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CHEMICAL TECHNOLOGY DIVISION
CHEMICAL DEVELOPMENT SECTION B
MONTHLY PROGRESS REPORT
MARCH 1960

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CHEMICAL TECHNOLOGY DIVISION

CHEMICAL DEVELOPMENT SECTION B

MONTHLY PROGRESS REPORT FOR CHEMICAL DEVELOPMENT SECTION B

MARCH, 1960

R. E. Blanco

OAK RIDGE NATIONAL LABORATORY
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ABSTRACT

Dissolution of Consolidated Edison Fuel

Consolidated Edison type fuel pellets (96% ThO_2-4% UO_2; 92% of theoretical density) were exposed in the ORR to power densities of 16 to 160 Mw/metric ton of thorium for 3 min. In no case were the fuel pellets shattered.

Zircex Process for Dissolution of Zirconium-bearing Fuels

Fused sodium or potassium hydroxide at temperatures of 400°C or higher was used to shatter Consolidated Edison pellets (93% of theoretical density) into fragments, most of which had thicknesses less than the radius of the original pellet. Similar pellets were dissolved in refluxing 14.8 and 7.4 M H_3PO_4 at rates of 1.4 and 0.08 mg/cm^2-min, respectively and in fused ammonium bifluoride at 220°C at a rate of 7 mg/cm^2-min.

Two runs using nickel turnings as packing in the uranium chloride condenser resulted in >10% uranium loss to the zirconium chloride condensate.

Dissolution of Sodium-bonded Fuels by Darex and Sulfex Processes

A literature survey was made of the thermodynamics and limits of flammability of gases expected when sodium-bonded, stainless steel-clad fuels are dissolved in dilute aqua regia or sulfuric acid. Vapor-phase explosions are a definite possibility with the aqua regia system when sodium is dissolved and hydrogen is formed. Significant amounts of hydrogen are not formed on dissolution of stainless steel under process conditions. Reactions between nitrogen oxides and hydrogen are highly exothermic and mixtures of the gases are explosive over wide concentration ranges.

Hydrogen in Darex Off-Gas

The hydrogen in off-gas from batch Darex type dissolutions of 304 stainless steel increased from about 0.15 vol % in 5 M HNO_3-2 M HCl to 2.0 vol % in 6 M HCl-1 M HNO_3. In 5 M HNO_3-2 M HCl and 4 M HNO_3-3 M HCl, a maximum concentration of hydrogen, 0.35-0.5 vol %, was observed when 30 to 50% of the total dissolving time had elapsed. In 6 M HCl-1 M HNO_3, the hydrogen concentration remained in the 1.5-3.5 vol % range throughout dissolution.

Tin Dissolution in HF-H_2O_2

Tin dissolved at rates exceeding 10 mg/cm^2-min in 5 M HF containing 2 M or more H_2O_2 at 13-70°C. The rate at 13°C decreased over 10-fold when the 5 M HF was replaced with 5 M NH_4F.

Recovery of Uranium and Thorium from Graphite Fuels

A technique for simultaneously disintegrating to -20 mesh and leaching 1.2 x 1.4 x 4.5 cm pieces of graphitized fuels by boiling in white, fuming nitric acid (90% HNO_3, 0.2% maximum dissolved oxides) has been developed. Two acid treatments and suitable water washes recovered 99.85% or more of the uranium in fuels containing at least 5% uranium. Metal recovery decreased to 99% when the uranium concentration in the fuel was 2%. When 70% acid was used instead of 90% in the second leach, metal recoveries decreased by at least 0.2%.

Immi Hot Cell Facility

The facility dissolution and feed clarification equipment operated satisfactorily on uranium-aluminum alloy which simulated Foreign Research Reactor fuel. The uranium extraction was inadequate (0.33% uranium loss) in the mixer-settler using the 6% TBP flowsheet because of insufficient organic-aqueous contact in the mixers or back mixing.

Dissolution of Yankee Atomic Fuel

Simulated Yankee Atomic Fuel containing fissia equivalent to 10,000 Mwd/T U was dissolved by both the Sulfex and Darex head end process. The acid insoluble residue obtained from the Sulfex process was 0.48% of the total fuel weight. Of this amount 0.44 wt % was SiO_2 and the remaining 0.04 wt % was fissia and other unidentified material. The latter corresponds to ~ 8.7% of the initial fissia. Using the Darex process, the residues were ~0.47 wt % of the fuel, of which 0.36 wt % was SiO_2 and the remaining 0.06 wt % was fissia. The latter corresponds to 9.5% of the initial fissia. These insoluble residues do not include those that might be derived from special brazing alloys used with complete fuel assemblies.

Solvent Extraction Studies

Uranium and thorium may be costripped from a neutral 30% TBP solution using an equal volume of 0.008 $\underline{M}$ $Al(NO_3)_3$ in seven stages. A larger volume of strip solution or more stages would be required to strip the uranium and thorium from organic solutions containing greater than 0.1 $\underline{M}$ HNO_3. Distribution coefficients of uranium and thorium have been determined in a system containing 30% TBP-Amsco; 0.2 to 20 g/l U, and 0 to 70 g/l Th.

Corrosion Studies

In Zirflex dissolver solutions, the presence of 0.003 to 0.03 $\underline{M}$ H_2O_2 lowered the corrosion rates of Hastelloy F, Type 309 SCb stainless steel and Ni-o-nel by factors varying from 5 to 10. In the presence of 0.03 $\underline{M}$ H_2O_2, maximum rates for a 9-hr exposure were 1.2, 1.7 and 2.2 for Hastelloy F, Type 309 SCb and Ni-o-nel, respectively. In Zirflex solutions and fluoboric-nitric acid solutions the presence of 0.4-0.6 Cr(VI) lowered the corrosion rate of titanium from 500 to 40-60 mils/mo. Titanium-0.2% Pd alloy showed somewhat higher corrosion rates than Ti-45A in these high fluoride solutions. The presence of 0.1 M borate in initial Thorex dissolver solution lowered the corrosion rate of titanium in the solution phase from 6-7 to 0.3 mils/mo and eliminated pitting in the vapor phase at low thorium concentration. The presence of borate did not eliminate pitting observed in the vapor above solutions containing high concentrations of thorium.

Specimens of Type 304L stainless steel exposed to Darex-Purex simulated waste solutions continued to show intergranular attack in solutions at 65° and $85^{\circ}C$ although over-all rates for approximately 2000 hr exposures were only 0.1 and 0.41 mils/mo, respectively. In N_2-CCl_4 at $600^{\circ}C$, Illium R, Nichrome V, Inconel and INOR-8 performed the most satisfactorily out of a group of 10 alloys though minimum rates in every case were ≥ 26 mils/mo.

Radiation Damage to Solvents and Diluents

Six samples of 1 M di-sec-butyl phenylphosphonate in Solvesso-100 were irradiated to levels of 45, 135, and 400 watt-hr/liter after being contacted with 0.3 or 1 N HNO_3. G values for both nitric acid destroyed and monobasic organic acid formed decreased with increasing dose.

Purification of Degraded Solvent by Distillation

Distillation of 30% TBP in Amsco 125-82, degraded either by irradiation to 120 watt-hr/liter with cobalt-60 gamma radiation or by extended use in the ORNL Purex pilot plant, was tested on a laboratory scale for use in solvent repurification operations. Using U-233/Ru-106 tracer extraction-scrub-strip tests as the basis for comparison, it was found that rapid distillational separation of diluent and TBP fractions from each other, followed by separate fractional distillation in a ~42 theoretical plate column, yielded products comparable to those from distillation of "as received" Amsco 125-82 and TBP. Materials losses were in the order of 20% but should be much lower in larger scale operations. Using a Zr-Nb tracer extraction-scrub test as the basis for comparison, molecular distillation was shown to yield diluent and TBP fractions as good as or better than the control materials. No efforts were made to obtain a good materials loss value in the molecular distillation test.

Waste Treatment

In the batch evaporation of simulated Purex 1WW waste concentrate containing additives to reduce sulfate volatility, ruthenium volatility was reduced from 66-79% to 15% by the presence of TBP and to 7-8% when the experiments were carried out in a NO atmosphere, with or without the presence of TBP. Using "Micro-Cel E" (a synthetic calcium silicate) as an additive reduced the ruthenium color in the condensate but not the Ru-106 tracer activity. Whether this is because the "cold" and "hot" ruthenium forms present were not in equilibrium is under further study.

Evaporation and calcination of small batches of simulated Purex 1WW in the presence of 8 to 270 ml TBP per liter failed to produce any violent reactions or any rapid rises in pot temperature.

The strongest solid block made from simulated Sulfex decladding waste had a compression test strength of 3000 psi. It was made by adding 0.26 parts by weight $Ca(OH)_2$, 0.26 parts sand and 0.55 parts Portland cement to one part waste. The resulting solid had a 45% greater volume than the starting waste. Blocks made without sand showed only a 23-28% volume increase but were weaker, 1250-1350 psi strength, though this may be strong enough for transportation and storage purposes.

Hydroxyl form strong base anion exchange resin removed 72% of the gross fission product activity from ORNL low level process water waste and raised the pH of the effluent water to 11.3, high enough to use with a phenolic cation exchange resin in a second column. This column removed 96% of the remaining mixed activity from a total of approximately 2000 volumes of water per volume of phenolic resin. The phenolic resin was regenerated with about 5 volumes of 5 M $NaNO_3$-0.5 M HNO_3. The volume of regenerant required might be reduced by a factor of two by the "split elution" technique but this has not yet been demonstrated.

Ion Exchange Studies

Making the 10X diluted synthetic Purex 1WW 0.124 M in oxalic acid increased the breakthrough capacity of Dowex 50 resin by a factor of 2-3 for strontium and by a factor greater than 3 for rare earths. The capacity of Dowex A-1 chelating resin for strontium and rare earths from 3X diluted Purex 1WW containing 0.33 M tartrate was increased about five times by raising the pH from 5.5 to 7.5.

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Work was continued on studies of the kinetics of the reduction of $CaSO_4$ by hydrogen. Two determinations of the reduction rate using a semi-automatic recording thermogravimetric balance indicated that the reaction was controlled by bed diffusion. The observed weight losses agreed with the theoretical for the reduction to CaS to within 10 parts in 1000. The hydrogen flow was 1.4 liters/min.

Under static conditions, the rate of reduction of $CaSO_4$ was nearly independent of pressure in the 200-600 mm range indicating that the reaction is not adsorption controlled. Three separate determinations were made where the dead volume in the system was varied. Calculation of absolute rates awaits measurement of the dead volumes.

CONTENTS

1.0 POWER REACTOR FUEL PROCESSING

1.1 Dissolution Studies (L. M. Ferris)

1.1.1 Dissolution of Consolidated Edison Fuel (A. H. Kibbey)

Twelve aluminum capsules containing 95.6% ThO_2-$UO_{2.05}$ pellets (92% of theoretical density) were inserted into the ORR at power levels ranging from 1 to 10 Mw. The specific power generated during the 3-min irradiation ranged from 16 to 160 Mw/metric ton of thorium. The experiments were designed to determine the extent of fracturing which occurred, the particle size of the fines produced, and the rate of dissolution of the pellets in boiling 13 $\underline{M}$ HNO_3-0.04 $\underline{M}$ NaF-0.1 $\underline{M}$ $Al(NO_3)_3$. All 12 capsules have been declad and the pellets inspected. No fracturing occurred except in one case where the capsule was dropped 2 floors down a drain in the ORR building.

The capsules contained two MgO spacer pellets in addition to the fuel pellets. These were removed manually after the aluminum jacket had been dissolved in 2 $\underline{M}$ NaOH-1.78 $\underline{M}$ $NaNO_3$. After dejacketing, the vessel was rinsed three times with dilute caustic. The maximum amount of fines found was less than 0.5% of the original pellets and could have been produced solely by attrition. No gross cracking of the pellets was observed.

The pellets were dissolved in a series of 5-hr digestions in boiling 13 $\underline{M}$ HNO_3-0.04 $\underline{M}$ NaF-0.1 $\underline{M}$ $Al(NO_3)_3$. In the first digestion a 200% excess of reagent is used while in each additional digestion only a half-volume is used. Preliminary data indicate that about 85% of the pellets is dissolved in the first, 5-hr, digestion and that after 3 additional digestions some residue remains. The residue was identified by x-ray analysis as ThO_2; however, the lattice constant is slightly lower than that expected for pure ThO_2, which is indicative of the presence of UO_2. This point is receiving further study.

In other studies of the dissolution of ThO_2-UO_2 pellets the fact that the rate of dissolution in 13 $\underline{M}$ HNO_3 is at its maximum when the fluoride concentration is about 0.07 $\underline{M}$, has been confirmed. These experiments were conducted in Teflon equipment and confirmed previous results obtained in glass.

1.1.2 Alternative Dissolution Methods for Consolidated Edison Pellets (T. A. Gens)

In the Darex and Sulfex decladding - Thorex core dissolution flowsheets for Consolidated Edison fuel, the low dissolution rate of dense (>90% of theoretical) Consolidated Edison core pellets in Thorex solution presents a difficult problem.[1] Alternative dissolution procedures, preferably compatible with the present flowsheets, are being sought.

Fused sodium or potassium hydroxide at temperatures of 400°C or higher was used to shatter Consolidated Edison pellets (93% of theoretical density) into many fragments, most of which had thickness less than the radius of the original pellet (Fig. 1). The pellets at room temperature were dropped into the fused caustic. The shattering phenomenon might be used in the present Sulfex decladding flowsheet if a material of construction sufficiently resistant to both sulfuric acid and fused caustic can be found. The fused caustic would be removed from the dissolver previous to Thorex dissolution of the fragments. Enough sodium or potassium hydroxide probably would be required in the shattering procedure to neutralize about one-half of the unused nitric acid in the Thorex solution upon blending the two streams after dissolution. The caustic would have to be blended with the Thorex solution before solvent extraction to recover uranium which enters the fused caustic during the shattering treatment. The uranium loss to the fused salt exceeded 0.1% of the total uranium in a run in which a pellet was shattered in fused potassium hydroxide at 500°C. No shattering occurred in liquid bismuth at 600°C or in fused potassium hydroxide at 500°C if the pellet and potassium hydroxide were warmed together from room temperature. Lithium hydroxide at 500°C repeatedly produced fragmentation into only three pieces or less.

