. Whetsel)

A program is planned to define the relationships between surface area and particle size. Sedimentation rates will be used to estimate particle size. Surface areas will be determined according to the BET method and the method of Mills and Whetsel (unpublished). This method consists in the adsorption of perfluoro acids or their salts from either organic or aqueous solution. In these determinations, perfluorooctanoic acid in carbon tetrachloride-ethyl ether is used. About 4 g of the acid is dissolved in a mixture of carbon tetrachloride and ethyl ether (390 ml of carbon tetrachloride and 10 ml of ether). The amount of acid is determined iodometrically. Forty milliliters of the reagent is mixed with 5 g of the oxide in a centrifuge tube, stirred, stoppered, and centrifuged. Twenty milliliters of the supernatant is removed and the amount of acid was determined iodometrically. By difference, the amount of adsorbed acid was determined. By assigning a $10\text{-}\text{\AA}^2$ cross sectional area to the acid molecule, it was determined that 6.88 mg would be equivalent to 1 m^2 . The perfluorooctanoic acid molecule is too big to enter the pores that are accessible to nitrogen. Accordingly it may be possible to determine the effect of porosity on sinterability. It is also possible that a short-chain acid or salt, such as the perfluorobutyric, may make it possible to further characterize the powders in terms of porosity.

In initial tests, six BET-analyzed oxides of known sintered density were tested according to the adsorption-from-solution method (Table 12). It appears that by use of the two methods it is possible to determine the degree of porosity. Surface areas by the adsorption of perfluorooctanoic acid and BET methods correlate fairly well and increase quite regularly with sintered density. The irregularities, i.e., in No. 94 and 130 may be due to the size of pores as discussed above.

3.13 Characterization of UO_2 Powder Reactivity by Acid Titration and Reduction of $Fe(III)$ (O. C. Dean)

The reactivity of hydrolyzed UO_2 with HCl has been studied as an index to the sinterability of a UO_2 precipitation.¹⁹ A pure sample of UO_2 , prepared by air-oxidation of uranium hydride, was titrated potentiometrically.

Table 12. Comparison of Surface Areas Determined According to the BET Method and the Method of Mills and Whetsel

Sample Number	Surface Area by Adsorption from Solution (m^2/g)	Surface Area by BET Method (m^2/g)	Sintered Density (%)
4	0.2	0.45	76.0
98	1.4	3.0	85.0
97	3.3	4.8	92.6
94	2.5	4.9	93.2
99	3.1	4.4	93.6
130	2.1	6.0	95.0

by the previously described procedure. There was no fluoride inflection in the curve, hence no correction. The acid titer or acid number, defined as milliequivalents of $\text{HCl} \times 100$ adsorbed per gram of UO_2 between the two equivalence points at pH 7 and 3, was 7.7 (Table 13). The BET surface area for this oxide was $2.4 \text{ m}^2/\text{gram}$. From Figure 1 in the reference above, surface area should predict a sintered density for the powder of 81% of theoretical, while acid number would predict 85%. Consequently, it was concluded that titration can be used to predict sintering characteristics. The sintering characteristics of this particular sample were not determined by pressing and sintering, however, because of the limited amount of powder available.

Ferric Iron Reduction by UO_2 and Sinterability

This study is an extension of the search to find simple, reliable, quickly-applied tests which will be an index to the reactivity (sinterability) of UO_2 powder. The reducing property of UO_2 was exploited in determining the relative rate of reduction of 0.01 N ferric ion in 50 ml of a 0.2 N sulfuric acid slurry of 10 grams of various oxides at 100 and at 25°C.

In the procedure at 100°C, 10 grams of UO_2 was introduced into 50 ml of a refluxing 0.2 N H_2SO_4 - 0.016 M Fe III solution under an argon blanket with vigorous stirring. After 1 min the slurry was vacuum-filtered. The filtrate was titrated to a "ferroin" end point with 0.1 N KMnO_4 to determine the amount of Fe^{+++} reduced to Fe^{++} . The procedure in the series at 25°C was the same, except that the slurry was held for 1 min at 25°C before filtration instead of 100°C. The iron number is defined as the milligrams of ferric ion reduced to ferrous ion per gram of UO_2 . Results for the oxides tested are shown in Table 13. For comparison, the surface area, sintered density and fluoride-corrected acid-number are included. Neither hot nor cold iron numbers correlated as well with sintered density as did surface area or acid number. The reduction of iron in both hot and cold tests was extremely rapid. About 90% of the ferric iron was reduced in the 1 min contact time. There was also evidence e.g., oxides numbers 98 and 825, that factors other than the surface of the oxide were involved in the reduction.

Table 13. Physical and Chemical Properties of Ceramic Grade UO₂ Samples

Oxide No.	Specific Area (m ² /g)	Sintered Density (% of Theoretical)	Acid No. ¹ ($\frac{\text{meq H}^+ \times 100}{\text{g UO}_2}$)	100°C Iron No. ₊₊ ($\frac{\text{mg Fe}}{\text{g UO}_2}$)	25°C Iron No. ₊₊ ($\frac{\text{mg Fe}}{\text{g UO}_2}$)
825	0.14	-	0.7	13.9	2.10
4	0.45	76	0.8	-	15.66
98	3.00	85.0	7.7	21.10	18.98
97	4.80	92.6	9.8	21.30	19.91
94	4.90	93.2	10.7	21.85	18.36
99	4.40	93.6	10.7	-	20.01
130	6.00	95.0	10.7	21.3	19.50

(1) Acid number = milliequivalents $\text{H}^+ \times 100/\text{g UO}_2$ required to titrate oxide from pH of 7 to 3.

3.2 Reduction of Uranium Fluoride with Sodium (O. C. Dean)

Reduction of $\text{UF}_4 \cdot 2 \text{NaF}$ with sodium was conducted in a stainless steel reactor lined with Norton high-density magnesia. The mole ratio of reactants was 1:2:6 for $\text{UF}_4:\text{NaF}:\text{Na}$, providing a sodium excess of 50%. The system was prepared as described previously²⁰ by careful vacuum outgassing of the fluoride mixture at 400°C for 16 hr to remove air and HF. The system was then back-flushed with argon at 25°C, and the sodium added. The system was again evacuated for 1 hr at 25°C, then at 200°C for 2 hr to remove reactive gases from the sodium. The temperature was then advanced to the melting point of the salt (700°C) and held for 1-1/2 hr. Finally, the temperature was increased to 850°C for 4 hr, then to 950°C for 6 hr to assure a molten mixture throughout the reaction period.

A metallic deposit on the reactor head and in the upper 1/3 of the reactor proved to be partly magnesium metal and partly sodium. The product in the crucible appeared to be largely UO_2 and NaF (no observable green UF_4). Apparently at 950°C, the sodium vapor reduces some of the magnesium oxide to magnesium. The sodium oxide product probably converted UF_4 to UO_2 . Some evidence for surface attack of the MgO could be seen, particularly at the surface of the fluoride melt. There was no spalling nor cracking of the magnesia liner.

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