In 1-hr tests, Consolidated Edison pellets (93% of theoretical density) were dissolved at rates of 1.4 and 0.08 mg/cm²-min in refluxing 14.8 and 7.4 $\underline{M}$ H_3PO_4, respectively. These rates are not high enough to appear attractive for a dissolution procedure.

Fused ammonium bifluoride at 220°C has been used to dissolve low density Consolidated Edison pellets (about 80% of theoretical) at rates of 6-7 mg/cm²-min.[2] In a 3-hr test, this reagent dissolved a dense Consolidated Edison pellet (93% of theoretical) at the same average rate, 7 mg/cm²-min. This reagent has the disadvantage that there does not appear to be a simple method of recovering the uranium and thorium after dissolution.

1.1.3 Dissolution of Sodium-Bonded Fuels by Darex and Sulfex Processes (K. S. Warren)

Sodium or NaK will be used as a bond between the stainless steel cladding and the core material in several power reactor fuel elements. Before attempting to dissolve fuels such as the SRE-1 (metallic uranium core) in dilute aqua regia or declad fuels such as the CPPD-1 (U-Mo alloy core) in sulfuric acid, the possibility of the gaseous products entering into explosive reactions with hydrogen produced by reaction of sodium or potassium with water must be considered. Standard state heats and free energies of several possible gas-phase reactions were computed and the limits of flammability of many of the mixtures were surveyed. A comprehensive report on this subject will be issued.[3]

The literature survey revealed that virtually all reactions between nitrogen oxides and hydrogen are highly exothermic and that mixtures of these

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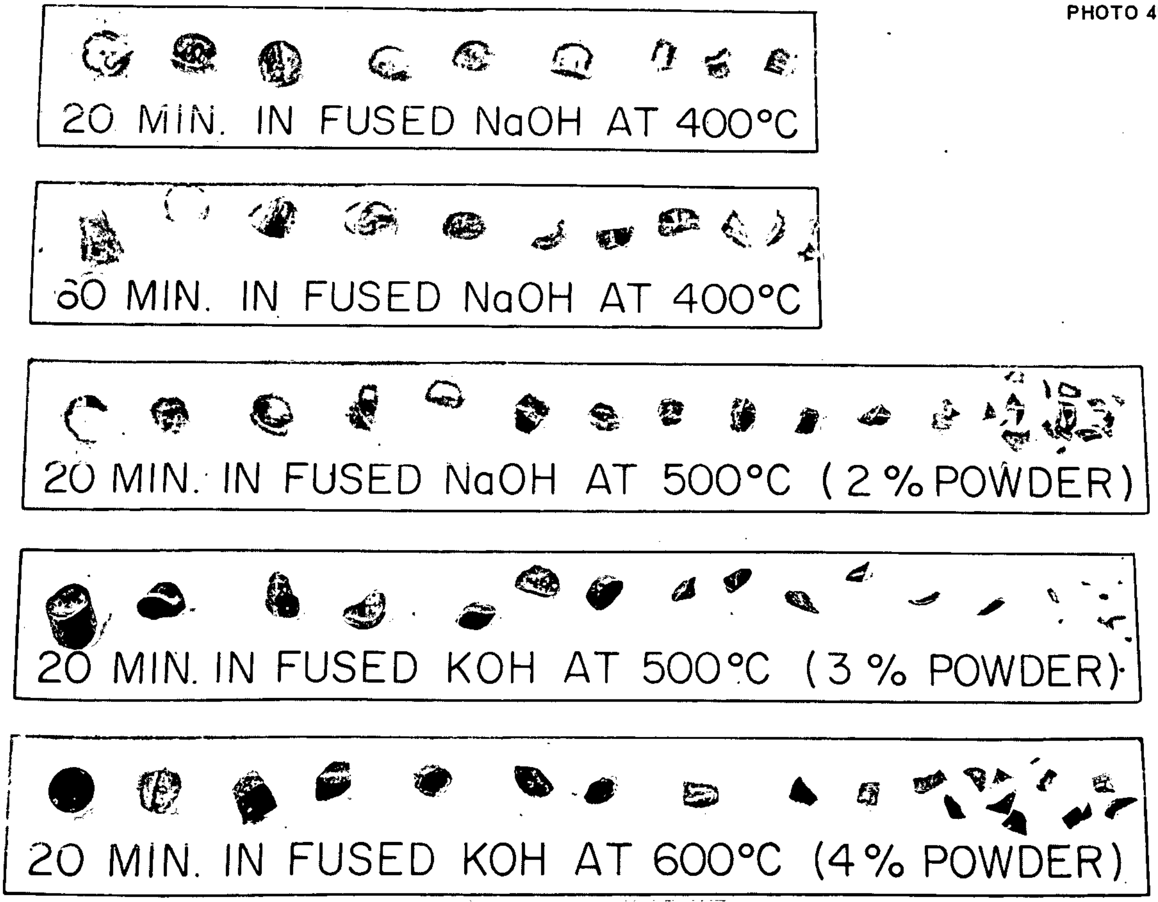

Fig. 1. Shattering of Consolidated Edison Pellets (93% of theoretical density) in fused KOH or NaOH.

components can be explosive in nearly all proportions. It was concluded, therefore, that exposure of sodium or NaK to dilute aqua regia is definitely hazardous. Furthermore, dissolution of metals in aqua regia under conditions where hydrogen is produced is also dangerous. On the other hand, there appears to be no great hazard from vapor-phase reactions when sodium or NaK is exposed to sulfuric acid. Since hydrogen is the only gaseous product, the stainless steel cladding from sodium-bonded fuels could, therefore, be dissolved in sulfuric acid if the reaction of sodium and water could be controlled or contained.

1.1.4 Hydrogen in Darex Off-Gas (T. A. Gens)

The amount of hydrogen evolved during Darex dissolution of 304 stainless steel is a problem of major concern because of the explosive potential of hydrogen in certain gas mixtures and the difficulty in removing hydrogen from the off-gas.[4]

Experiments were made to determine the volume percent hydrogen in the off-gas from Darex-type dissolutions as a function of the fraction of total dissolving time (Fig. 2) and the total gas evolved throughout dissolution (Fig. 3). In the latter experiments the total volume of gas was calculated, based on the assumption that 0.75 mole of NO and 0.75 mole of NO_2, and no significant quantities of other gases, are evolved per mole of 304 stainless steel dissolved. On the basis of this calculation, the hydrogen in the off-gas from batch Darex-type dissolutions of stainless steel increased from about 0.15 vol % in 5 M HNO_3-2 M HCl to 2.0 vol % in 6 M HCl-1 M HNO_3 (Fig. 3). Periodic sampling of the off-gas stream from similar dissolutions (Fig. 2) showed that the rate of hydrogen evolution did not fluctuate greatly throughout dissolution. In 5 M HNO_3-2 M HCl and 4 M HNO_3-3 M HCl a maximum concentration of hydrogen, 0.35-0.5 vol %, was observed when 30 to 50% of the total dissolving time had elapsed. In 3 M HNO_3-4 M HCl, the maximum hydrogen concentration, 0.7 vol %, was observed just after dissolution started. This concentration decreased to nearly 0.2 vol % when 30% of the total dissolving time had elapsed and remained constant during the remainder of dissolution. In 1 M HNO_3-6 M HCl, the hydrogen concentration remained in the 1.5-3.5 vol % range throughout dissolution.

Experiments are planned in which the evolution of nitrous oxide, N_2O, will be measured.

1.1.5 Zircex Process for Dissolution of Zirconium bearing Fuels (T. A. Gens)

In the Zircex process, U-Zr alloy fuels are hydrochlorinated at 350-800°C to produce and separate volatile zirconium chloride and from relatively nonvolatile uranium trichloride.[5] After hydrochlorination, the residue consisting of mixed oxides and chlorides of uranium and zirconium is converted to volatile chlorides by chlorination at 600°C with carbon tetrachloride vapor in nitrogen carrier gas.[6] The uranium chloride is selectively

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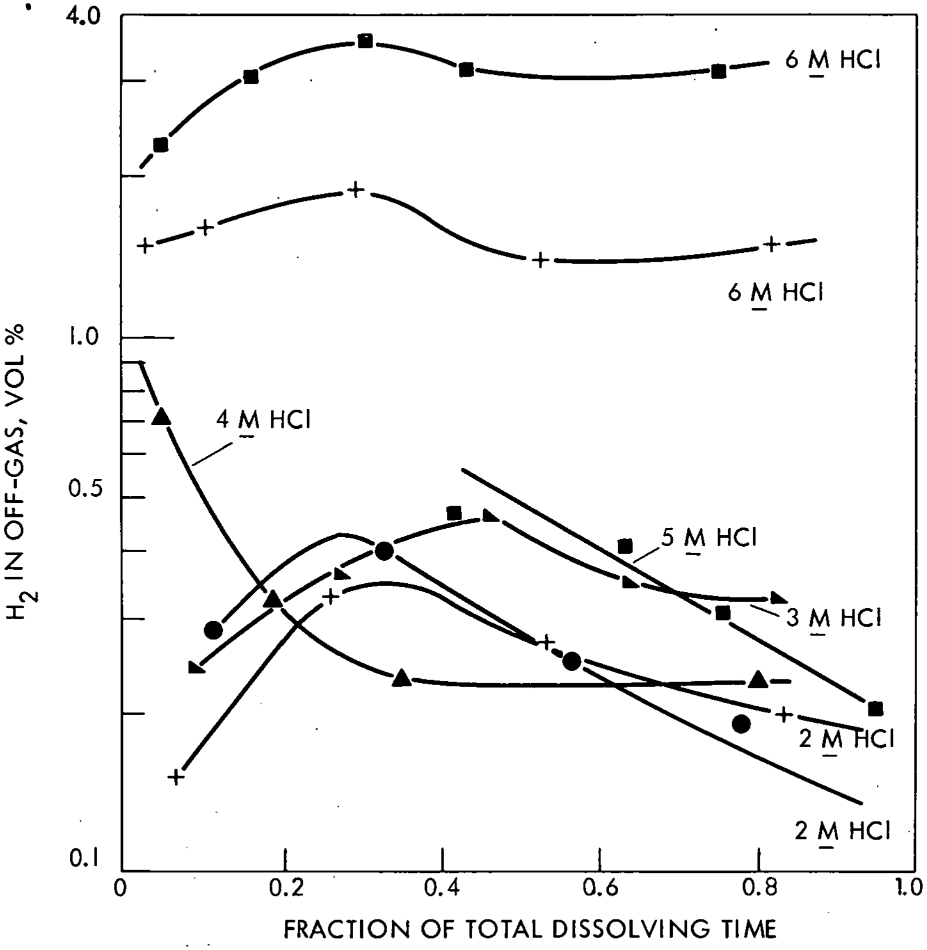

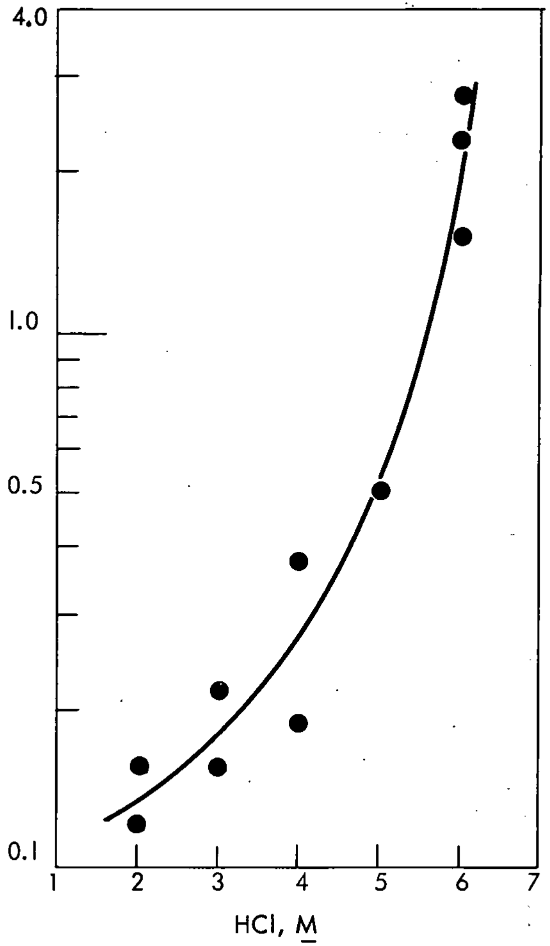

Temperature, reflux; samples, 2-3 g 304L SS (40 mil thickness); volume of reagent/g SS, 20 cc; total M HCl + HNO_3, 7; total dissolving time, 5 min (2 M HCl) - 22 min (6 M HCl).

Fig. 2. Hydrogen in Darex off-gas as a function of dissolving time on dissolution of stainless steel.

Fig. 3. Total hydrogen in Darex off-gas on dissolution of stainless steel.

condensed from the exit gases at 300°C. The zirconium chloride, which still has a vapor pressure of 0.3 atm at 300°C[5] passes through the 300°C condenser and is condensed in a separate chamber at ambient temperature. Experimental work is underway to develop satisfactory methods for selective condensation of uranium chloride which can be followed by either aqueous or direct fluorination[7] recovery procedures for uranium.

A recovery procedure in which <0.1% of the uranium was lost to the zirconium chloride condensate was developed with the use of glass wool packing in the 300°C condenser.[8] The uranium can be recovered from the packing with aqueous solution. A satisfactory direct fluorination recovery procedure has not been developed as yet. Two runs using copper turnings as packing in the 300°C condenser resulted in excellent separation of uranium chlorides (>99.99%) but the copper turnings ignited during fluorination of the uranium chlorides at 200°C. Two runs using nickel turnings resulted in >10% uranium loss to the zirconium chloride condensate, probably because the nickel turnings did not pack into the 300°C condenser as easily as copper turnings. Other runs are planned in which different types of nickel packing are used.

1.1.6 Dissolution Rate of Tin in NH_4F-H_2O_2 and HF-H_2O_2 (T. A. Gens)

In developing the Perflex flowsheet for dissolving U-Zr-Sn alloys in HF-H_2O_2,[9] it was necessary to determine if tin dissolved rapidly in HF-H_2O_2.

Tin metal dissolved in 5 M HF-H_2O_2 at rates exceeding 10 mg/cm^2-min between 13 and 70°C at hydrogen peroxide concentrations between 2 and 7 M (Fig. 4). At 13°C in 5 M HF, hydrogen peroxide dissolved tin much more rapidly than did HF-HNO_3 (Fig. 5). At 70°C both hydrogen peroxide and nitric acid dissolved tin rapidly in 5 M HF, with nitric acid causing faster dissolution at concentrations over 6 M (Fig. 6). By replacing hydrogen ion with ammonium ion, the pH of the solution was increased. This pH increase greatly decreased the effectiveness of both peroxide and nitrate in tin dissolution (compare Figs. 5 and 7).

1.1.7 Recovery of Uranium and Thorium from Graphite Fuels (M. J. Bradley)

Fifteen-gram samples of graphitized uranium-thorium-graphite fuel were simultaneously disintegrated and leached by boiling 1.2 x 1.4 x 4.5 cm pieces in 50 ml of 90% HNO_3 for 4 hr. The mixture was filtered, residue washed with three 25-ml portions of cold water, and residue divided into two portions to test the effect of acid concentration in the second leach. Half was leached again with 25 ml of 90% HNO_3; the other half with 25 ml of 70% HNO_3. Finally the residues were washed once more with 25 ml of cold water. Vacuum filtration was used throughout. The final graphite residue was a -20 mesh powder.

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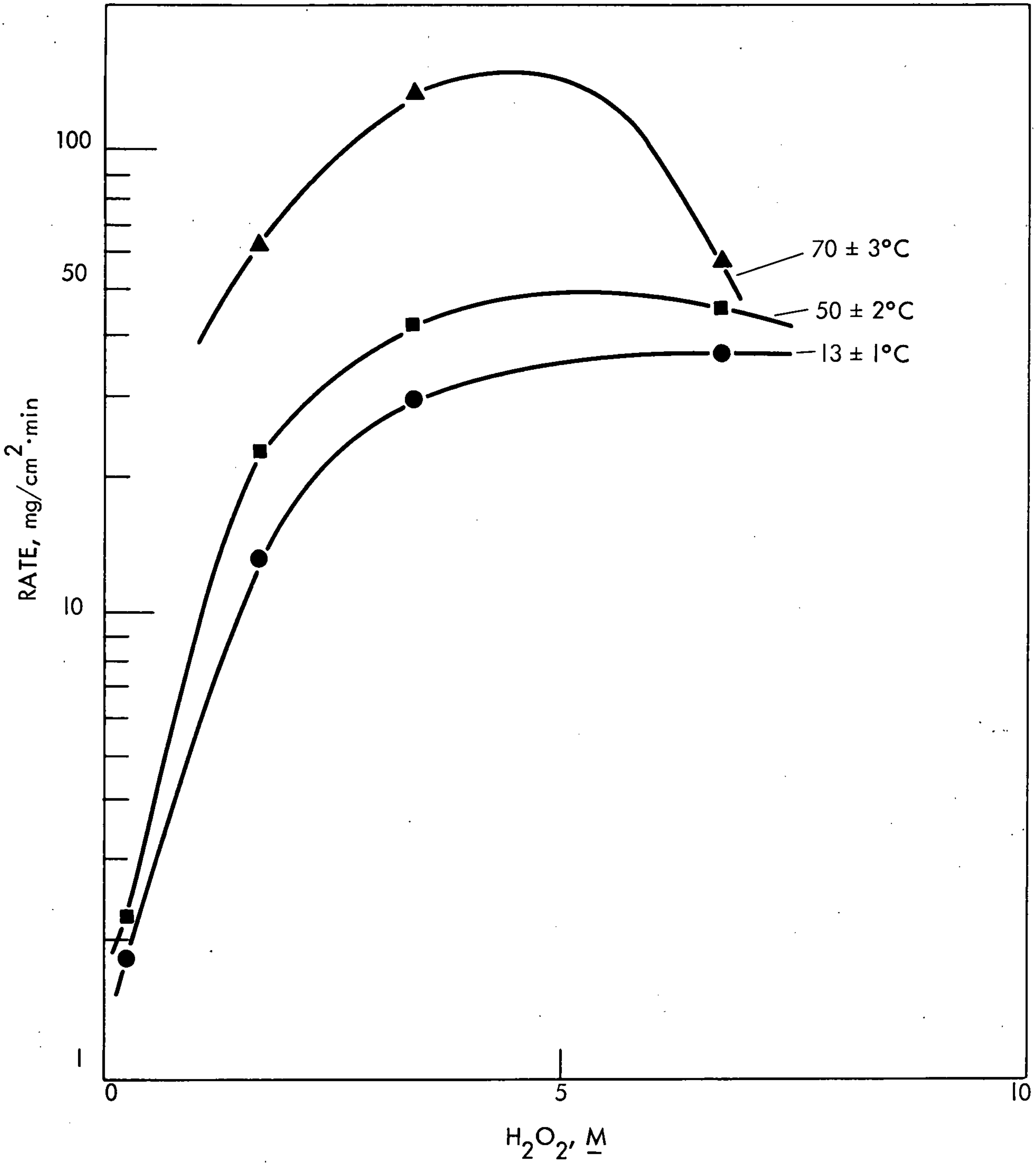

Fig. 4. Initial dissolution rate of tin in 5 M HF-H_2O_2.

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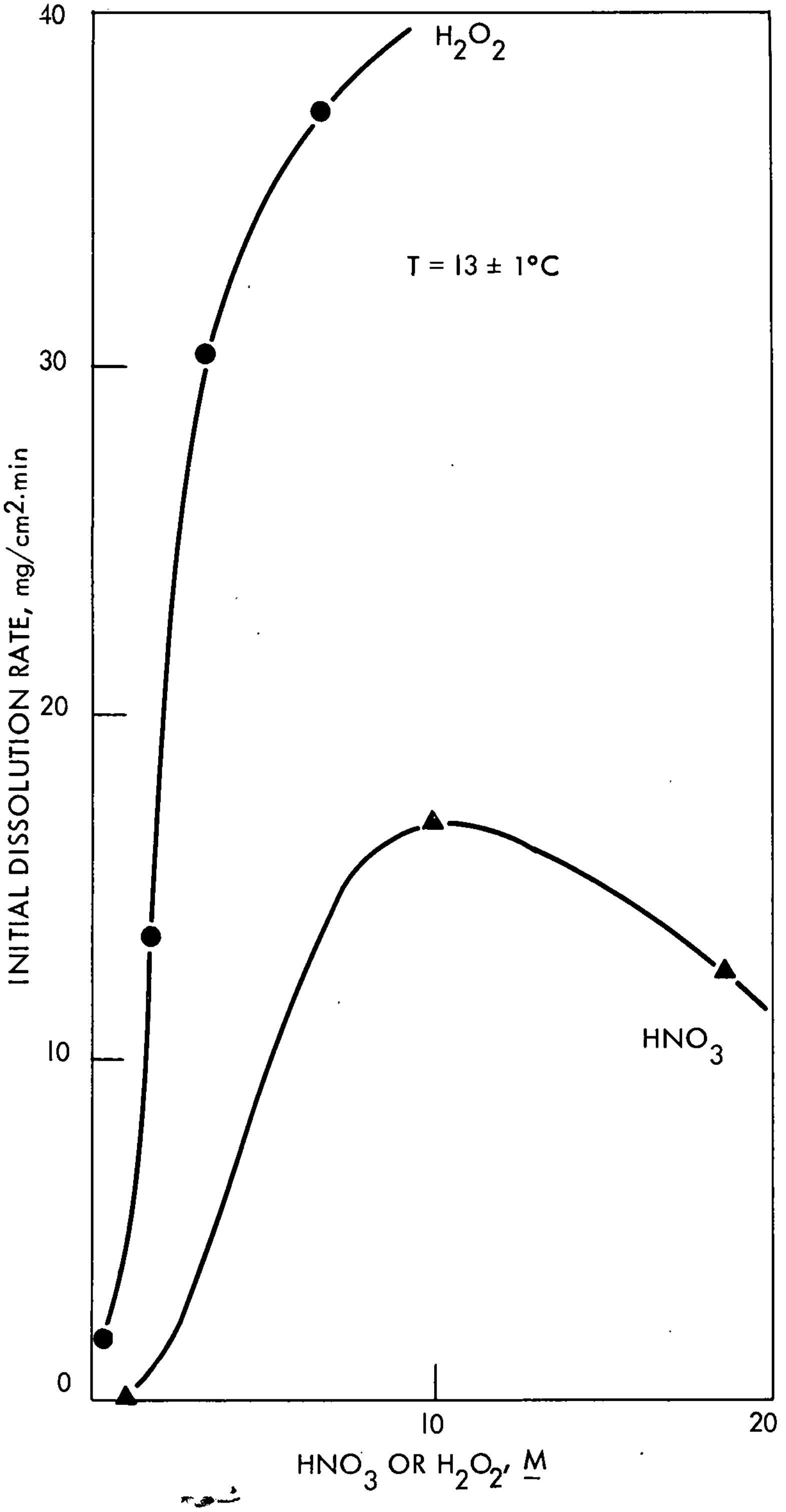

Fig. 5. Comparison of tin dissolution rates in 5 M HF-H_2O_2 and 5 M HF-HNO_3.

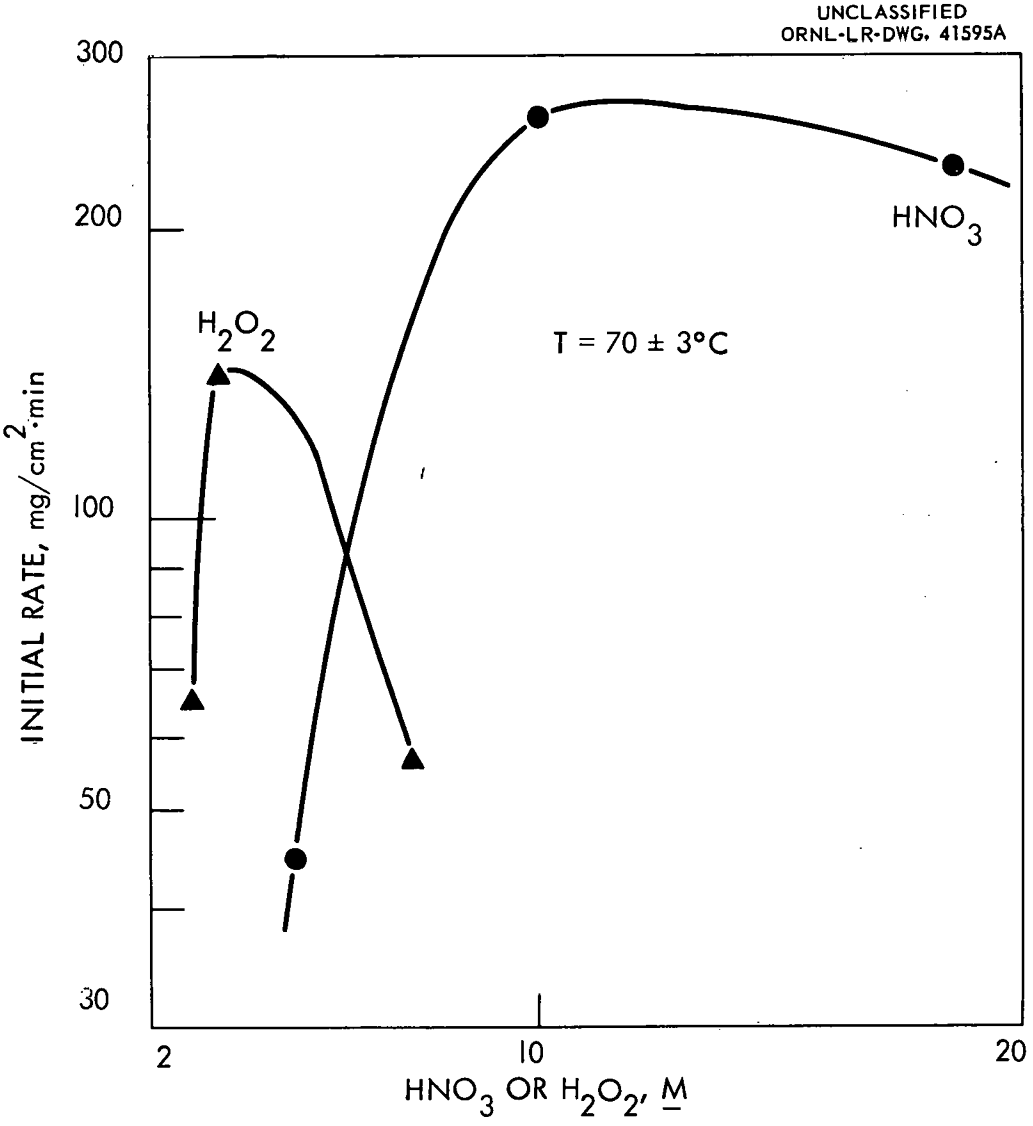

Fig. 6. Comparison of tin dissolution rates in 5 M HF-H_2O_2 and 5 M HF-HNO_3.

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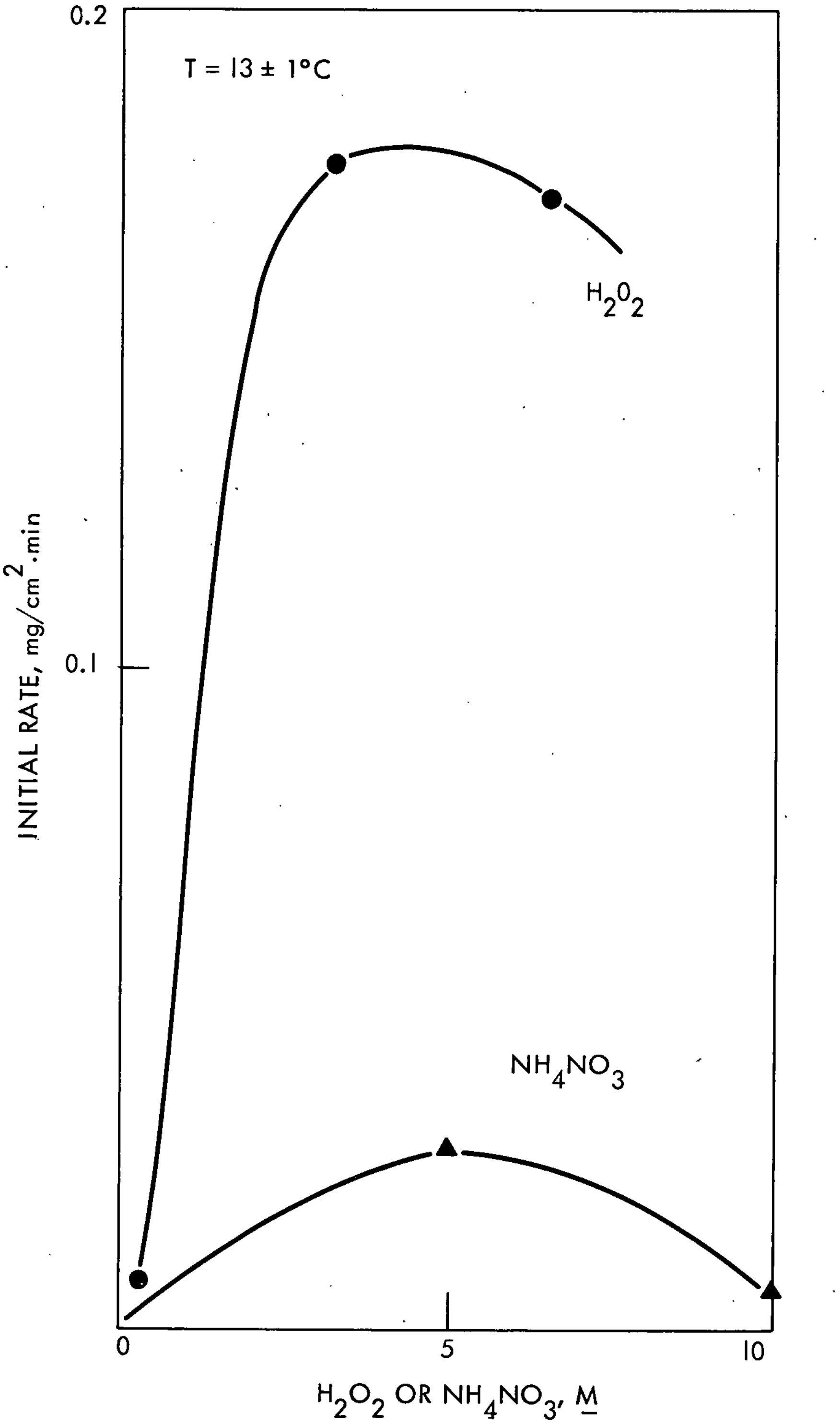

Fig. 7. Comparison of tin dissolution rate in 5 $\underline{M}$ NH_4F-H_2O_2 and 5 $\underline{M}$ NH_4F-NH_4NO_3.

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Two leaches with boiling 90% HNO_3 (21.2 M) recovered 99.85% or more of the metal in fuels containing 5-13% uranium (Table 1). Metal recoveries decreased with decreasing uranium concentration in the fuel, although this effect was less pronounced with the 90% HNO_3 leach process than with the grind-leach (Fig. 8). With the exception of the first run in Table 1, two, 4-hr leaches with boiling 90% HNO_3 of 1.2 x 1.4 x 4.5 cm pieces and suitable washing techniques left a graphite residue containing 70-160 ppm uranium (avg. 110 ppm) irrespective of the original uranium concentration in the fuel. When 70% acid (15.8 M) was used instead of 90% acid for the second leach, all of the graphite residues contained between 250 and 450 ppm uranium (avg. 310 ppm). This tendency to approach a limiting uranium concentration in the graphite was also observed by Fromm,[10] and is probably due to formation of graphite residue compounds analogous to those studied by Hennig.[11] Decreasing the acid concentration of the second leach from 90% to 70%, lowered the uranium recovery by 0.2% or more (Table 1). Thorium had no effect on the uranium recovery from the sample studied, which contained the oxides as separate particles.

Of the aqueous techniques studied thus far, simultaneous disintegration and leaching in boiling, white, fuming nitric acid (90% HNO_3, 0.2% maximum dissolved oxides) gave optimum uranium recovery from fuels containing 0.7%-14% uranium, with the minimum number of steps. Comparable uranium recoveries from fuels containing greater than 5% uranium were obtained by grinding to -200 mesh and leaching with 70% acid. With fuels containing less than 5% uranium, the graphite had to be rendered more porous by a swelling agent such as 90% nitric or bromine before satisfactory recovery was achieved by leaching. Since disintegration and leaching are carried out simultaneously with fuming nitric acid, one step has been eliminated - i.e., fine mechanical grinding or halogen disintegration. No extraneous ions such as halides, which must be removed prior to solvent extraction, and no nonremovable ions which would increase waste volumes are added. Although the fuel samples used in the study were relatively small (1.2 cm thick), somewhat larger pieces could probably be disintegrated by increasing the reaction time. Solid-liquid separations still present a serious engineering problem for any aqueous leach method.

1.2 Flowsheet Demonstration on Irradiated Fuel (J. R. Flanary)

1.2.1 Immi Hot-Cell Facility (J. H. Goode)

Foreign Research Reactor Processing. A total of five feed preparation runs have been made in the Immi facility with unirradiated fuel, two using 2S aluminum sheet and three using uranium-aluminum alloy as fuel charges. Operation of the dissolver-condenser-off gas system was satisfactory from the standpoint of temperature control, off-gas scrubbing efficiency, and capability of handling the volume of nitrogen oxides resulting from batch dissolution of about 2 kg of uranium-aluminum alloy in 50 liters of mercury-catalyzed nitric acid. Optimum dissolvent acid concentration, in

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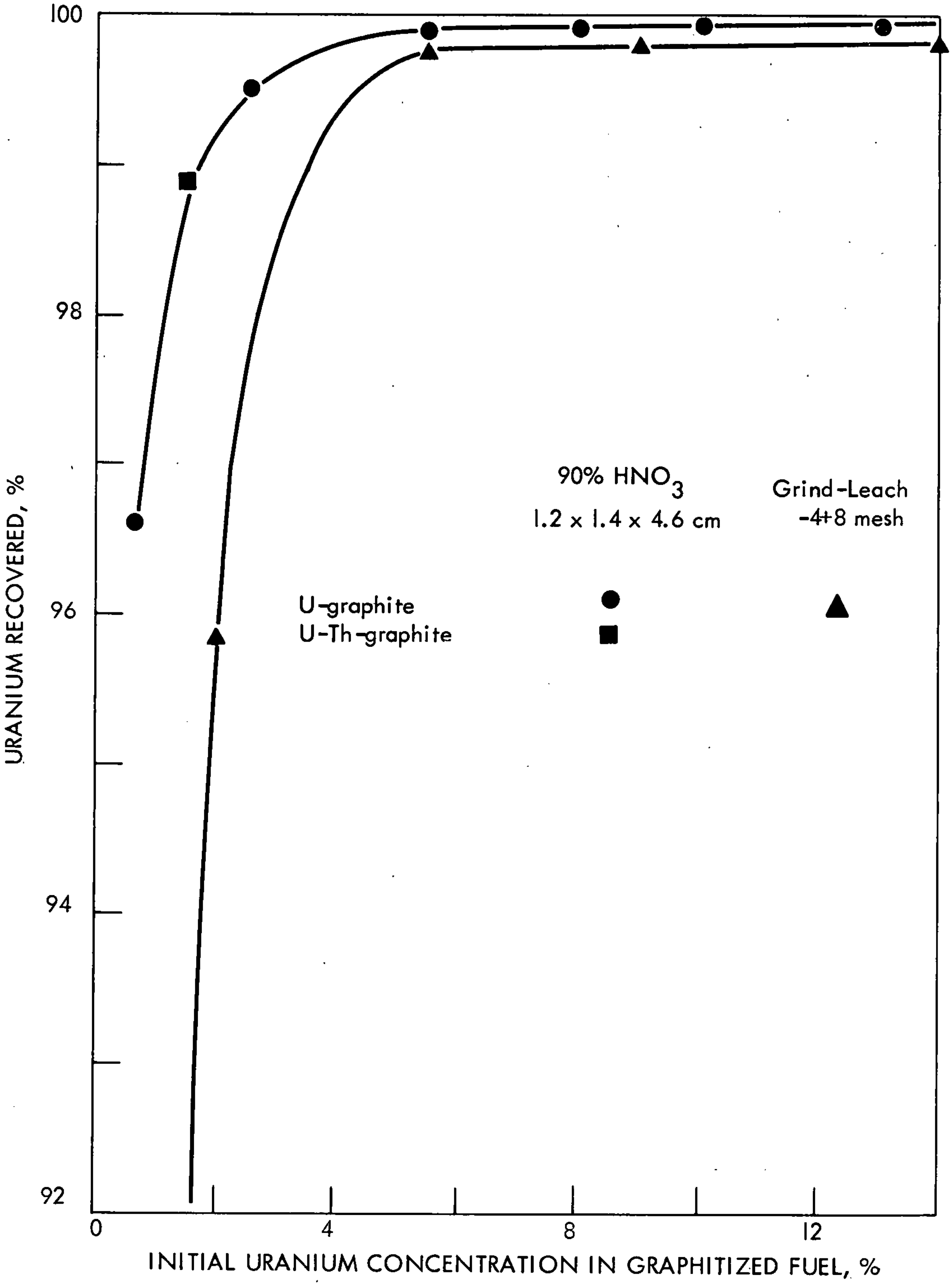

Fig. 8. Comparison of 90% HNO_3 and grind-70% HNO_3 leach methods. Two leaches with boiling acid in both cases.

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Table 1. Recovery of Uranium from Graphite Fuels by Disintegration in Boiling 90% HNO_3

Procedure: 15 g sample digested in 50 ml of boiling 90% (21.2 M) HNO_3 for 4 hr. Residue filtered and washed three times with water. Residue divided into two portions - half leached again with 25 ml of boiling 90% acid, half with 25 ml of boiling 70% (15.8 M) acid.

Fuel Composition, %		2nd Leach HNO_3 Conc., M	Metal Recovered, %							
			1st HNO_3 Leach + 2 Water Washes		3rd Water Wash		2nd HNO_3 Leach + 1 Water Wash		Graphite Residue[a]	
U	Th		U	Th	U	Th	U	Th	U	Th
0.63	0	21.2	91.6		0.02		4.0		4.4[b]	
		15.8	91.6		0.02		3.6		4.9[b]	
0.70	0	21.2	89.1		0.1		8.4		2.3	
		15.8	89.1		0.1		7.4		2.5	
0.68	0	15.8	87.2		0.2		6.2		6.4	
1.44	6.33	15.8	96.3	85.4	0.07	0.8	2.6	7.0	1.1	6.8
2.53	0	21.2	96.8		0.2		2.5		0.5	
		15.8	96.8		0.2		1.9		1.1	
5.41	0	21.2	98.1		0.2		1.6		0.15	
		15.8	98.1		0.2		1.3		0.35	
8.03	0	21.2	98.2		0.1		1.6		0.08	
		15.8	98.2		0.1		1.4		0.34	
10.2	0	21.2	98.4		0.1		1.4		0.05	
		15.8	98.4		0.1		1.2		0.33	
13.0	0	21.2	99.0		0.1		0.8		0.06	
		15.8	99.0		0.1		0.7		0.20	

[a] Combustion analysis.

[b] 6-hr leaches.

the Immi dissolver and condenser system, for the Foreign Research Reactor fuel, was established at 7 M HNO_3-0.005 M Hg^{++}.

Feed Clarification. Gelatin treatment for the coagulation of silica and operation of the sand filter unit appeared satisfactory. One test showed a 20 liters holdup of water could exist in the sand filter, which would dilute the dissolver product being filtered unless thoroughly drained before solution transfer was begun. An extended drainage period for the filter was included in the Immi operating manual. The dissolver was successfully used in its other function, as an evaporator, during this test.

Solvent Extraction. Three solvent extraction runs have been made in the Immi unit as part of the startup tests. The first run was troubled by improper control of interfaces and siphoning of metered streams; these deficiencies were corrected by installing new orifices in the interface control valves, replacing a plugged air line to the "C" Bank mixer-settler, and drilling vent holes in each of the settling sections of the mixer-settlers to prevent air-locking and over-flow of solvent out of the mixers. Siphon-breaks were installed on all pump lines leading into the cell.

In the second test a 900 rpm impeller speed in the "A" Bank apparently did not provide adequate mixing, as indicated by flowing stream samples showing excessive uranium loss (0.02 mg/ml or 0.33%) to the aqueous raffinate. In the third run, impeller speed increased to 1100 rpm apparently did not improve the uranium extraction.

Uranium Analysis. Some doubt exists as to the reliability of the samples used to calculate the losses. Wide variations in analysis occurred in samples of low uranium content. These samples, pulled by vacuum through dip tubes extending into both phases of the settling sections of the mixer-settler banks, were not consistent among successive samples of the same phase or with composite end-stream samples taken from the catch tanks. This difficulty also occurred with the "B" and "C" Bank samples of low uranium content, and in alternate stage samples taken for determination of stage efficiency. Samples of high uranium content (AP, BU, and CU) were reasonably consistent, indicating equilibrium had been established in the mixer-settlers. Table 2 lists the analytical results of the 3rd extraction run, and shows the erratic results obtained. Efforts were made to avoid cross-contamination of samples by thorough rinsing of the sampling devices and dip tubes before taking the final sample, taking samples in order of increasing uranium concentration and by using separate samplers for the organic and aqueous phases.

Nonstandard Processing Conditions. Flow checks over the entire run indicated the solvent flow rate in the "A" Bank was about 11% lower than the flowsheet value; however, it was only 40% saturated with uranium and should not have contributed to the excessive losses. Concentrations of all ingoing streams were of flowsheet value. The flowsheet has been demonstrated batch-countercurrently to require 4 theoretical extraction stages for a uranium loss of less than 0.01%. The flowing stream and stage samples showed that the 11 extraction stages in the mixer-settler were equivalent to not more than 3 theoretical stages.

Mixing Speed. The 900 rpm used in the second run appeared to be adequate for proper mixing and pumping. Increasing the speed to 1100 rpm in the third run produced a near-emulsion in the mixing section of each stage, although the phases separated satisfactorily in the settling sections.

Phase Contact and Settling Time. The flow rates in the extraction bank "A" were such that the feed and solvent were contacted in each mixing chamber for about 0.5 min and settled for about 1.6 min, giving a total residence time in the bank of about 37 min. Flow rates will be varied to determine the relation between contact time and efficient extraction.

Back-mixing of Phases. Another possible cause of uranium loss to the raffinate may be back-mixing of uranium down the bank toward the raffinate discharge point. Tests with an earlier model of the mixer-settler on an APPR flowsheet using 5% TBP and about the same total flow through the bank, showed uranium losses of nearly 1% to the raffinate; back-mixing was visible in some of the stages.

Table 2. Uranium Concentrations of Flowing Streams Samples - Run 3

(Foreign Research Reactor Flowsheet, Immi mixer-settlers)

Running Time, hr	Uranium - mg/ml					
	AW	AP	BP	BU	CU	CW
1	0.001	5.71	-	-	-	-
3	0.029	9.21	0.0035	6.54	19.72	0.0026
6	0.029	9.93	0.0078	7.54	14.09	<0.0001
8	0.044	9.96	0.0079	7.54	14.63	0.0076
11	0.003	10.51	0.0006	7.54	14.94	0.0048
15.2[a]	0.176	-	0.0002	-	10.96	0.0078
Theoretical	<0.0006	9.4	<0.0006	7.5	15.0	<0.0006

[a] Composited end streams in catch tanks.

Material balances for uranium and nitric acid, based on flowing stream samples taken from the three banks at equilibrium, were very close to 100%. An over-all uranium balance, based on the feed and composited end streams, however, was only 86%.

A series of Purex runs will be made to further evaluate mixer-settler performance with higher concentration streams and different flowrates.

1.2.2 Dissolution of Yankee Atomic Fuel (C. P. Johnston)

Simulated Yankee Atomic fuel containing a fissia concentration equivalent to 10,000 Mwd/T U was dissolved by the Sulfex and Darex head end processes to determine the amount of acid insoluble residues formed.

Unirradiated UO_2 pellets containing ZrO_2-1600 ppm, Mo-110, Ru-620, $BaCO_3$-975, NdO_2-1150, CeO-1200, La-520, Pr-440, Sm-185 and Y_2O_3-200 (a total of 0.8% fissia in the UO_2) was used as a starting material in the experiments to simulate the fissia produced in Yankee Atomic fuel irradiated to 10,000 Mwd/T U. These pellets were prepared by mixing the oxides and carbonates, pelletizing, and heating to ~1800°C.

In the first experiment with the Sulfex process, 16.5 g of type 304L stainless steel was treated with 165 ml of 6 M H_2SO_4 at 105°C in a nitrogen atmosphere for 30 min. Uranium oxide pellets (27.4g) were then added to the solution and boiling continued for an additional 60 min to completely dissolve the stainless steel. The H_2SO_4-stainless steel solution was filtered, and the residue washed and dried separately from the undissolved UO_2 pellets. The pellets showed no weight loss and were dissolved in 60 ml of 10 M HNO_3. The resulting solution was adjusted to Purex feed composition, 2 M HNO_3 and 320 mg U/ml, and filtered, yielding a solid residue insignificant in weight.

Three experiments were performed using the Darex process to dissolve jacket and core in boiling 5 M HNO_3-2 M HCl followed by removal of the chloride and subsequent dilution to appropriate feed composition, 2 M HNO_3, 130 mg U/ml and 60 mg SS/ml, for solvent extraction. The acid insoluble residue recovered by filtration was washed with water, dried, and weighed. In the first two experiments, proportionate weights of Type 304L stainless steel and UO_2 pellets were dissolved simultaneously. In the third experiment a synthetic stainless steel solution was used, to minimize the quantity of silica contributed by the stainless steel jackets, along with the UO_2 pellets (Table 3).

The residue from the H_2SO_4-stainless steel solution in the first experiment contained 0.210 g dry solids of which 0.191 g was silica. The remainder, assumed to be insoluble fissia, is equivalent to 8.7% of the total fissia in the pellets. By semi-quantitative spectrographic analysis, the composition of the fissia residue was 1.8% Zr and 1.1% Mo. Only traces of the other fissia elements were detected. Therefore, about 97% of the fissia residue remains unidentified.

The following procedure was used in the gravimetric analysis of the insoluble residues. The wet or air dried residue was heated at 200°C for 2 hr to remove water, and reweighed. Next, the dry residue was fumed with

H_2SO_4-HF mixture to remove SiO_2 as volatile SiF_4 followed by reweighing the dry residue as insoluble fissia and extraneous material. The semi-quantitative spectrographic analysis of the insoluble residue containing SiO_2 showed zirconium and molybdenum weights of 1 mg and 0.04 mg, respectively. These values correspond to about 5 and 0.2%, respectively, of these elements initially in the pellets. It seems illogical that 5% of the zirconium and 0.2% of the molybdenum would be leached from the apparently intact UO_2 pellets which showed essentially no uranium loss to the H_2SO_4-stainless steel solution. Zirconium should not be found in 304L stainless steel whereas molybdenum could be present as an impurity.

In Darex runs 1 and 2, the amount of insoluble fissia varied from 1.1 to 9.5% of the total fissia in the pellets, as determined gravimetrically by difference (Table 3). In Darex run 3 where a synthetic stainless steel solution was substituted for 304L stainless steel to eliminate most of the silica, a dry residue of 0.025 g was produced containing only 0.005 g SiO_2. The remainder, taken as insoluble fissia, is equivalent to 3.4% of the total fissia in the pellets. Spectrographic analysis of this residue indicates 20% SiO_2, 20% Zr, 2% Ru, 0.2% Mo, along with lesser amounts of the other fissia elements.

In Table 4, the insoluble residue, total, silica, and fissia, is shown on the basis of weight percent of the simulated fuel for each experiment.

Table 3. Insoluble Residue from Sulfex and Darex Head-end Processes with Simulated Yankee Atomic Fuel Containing Fissia Expected from 10,000 Mwd/T U from Irradiation

	Simulated Yankee Atomic Fuel[a]			Dry Residue			Percent of Initial Fissia in Residue
Run No.	SS, g	UO_2, g	Fissia, g	Total, g	SiO_2,[c] g	Fissia,[d] g	
Sulfex							
1	16.5	27.4	0.219	0.210	0.191	.019	8.7
Darex							
1	12	34	0.272	.170	.167	.003	1.1
2	29.8	75	0.20	.318	.261	.057	9.5
3	27.5[b]	73.8	0.59	.025	.005	.020	3.4

[a] The Yankee Atomic fuel consists of a cluster of Type 304L SS clad, UO_2 rods with 304L SS end plugs. The SS/UO_2 weight ratio per rod is 0.242, and 0.337 for an entire assembly. The sintered UO_2 pellets were specially prepared for these experiments by blending with uranium dioxide calculated proportions of the fission product oxides and carbonates according to the mass yield of the radioelements after 10,000 Mwd/T U irradiation.

[b] Calculated wt of SS.

[c] Silica determined by gravimetric analysis of residue except in Darex 3 which was determined by spectrographic analysis.

[d] Insoluble fissia in Sulfex 1 identified as Zr and Mo. In Darex 3, insoluble fissia identified as mainly Zr, Ru, and Mo.

Table 4. Percentage Insoluble Residue Expected from Sulfex and Darex Head-end Processes Using Prototype Yankee Atomic Fuel Pins Irradiated to a Nominal 10,000 Mwd/T U

Run No.	Simulated Fuel Charge, g	Dry Insoluble Residue, Wt %[a]		
		Total	Silica	Fissia
Sulfex				
1	43.9	0.48	0.44	0.044
Darex				
1	46	0.37	0.36	0.006
2	104.8	0.31	0.25	0.06
3	101.3	0.02	0.005	0.02

[a] These values do not take into account insolubles introduced by brazing alloy or other special materials which may be used in fabrication of reactor fuel assemblies.

1.3 Solvent Extraction Studies (R. H. Rainey, J. G. Moore)

1.3.1 Stripping Uranium and Thorium from 30% TBP-Amsco

The Power Reactor Fuel Processing pilot plant is being redesigned to keep all high activity processing in Building 3019. This may require partitioning of thorium from uranium in the first solvent extraction cycle with subsequent cycles for thorium and uranium purification. Therefore, studies are being made on the Acid-Thorex flowsheet for both partitioning and co-stripping of thorium and uranium from the organic phase.

The concentration of thorium, uranium, nitric acid, and gross gamma activity has been determined at various stages of the extraction-scrub column of the Acid-Thorex flowsheet (Table 5). The extraction factor for thorium was 1.5 at the feed plate (E-1), about 4 in the scrub section and increased to a maximum of 28 in the extraction section; whereas the extraction factor for uranium was greater than 30 throughout the column. The extraction factor for nitric acid varied from 0.5 to 1.5 and indicated considerable reflux of acid in the column. This reflux of acid minimized the amount of acid which must be added to the column. Extraction of gamma activity was very low in the extraction section of the column. Scrubbing efficiency decreased continuously in the scrub section due to selective removal of less extractable species.

Thorium and uranium were co-stripped from 30% TBP containing 0.01 N HNO_3 by using equal volumes of 0.008 M $Al(NO_3)_3$ in 7 stages with a loss of 0.08% of the uranium to the organic phase. The maximum concentration of uranium was 10 g/l in both the aqueous and organic phases at the second

Table 5. Composition of Stages of Acid-Thorex Flowsheet

Flowsheet Conditions

Feed: 275 g/l Th, 17.6 g/l U, 0.2 N AD, 1.28 x 10^7 Gr γ c/m/ml, 6.5 x 10^5 Ru γ c/m/ml, 1.1 x 10^7 Zr-Nb γ c/m/ml, 7.9 x 10^5 Pa γ c/m/ml.

Scrub: No. 1 - 5 N HNO_3
No. 2 - 0.01 M H_3PO_4, 0.01 M $Fe(NO_3SO_2)_2$

Acid: 13 N HNO_3

Solvent: 30% TBP-Amsco

Volume Ratio: Feed/Scrub No. 1/Scrub 2/Acid/Solvent = 1/0.2/0.8/0.3/7

Solutions are introduced into the column at the following stages:
Scrub No. 2 at Sc6, Scrub No. 1 at Sc3, Feed at Ex1, Acid at Ex4, Solvent at Ex5.

	Thorium				Uranium				Nitric Acid				Gross γ Thru Pb			
Stage	Org (g/l)	Ag (g/l)	DC_a^o	EF_a^o	Org (g/l)	Ag (g/l)	DC_a^o	EF_a^o	Org M	Ag M	DC_a^o	EF_a^o	Org c/m/ml	Ag c/m/ml	DC_a^o	EF_a^o
Sc 6	40	86	0.47	4.1	2.6	0.31	8.5	74	0.07	0.42	0.17	1.5	360	$2.2x10^3$	0.17	1.5
Sc 4	50	103	0.49	4.3	2.7	0.28	9.7	85	0.19	1.26	0.15	1.3	860	$1.9x10^4$	0.046	0.4
Sc 2	53	91	0.58	4.1	2.7	0.28	9.7	70	0.23	1.60	0.14	1.0	$3.1x10^3$	$1.8x10^5$	0.017	0.12
Ex 1	56	126	0.44	1.5	2.5	0.30	8.5	30	0.13	1.03	0.13	0.5	$2.5x10^5$	$6.8x10^6$	0.038	0.13
Ex 3	12	1.5	7.95	28	0.002	0.0001	20	70	0.50	2.36	0.21	0.7	$1.2x10^5$	$6.5x10^6$	0.018	0.063
Ex 5	0.27	0.28	0.98	3.0	-	-	-	-	0.47	1.85	0.25	0.8	$1.6x10^4$	$5.4x10^6$	0.030	0.09

stage. A McCabe-Thiele diagram using thorium extraction data from Siddal* and thorium-uranium equilibrium data (see below) indicates that 1.2 volumes of 0.008 M $Al(NO_3)_3$ would leave less than 0.01% of the uranium in the organic after 4 stages. The maximum concentration of uranium was 5 g/l in the organic and 2 g/l in the aqueous in the first stage.

Co-stripping organic feeds containing larger amounts of acid is more difficult. For example, stripping solutions containing 0.11 to 0.22 N HNO_3 with equal volumes of 0.008 M $Al(NO_3)_3$ left 0.3% of the uranium in the organic after seven stages. The maximum concentration of uranium was 13 g/l in the organic and 15 g/l in the aqueous phase of the second stage.

1.3.2 Co-extraction of Uranium and Thorium with 30% TBP-Amsco

Distribution coefficients of uranium, thorium, and nitric acid are being determined for the range of conditions encountered in the Acid-Thorex flowsheet. Only the data for uranium and thorium solutions containing less than 0.03 M HNO_3 are complete at this time (Table 6). These data illustrate the strong salting effect of thorium on the extraction of uranium. The distribution coefficient of uranium from an aqueous solution containing 20 g/l uranium to 30% TBP is 0.36 in the absence of thorium but increases to 3.5 in the presence of 50 g/l Th.

The uranium acts as a salting agent for low concentrations of thorium but decreases the distribution coefficient when the thorium concentration is greater than about 30 g/l. At 10 g/l Th the distribution coefficient increases from 0.012 in the presence of 5 g/l U to 0.026 in the presence of 20 g/l U. Whereas at 50 g/l Th the distribution coefficient decreases from 0.19 in the presence of 5 g/l U to 0.17 in the presence of 20 g/l U.

1.4 Corrosion Studies (Work done by members of the Reactor Experimental Engineering Division) (W. E. Clark)

Work has continued on the corrosion of various alloys in Zirflex-type solutions, on titanium in various Thorex environments and in high fluoride solutions, on stainless steel in Darex-Purex waste solution, and on various alloys under possible Zircex process conditions.

1.4.1 Zirflex Process

Several experiments were carried out to determine whether hydrogen peroxide acts as an effective corrosion inhibitor in the usual Zirflex decladding solution (6 M NH_4F, 1.0 M NH_4NO_3). The results (Table 7) show that the presence of 0.03 M H_2O_2 during a 3-hr exposure decreases the corrosion rates of Hastelloy F, Ni-o-nel and Type 309 SCb from 5.5 to 1.7 mils/mo from 19 to 2.4 mils/mo and from 12 to 1.5 mils/mo, respectively.

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* Siddal Laboratory

Table 6. Extraction of Thorium and Uranium by 30% TBP-Amsco (< 0.03 M Acid)

(Equal volumes of feed and solvent phases)

U in Feed	U_a	U_o	UDC_a^o	Th_a	Th_o	$ThDC_a^o$
No Thorium in Feed						
g/l	g/l	g/l	-	g/l	g/l	-
0.2	0.20	0.002	0.010	-	-	-
1.0	0.94	0.015	0.016	-	-	-
3	2.87	0.077	0.027	-	-	-
5	4.42	0.307	0.07	-	-	-
10	8.42	1.66	0.20	-	-	-
20	14.3	5.10	0.36	-	-	-
5 g/l Thorium in Feed						
0.2	.18	0.19	0.11	5.22	0.012	0.0023
1	.85	0.15	0.18	5.16	0.014	0.0027
3	2.42	0.49	0.20	5.16	0.020	0.0039
5	3.81	0.97	0.25	5.31	0.029	0.0055
10	7.07	2.94	0.42	4.93	0.042	0.0085
20	12.3	7.78	0.62	5.17	0.083	0.011
10 g/l Thorium in Feed						
0.2	0.14	0.044	0.31	9.68	0.074	0.0076
1	0.64	0.29	0.45	10.1	0.086	0.0085
3	1.92	1.08	0.56	10.1	0.109	0.011
5	3.12	1.80	0.58	10.0	0.123	0.012
10	5.65	3.81	0.67	9.54	0.207	0.022
20	10.3	9.36	0.91	9.47	0.246	0.026
20 g/l Thorium in Feed						
0.2	0.083	0.91	1.10	19.9	0.70	0.035
1	0.43	0.48	1.11	19.2	0.75	0.039
3	1.25	1.81	1.45	20.0	0.77	0.039
5	2.12	2.95	1.39	19.3	0.81	0.042
10	4.08	5.98	1.46	19.3	0.82	0.043
20	7.76	12.2	1.57	19.6	0.95	0.048

Table 6 (Cont.)

U in Feed	U_a	U_o	UDC_a^o	Th_a	Th_o	$ThDC_a^o$
30 g/l Thorium in Feed						
0.2	0.057	0.106	1.86	26.8	2.15	0.080
1	0.35	0.44	1.26	27.8	2.37	0.085
3	0.92	2.17	2.36	28.0	2.46	0.088
5	1.51	3.55	2.35	28.1	2.58	0.092
10	3.09	7.13	2.31	26.7	2.49	0.093
20	6.05	13.9	2.30	27.4	2.46	0.090
40 g/l Thorium in Feed						
0.2	0.036	0.134	3.72	36.6	5.12	0.14
1	0.25	0.58	2.32	36.6	5.12	0.14
3	0.71	2.39	3.37	35.8	5.33	0.15
5	1.18	3.84	3.25	35.8	5.12	0.14
10	2.41	7.63	3.17	35.8	5.05	0.14
20	4.89	14.5	2.97	36.3	4.75	0.13
50 g/l Thorium in Feed						
0.2	0.034	0.135	3.97	42.5	8.37	0.20
1	0.20	0.66	3.30	42.4	8.12	0.19
3	0.61	2.57	4.21	42.4	8.04	0.19
5	1.00	4.16	4.16	42.7	8.10	0.19
10	2.08	8.22	3.95	43.9	7.79	0.18
20	4.21	14.9	3.54	44.1	7.43	0.17
70 g/l Thorium in Feed						
0.2	0.025	0.118	4.73	54.0	14.1	0.26
1	0.18	0.85	4.73	54.5	14.8	0.27
3	0.49	2.48	5.04	55.5	14.1	0.25
5	0.81	4.17	5.14	55.5	13.7	0.26
10	1.72	8.40	4.88	55.5	13.0	0.23
20	3.82	15.8	4.14	55.5	12.1	0.22

In order to determine the effect of maintaining a steady concentration of peroxide, Ni-o-nel specimens were exposed for 11 hr in a 500-ml container through which boiling $6\ \underline{M}\ NH_4F$, $1.0\ \underline{M}\ NH_4NO_3$, $0.003\ \underline{M}\ H_2O_2$ was allowed to flow at an average rate of about 25 ml per minute. The liquid level was set to fluctuate so that interface corrosion specimens were alternately wetted and drained. The results (Table 8) indicate that the protective effect of peroxide is real since its presence has reduced the maximum rate from 21 (Table 7) to 3.5 mils/mo.

Table 7. Effect of Hydrogen Peroxide on the Corrosion of Several Alloys in a Boiling 6.0 M NH_4F-1.0 M NH_4NO_3 Solution

Specimen Position	Alloy	Corrosion Rate (mpm) No Additive 3 hr	6 hr	9 hr	0.03 M H_2O_2[a] 3 hr	6 hr	9 hr
V	Hastelloy-F	0.3	0.3	0.2	0.7	0.2	0.3
	309 SCb	0.4	0.3	0.4	0.7	0.2	0.5
	Ni-o-nel	1.0	0.5	0.6	1.0	0.3	0.6
I	Hastelloy-F	4.3	5.1	6.0	1.4	1.0	1.1
	309 SCb	5.2	5.7	5.2	1.3	1.0	1.4
	Ni-o-nel	8.4	11.0	13.0	2.7	2.1	2.1
S	Hastelloy-F	5.5	6.0	7.1	1.7	1.2	1.2
	309 SCb	11.0	11.0	12.0	1.5	1.5	1.7
	Ni-o-nel	19.0	20.0	21.0	2.4	2.1	2.2

[a] Fresh solution used for each period. H_2O_2 was added once at the beginning of each test.

Table 8. Corrosion of Ni-o-nel in a Boiling 6.0 M NH_4F, 1.0 M NH_4NO_3, 0.003 M H_2O_2 Solution

(Test period 11 hr; fresh solution added at a rate of 25 ml/min; volume of test vessel approximately 500 ml)

	Vapor	Interface	Solution
Corrosion rate (mpm)	0.8	2.8	0.7
	0.4	3.5	1.1

1.4.2 Titanium in Fluoride Dissolver Solutions

Since scouting tests have shown a possibility that titanium could be used as a container for the dissolution of zirconium in the presence of chromate, a series of 24 hr exposures was carried out in which specimens of titanium 45-A and Ti-0.2% Pd alloy were exposed to boiling solutions of 6 M NH_4F-NH_4NO_3 with and without additions of HF and chromate. The results of these tests together with those from a fluoboric-nitric acid solution containing chromate are listed in Table 9. Corrosion rates in solutions containing no chromate were catastrophic. In the presence of 0.2 M dichromate (0.4 M total Cr(VI)) Zirflex solution gave rates of 40-60 mils/mo while the fluoborate-nitrate solution gave a rate of 50 mils/mo for titanium and 110 mils/mo for the Pd alloy. The results definitely indicate the passivating effect of chromate though rates are still too

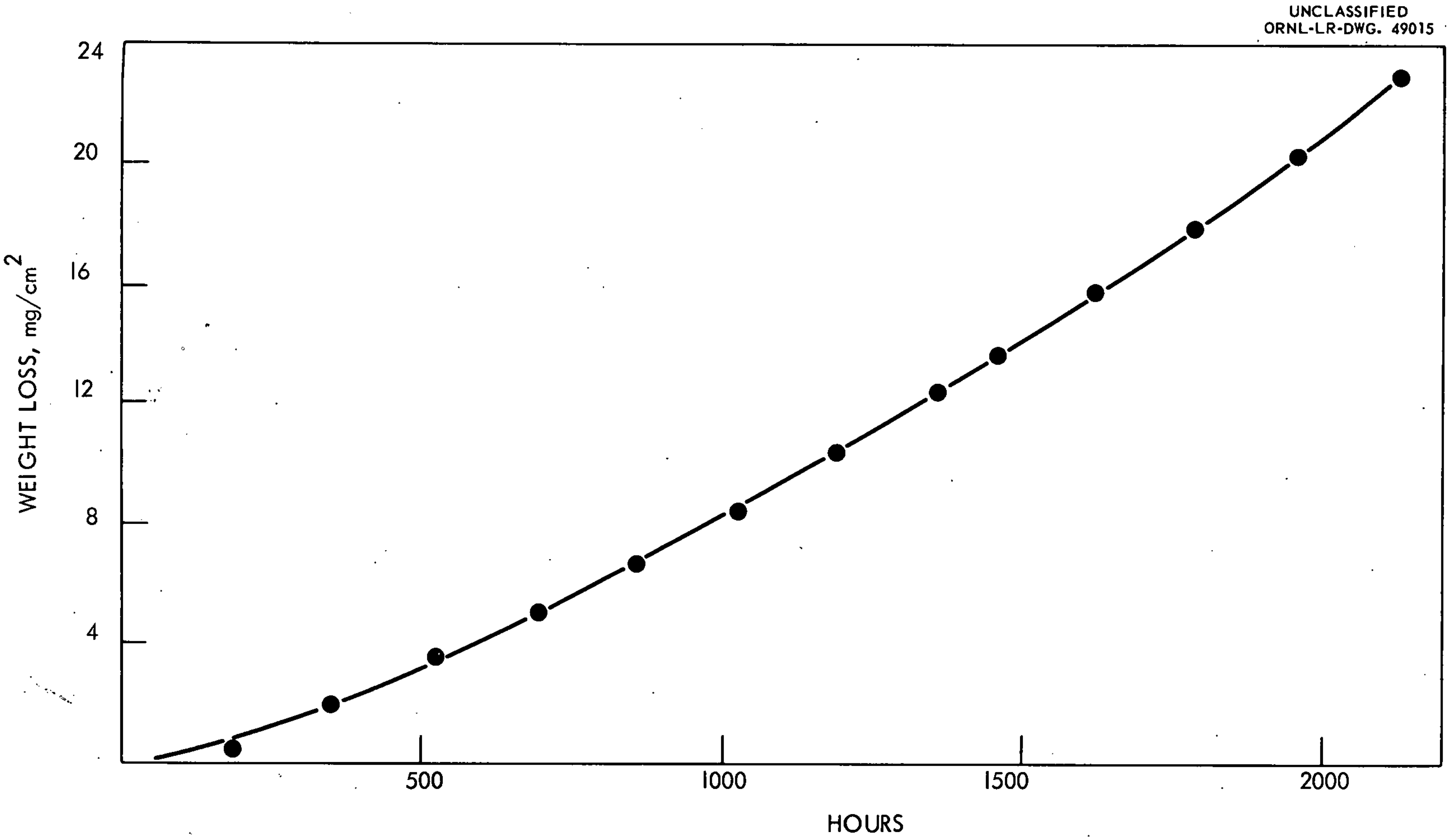

Fig. 9. Average weight loss of two welded type 304L stainless steel specimens in simulated Darex-Purex waste solution at 80°C (Solution: 5.0 $\underline{M}$ HNO_3. 1.82 $\underline{M}$ stainless steel, 100 ppm Cl^-).

high to allow the use of titanium as a container material in these solutions. The palladium alloy appears to be no more resistant to these environments than Ti-45A and perhaps is less so.

Table 9. Corrosion of Titanium-45A and Titanium-0.2% Palladium Alloy in Boiling Fluoride-Containing Solutions

(Test Period: 24 hr)

Solution	Specimen	Corrosion Rate (mpm)		
		Vapor	Interface	Solution
6.0 $\underline{M}$ NH_4F-1.0 $\underline{M}$ NH_4NO_3	Ti-45A	59.0	>500[a]	>500[a]
	Ti-0.2% Pd	13.0	>500[a]	>500[a]
6.0 $\underline{M}$ NH_4F-1.0 $\underline{M}$ NH_4NO_3-0.2 $\underline{M}$ $(NH_4)_2$ Cr_2O_7	Ti-45A	4.3	41.0	41.0
	Ti-0.2% Pd	7.4	52.0	59.0
6.0 $\underline{M}$ NH_4F-0.5 $\underline{M}$ NH_4NO_3-0.5 $\underline{M}$ HF	Ti-45A	13.0	211.0	>500
	Ti-0.2% Pd	190[b]	>500[b]	>500[b]
0.5 $\underline{M}$ HBF_4-0.3 $\underline{M}$ $(NH_4)_2Cr_2O_7$-3.0 $\underline{M}$ HNO_3	Ti-45A	3.1	40.0	50.0
	Ti-0.2% Pd	g	90.0	110.0

[a] These specimens disintegrated.

[b] This test was stopped before 24 hr because of rapid disintegration of the specimens.

1.4.3 Thorex Process

Continued exposure of titanium to Thorex dissolver solutions containing 0.1 $\underline{M}$ borate confirmed the fact that the presence of borate inhibits corrosion by the solution without causing pitting in the vapor phase contrary to the case when aluminum is present. The only pitting observed was in the vapor phase above the final solution (Table 10), the depth of the pits corresponding to approximately 3.6 mils/mo.

Titanium specimens welded in a dry-box were exposed for 1000 hr to beginning and middle Thorex solutions (Table 11) in order to determine whether or not the etching previously observed in the heat-affected zone[12] was caused by atmospheric contamination of the metal during welding. There appeared to be no clear advantage in using dry-box welds in the Thorex solutions. Specimens exposed to the beginning solution were selectively etched in the heat-affected zone as previously observed. Specimens in interface and solution positions of the middle solution remained in good condition; however, the vapor specimens suffered the usual gold-colored etch and one of them was etched deeply enough to be considered catastrophic. Additional work should be done with the middle and final Thorex solutions to eliminate the pitting and etching which has been observed in almost every test with these solutions.

Table 10. Corrosion of Titanium-45A Welds in Beginning[a] and Final[b] Thorex Solutions Containing 0.1 M $Na_2B_4O_7$

Specimen Position	Corrosion Rate (mpm)			
	840 hr		1000 hr	
	Beginning	Final	Beginning	Final
V	1.1	0.1	1.1	0.1
	1.0	0.1	1.1	0.1
I	0.3	0.1	0.3	0.2
	0.3	0.1	0.3	0.1
S	0.3	0.2	0.3	0.2
	0.3	0.3	0.3	0.3

[a] 13.0 M HNO_3, 0.04 M NaF.
[b] 8.5 M HNO_3, 0.04 M NaF, 1.0 M $Th(NO_3)_4$.

Table 11 shows results obtained for exposure of Titanium-45A dry-box welds to beginning and middle Thorex solutions. Dry-box welds were used to determine if the etching observed in the heat-affected zones during previous tests was due to atmospheric contamination of the metal by welding.

Table 11. Corrosion of Titanium-45A Dry-Box Welds in Beginning[a] and Middle[b] Thorex Solutions

Position	Corrosion Rate (mpm)			
	840 hr		1000 hr	
	Beginning[a]	Middle[b]	Beginning[a]	Middle[b]
V	3.8	0.08	3.9	0.07
	3.7	0.05[c]	3.7	0.04[c]
I	5.8	0.08	5.8	0.09
	5.9	0.14	5.8	0.14
S	6.1	0.20	6.1	0.19
	5.9	0.11	5.9	0.10

[a] 13.0 M HNO_3, 0.04 M NaF.
[b] 10.8 M HNO_3, 0.04 M NaF, 0.5 M $Th(NO_3)_4$.
[c] This specimen failed by deep localized penetration.

Welded titanium specimens are being exposed in various positions during feed adjustment boildown of Thorex solutions containing 0.1 M borate. After 5 boildowns all specimens showed negligible corrosion rates. These tests will be continued to at least 25 boildowns in order to evaluate the possibility of localized attack in the condenser.

1.4.4 Darex-Purex Waste Solutions

The exposure of welded Type 304L stainless steel specimens to simulated Darex-Purex waste solutions has been terminated after 2000 hr. As reported last month,[13] the specimens exposed at 80 and 65°C, showed intergranular attack. This type of attack will probably continue because of the increasing slope of the weight loss versus time curve for the 80-day solution specimens (Fig. 9). Corrosion rates for all the specimens exposed at 80, 65, and 50°C are shown in Table 12.

Table 12. Corrosion Rates of Welded Type 304L Specimens in Simulated Darex-Purex Waste Solutions[a]

Temperature (°C)	Corrosion Rate (mpm)			
	Vapor	Interface	Solution	Solution (Unwelded)[b]
80	0.02	0.23	0.40	0.41
(2132 hr)	0.02	0.22	0.38	0.41
65	0.01	0.05	0.09	0.10
(1945 hr)	0.01	0.05	0.09	0.10
50	0.01	0.03	0.03	0.03
(2371 hr)	0.01	0.03	0.04	0.03

[a] 5.0 M H^+, 1.82 M stainless steel, 100 ppm Cl^-, balance NO_3^-.
[b] Stressed U-bends.

Intergranular attack occurred on all the solution and interface specimens at 65 and 80°C; however, none could be detected on any of the 50°C specimens. The experiment is being repeated with Type 347 stainless steel specimens to determine if a stabilized steel will resist the intergranular attack. Types 304L and 347 stainless steel are also being exposed to a simulated waste solution containing only 2.0 M HNO_3 instead of 5.0 M to determine if the lower acid concentration will prevent intergranular attack.

1.4.5 Zircex Process

Since the most aggressive corrosion in the currently proposed Zircex process was observed during the exposure to N_2-CCl_4,[13] "elimination tests" were run on the various alloys under consideration using only that part of the test cycle. The results (Table 13) show that Illium R, Nichrome V, Inconel and INOR-8 are the most promising of the materials tested though all rates observed for even these alloys are greater than 26 mils/mo (Table 13). Rates will doubtless decrease considerably over the entire cycle[13] though even so it appears that over-all rates may well be 5 mils/mo or higher.

Table 13. Corrosion of Various Alloys in a Flowing Mixture of Nitrogen and Carbon Tetrachloride at 600°C

Alloy	Corrosion Rate (mpm) 2 hr	4 hr
Illium-R	68.0, 76.0	59.0, 27.0
Hastelloy-F	82.0, 140.0	Discontinued
Hastelloy-C	56.0, 57.0	108.0, 80.0
Haynes-25	196.0, 132.0	Discontinued
Nichrome-V	56.0, 63.0	41.0, 46.0
Inconel	53.0, 34.0	70.0, 26.0
INOR-8	- 33.0	47.0, 54.0
Elgiloy	181.0, 97.0	Discontinued
Multimet	- 175.0	Discontinued
Ni-o-nel	101.0, 54.0	Discontinued

These tests will be continued to determine the effects of adding small amounts of carbon monoxide and/or air to the gas stream.

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

1.5.1 Di-Sec-Butyl Phenylphosphonate Systems

Six samples of 1 M di-sec-butyl phenylphosphonate (DSBPP) in Solvesso-100 were irradiated to levels of 45, 135, and 400 watt-hr/liter after being contacted with equal volumes of 0.3 or 1 N HNO_3. The solutions were analyzed for nitric acid before and after irradiation and for monobasic organic acid after irradiation. Nitric acid decomposed, $G(-HNO_3)$ and monobasic acid formed, G(Monobasic Acid), both decreased as the total dose increased (Table 14). A similar decrease in monobasic acid formation with increasing dose was observed for another set[14] of 1 M DSBPP-Solvesso-100 solutions that had not been contacted with nitric acid.

1.5.2 Purification of Degraded Solvent by Distillation (W. Davis, Jr.)

Distillation has been tested on a laboratory scale as a method for purifying solutions of TBP in Amsco that were degraded by radiation and/or thermal dealkylation. Most of the distillations were performed at Georgia Institute of Technology[15] in a column operated at 20 to 50 mm Hg pressure. Two molecular distillations performed at ORNL are also summarized.

Table 14. Yields in the Radiation Decomposition of 1 M DSBPP in Solvesso-100

Contacting HNO_3, M	Initial HNO_3 in Org. Phase, M	Dose, w-hr/l	Acid Yields, molecules/100 ev G(Monobasic Acid)	G($-HNO_3$)
1	0.171	45	0.79	2.88
1	0.171	135	0.45	2.53
1	0.171	400	0.20	0.97
0.3	0.0324	45	0.21	0.63
0.3	0.0324	135	0.17	0.36
0.3	0.0324	400	0.13	0.17

Distillation of Irradiated 30% TBP in Amsco 125-82 at 20 to 50 mm Hg Pressure (Work performed at Georgia Institute of Technology of Subcontract 1374)[15]

Solutions of 30% TBP in Amsco 125-82 were irradiated at ORNL to ~120 watt-hr/liter in a 10,000 curie cobalt-60 source while being agitated with an aqueous solution containing 1.3 M U(VI) and 1.84 M HNO_3. The initial aqueous phase composition was chosen to represent a composite of feed and scrub streams of a Purex process described by Irish and Reas.[16] After irradiation, the organic and aqueous phases were separated and the organic phase contacted eight times with 0.01 M HNO_3. The first four contacts (stripping operations) were performed with a volume ratio, V_o^a, of 0.32 and the last four with V_o^a of 0.80. The resulting organic phase was used in the Georgia Technology distillation studies.

Column distillation of the composite TBP-Amsco, as received or after washing with aqueous sodium carbonate solution, left large quantities of black residues. For this reason, such distillation technique was abandoned in favor of a rapid volatilization operation which yielded first a diluent fraction and then a TBP fraction. Although pot residues contained ~20% of the charge, it is expected that losses will be considerably smaller in larger scale operations.

The two fractions obtained from rapid volatilization were distilled individually in a ~42 theoretical plate column and separated into 7 to 24 fractions. Each fraction was then used to make a solution of ~30% TBP, by adding "as received" TBP to fractions from the Amsco distillation or by adding "as received" Amsco to TBP fractions. These solutions were then contacted with aqueous solutions containing tracer concentrations of U-233 and Ru-106. The aqueous solutions used in extraction-scrub studies also contained 4.86 M HNO_3 while those used in extraction-strip studies contained 4.47 M HNO_3. These tests showed separate fractional distillation of Amsco 125-82 and TBP obtained from the rapid separation of the two after irradiation to the ~120 watt-hr/liter level yields products that are comparable to distillates from unirradiated materials.

Molecular Distillation of Irradiated 30% TBP in Amsco 125-82. A sample of the irradiated, stripped organic phase described above was exhaustively stripped with 2.5% aqueous sodium carbonate to remove residual uranium, nitric acid, and acidic products of TBP radiation degradation. The resulting TBP-Amsco solution was then used in one test in a falling film molecular still. In this test the Amsco fraction was separated as a water clear fraction with the pot temperature ≤35°C; TBP was separated as two water clear fractions with the pot temperature ≤70°C, corresponding to a pressure of ≤0.2 mm Hg; the pot residue, ~1% of the total charge, was not charred or blackened but of orange-red color. Infrared analysis showed it to contain large quantities of nitro compounds.

Molecular Distillation of Degraded 30% TBP in Amsco 125-82 from the 3019 Pilot Plant

On April 13, 1959, more than one gallon of highly degraded solvent was removed from the high pressure side of pump T-4-P in the 3019 pilot plant, i.e., before the 1CW solvent entered the solvent recovery equipment.[17] Samples of this material were used by Blake, Gresky, Schmitt, and Oxendine to study chemical methods of solvent recovery. Another sample, 368 ml, was molecularly distilled in ~75 ml batches at 32 to 40°C, from which a water clear Amsco fraction was obtained. The residual 136 ml of TBP-impurity fraction was then washed five times with equal volumes of 2.5% aqueous sodium carbonate and finally recharged to the molecular still. Four distillate fractions were taken at a pot temperature ≤70°C, or ≤0.2 mm Hg, as follows: (1) 43.5 ml of water clear TBP; (2) 35 ml of water clear TBP; (3) 16 ml of faintly yellow colored TBP; (4) a residue of 14.5 ml (~4% of the initial TBP-Amsco charge or ~11% of the TBP charge) of orange-red, viscous liquid.

The diluent fraction and the three TBP fractions were diluted with fresh TBP or fresh Amsco 125-82 to 1 M TBP, scrubbed with equal volumes of 2% aqueous sodium carbonate solution and subsequently tested for tracer Zr-Nb extraction and stripping properties by Blake, Gresky, Schmitt, and Oxendine.[18] The results of these tests are summarized as follows: (1) the diluent fraction from molecular distillation is very similar to fresh Amsco 125-82; (2) the first TBP fraction extracted only about 1/2 as much Zr-Nb as did the control solution and also could be stripped to 1/3 to 1/2 of the Zr-Nb activity of the control; (3) the second and third TBP fractions behaved toward Zr-Nb extraction and stripping very much like the control sample.

Future work on Distillational Purification of Degraded Solvent.

Data on low pressure distillation, i.e., the results from Georgia Institute of Technology, and the two molecular distillations performed at ORNL, show that 30% TBP in Amsco 125-82, degraded either by cobalt-60 radiation or in the Purex process of the ORNL pilot plant, can be purified to acceptable products on a laboratory scale of 0.1 to 2 liters. It is uncertain whether such purification is possible on pilot plant or production plant scale because certain engineering data have not yet been obtained. Specifically, materials losses in a true flash distillation followed by fractional distillation of separated diluent and TBP need to be evaluated as does the possibility of flash distillation without subsequent fractional distillation. This latter possibility is suggested by the apparent concentration of impurities in the high boiling fractions during molecular distillation. Molecular distillation data or calculations on a larger scale are needed to determine the feasibility of this unit operation to solvent recovery since materials loss can be very small.

2.0 WASTE TREATMENT

(J. T. Roberts)

2.1 Evaporation and Calcination of Purex Waste (H. W. Godbee, P. S. Lawson)

An experiment was performed in the equipment previously described[19] for evaporating and calcining high level waste and condensing and scrubbing the off-gases in a closed system (Fig. 10). The furnace was held at a temperature of 500°C since previous boil-off rate studies with water in this equipment had shown that the pressure in the calciner did not exceed 1 psig at this temperature.

A Purex 1WW concentrate (Table 15) to which had been added 102 g $NaNO_3$/l, 24.6 g $Ca(NO_3)_2$/l, and 11.2 g Micro-Cel E*/l was fed to the calciner at a rate of 28 ml/min. The average condensate rate was 26 ml/min. After an hour and 27 min operation, the pressure in the calciner reached 1 psig. This pressure actuated a pressure switch in the recycle gas line which shut off the furnace and recycle gas pump and caused cooling air to blow over the furnace. After cooling, inspection of the top flange showed that approximately the first inch of the off-gas line (3/8" SS tubing) was filled with a brown solid (entrained solid) which also had built up to a thickness of about 1/4 in. around and over the entrance to the off-gas line (3/8 in. pipe tap through top flange). The exit of the recycle gas line (3/8 in. pipe tap through top flange) was completely free of solids built up. The total volume of the calciner was 3.6 liters. The bottom liter of the calciner contained 1035 g of a light brownish-yellow solid. The top 2.6 liters was empty except for a light coating of brown flakes on the walls.

Table 15. Composition of Simulated Purex 1WW Waste Concentrate (Molarity)

H^+	NO_3^-	SO_4^{-2}	Na^+	Al^{+3}	Fe^{+3}	Cr^{+3}	Ni^{+2}	Ru
5.6	6.1	1.0	0.6	0.1	0.5	0.01	0.01	0.002

* A synthetic calcium silicate product of Johns-Manville.

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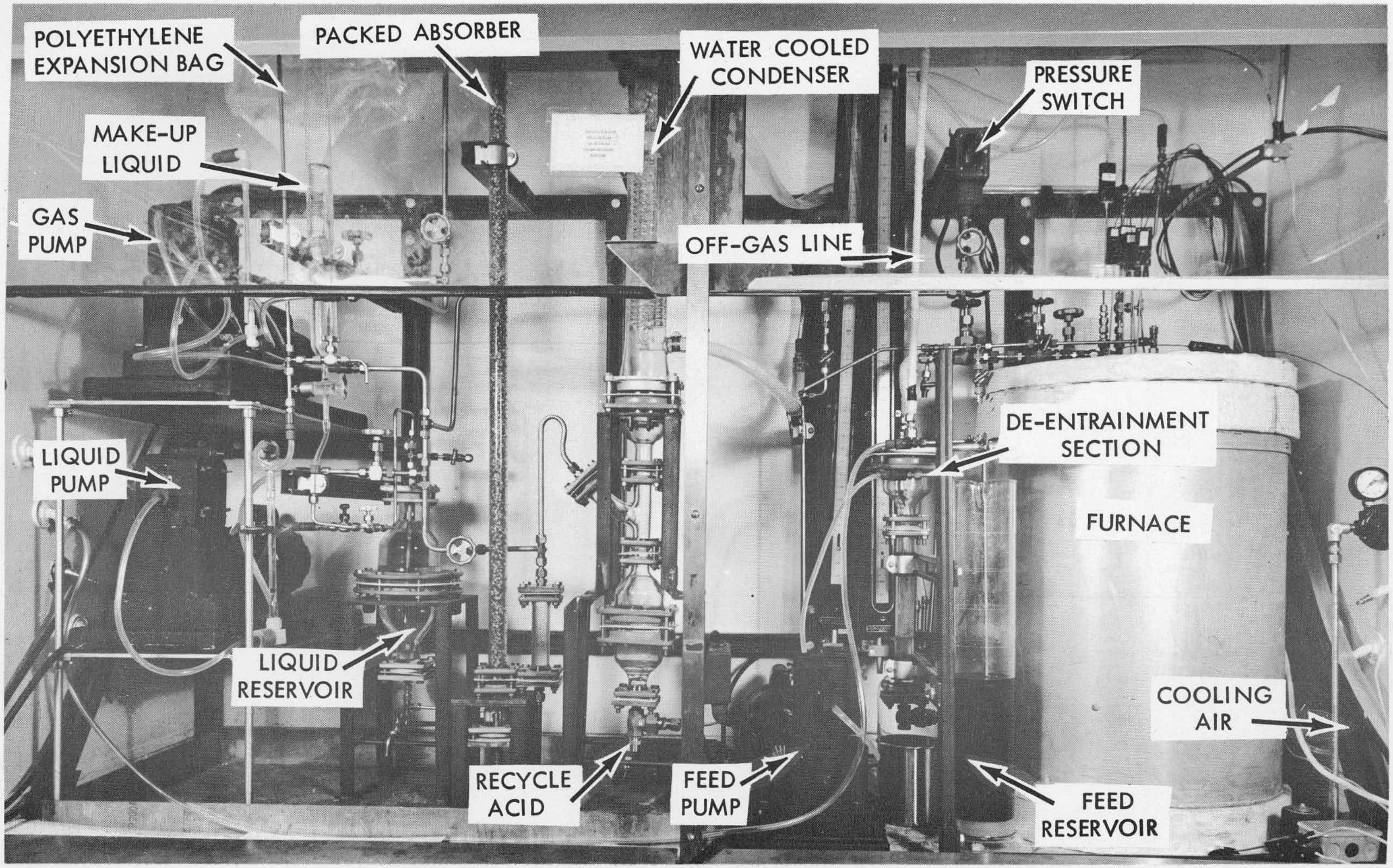

Fig. 10. Apparatus for calcining wastes and scrubbing off-gases.

The 3/8 in. off-gas line has been replaced with a 1 in. line and an experiment is proceeding in this modified equipment.[20] A larger off-gas line will not stop entrainment but the increased pressure drop caused by deposition of entrained solids should be less and it should take longer to completely plug the line. In larger scale equipment a "knocker" may be required to prevent the deposition of solids.

2.2 Volatility of Ruthenium During Evaporation and Calcination

(H. W. Godbee, P. S. Lawson)

Experiments were performed to study the effect of additives on ruthenium volatility when simulated Purex 1WW waste is evaporated and calcined. Samples of 1WW solution (Table 15) containing about 1 millicurie of ruthenium-106 tracer per liter of waste plus additives were evaporated and calcined to 400-500°C in a glass flask fitted with a glass condenser. The solution also contained 0.18 g/l of stable ruthenium.

In one experiment $NaNO_3$ (102 g/l) and $Ca(NO_3)_2$ (33 g/l) were added to the waste. Although some ruthenium plated on the condenser early in the evaporation, it was washed into the distillate by condensate later in the run. This plating-out effect probably causes the slope of the fraction-of-original-ruthenium-in-condensate vs volume-fraction-of-total-feed-in-condensate curve (Fig. 11) to be erroneously low near the origin. Total Ru-106 found in the condensate was 79% of the original. In another experiment, $NaNO_3$ (102 g/l), $Ca(NO_3)_2$ (24.6 g/l), and Micro-Cel E (11.2 g/l) were added to the waste and again ruthenium plated on the condenser. In this case, all of the black deposit was not washed out by condensate. About 66% of the original Ru-106 was found in the liquid condensate (Fig. 11). This experiment was repeated with the addition of 1 ml of TBP/liter of feed. Ruthenium appeared in the condensate after approximately 30% of the feed volume had distilled. Ru-106 accumulated in the liquid condensate was 15% of that in the feed (Fig. 11). This experiment was repeated again with nitric oxide (NO) introduced to the vapor space of the evaporator throughout the run. Ruthenium first appeared in the condensate when about 50% of the feed volume was distilled. The Ru-106 accumulated in the liquid condensate was 7% of that in the feed (Fig. 11). A fifth experiment was carried out in which $NaNO_3$, $Ca(NO_3)_2$, and Micro-Cel E, but no TBP, was added to the 1WW solution and NO passed through during evaporation and calcination. Ruthenium first appeared in the condensate when approximately 83% of the original feed volume was distilled. The total Ru-106 accumulated in the condensate was 8% of that in the feed (Fig. 11). In a sixth experiment, with <u>no</u> additives, 48% of the total Ru-106 in the feed was found in the condensate, however, the black ruthenium deposit on the condenser wall continued to build up throughout the evaporation. Soaking the condenser overnight in aqua regia did not remove any appreciable quantity of the deposit.

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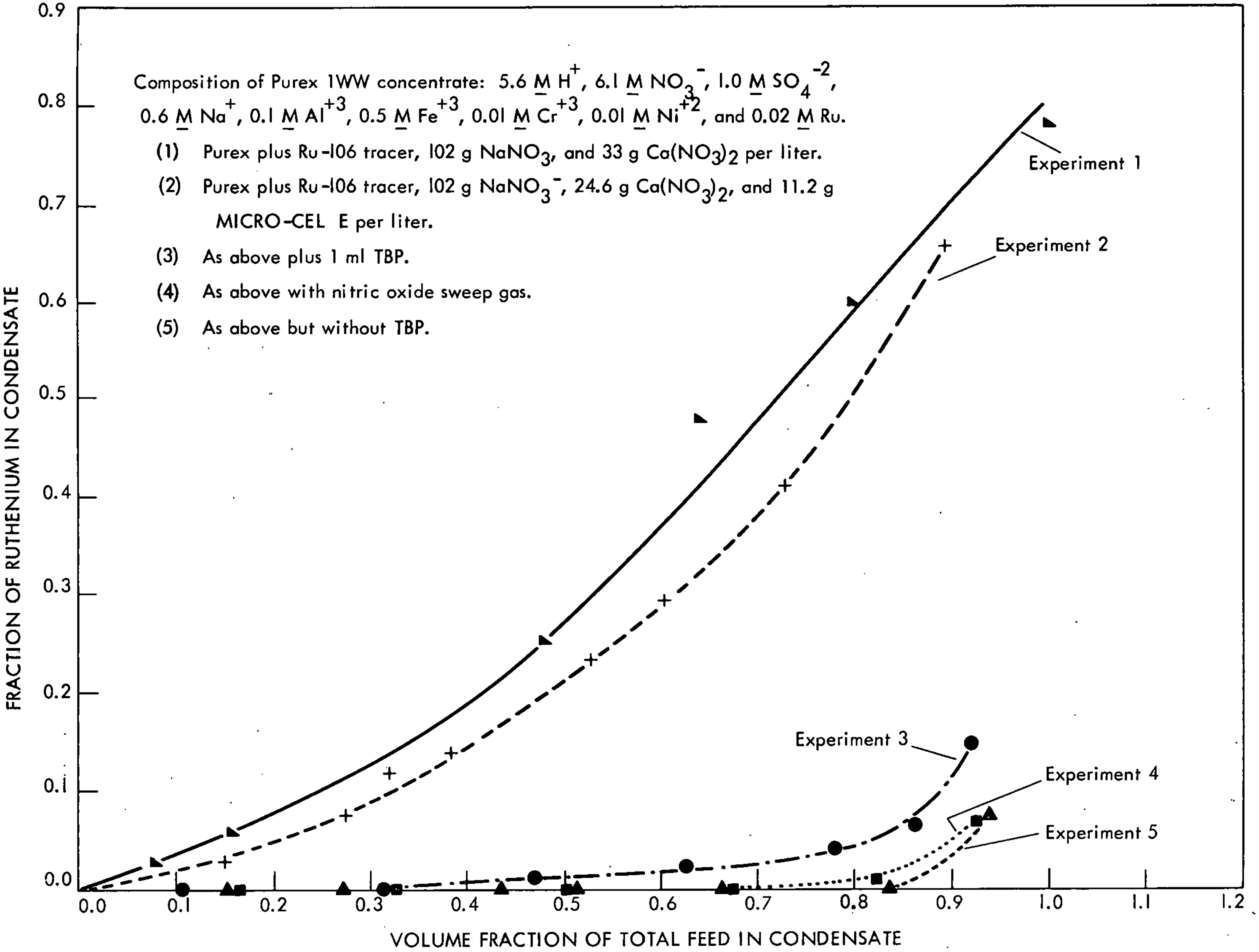

Composition of Purex 1WW concentrate: 5.6 M H^+, 6.1 M NO_3^-, 1.0 M SO_4^{-2}, 0.6 M Na^+, 0.1 M Al^{+3}, 0.5 M Fe^{+3}, 0.01 M Cr^{+3}, 0.01 M Ni^{+2}, and 0.02 M Ru.

(1) Purex plus Ru-106 tracer, 102 g $NaNO_3$, and 33 g $Ca(NO_3)_2$ per liter.

(2) Purex plus Ru-106 tracer, 102 g $NaNO_3^-$, 24.6 g $Ca(NO_3)_2$, and 11.2 g MICRO-CEL E per liter.

(3) As above plus 1 ml TBP.

(4) As above with nitric oxide sweep gas.

(5) As above but without TBP.

Fig. 11. Volatility of ruthenium during evaporation of Purex 1WW concentrate plus additives in glass equipment.

The above results with Micro-Cel E (synthetic calcium silicate) do not support the previous observation,[20] based on condensate color, that silicates suppress ruthenium volatility. Also the volatility (~48%) of ruthenium from these synthetic Purex solutions with no additives is greater than the volatility (~28%) reported previously[21,22] for a slightly different Purex composition containing mixed fission product tracer instead of the pure Ru-106 tracer as in the above experiment.

2.3 Organo-Nitrate Reactions during Evaporation and Calcination

(H. W. Godbee, P. S. Lawson)

A series of experiments were performed to study the nitrate-organic reactions when simulated Purex 1WW concentrate containing butyl phosphates is evaporated and calcined. The experiments consisted of boiling down 125 ml samples of Purex 1WW concentrate (Table 15) with either TBP, mono-butyl phosphoric acid, or di-butyl phosphoric acid plus various inorganic additives. The equipment consisted of a distilling flask fitted with gas and liquid phase thermocouples and a glass condenser.

Samples of Purex, to which had been added 102 g $NaNO_3$, 24.6 g $Ca(NO_3)_2$, and 11.2 g Micro-Cel E per liter of waste, in order to suppress sulfate volatility, were evaporated in three separate experiments in which 1, 2 or 3 milliliters of TBP had been added to the simulated waste samples. In each of these experiments, the fact that organic was steam-stripped into the distillate almost immediately was evident from the cloudiness of the condensate. The stripping was not complete, however, as indicated by suppression of ruthenium volatility by TBP or TBP degradation products at higher temperatures. Reflux periods prior to evaporation and very low boil-off rates were tried in order to minimize stripping, as well as decrease foaming and bumping during evaporation, but with little success. No violent reactions or rapid rises in pot temperatures were evident during the experiments.

In another experiment, a mixture of 27 ml TBP and 100 ml of Purex 1WW was evaporated and calcined to 475°C. The evaporation was carried out slowly to minimize foaming and bumping. When the liquid temperatures reached 132°C, copious evolution of white fumes was observed. At the end of the calcination, the residue in the distilling flask was a black, puffy solid. A mild reaction, indicated by bubbling, occurred in the distillate at the interface between the organic and inorganic phases.

Two experiments were performed in which 0.5 ml of either mono- or di-butyl phosphoric acid was added to the $1WW$-$NaNO_3$-$Ca(NO_3)_2$-Micro-Cel mixture described above. In these evaporations, the organic did not appear to be stripped into the distillate. No exothermic reactions were observed.

2.4 Treatment of Decladding Wastes for Disposal (W. E. Tomlin)

Based on the compression test of a 2 in. cube briquette, a satisfactory method of solidifying Sulfex decladding solution has been found. The solid has the following composition (parts by weight): declad solution 1.0, $Ca(OH)_2$ 0.26, sand 0.26, cement 0.55. After curing for 27 days, the compression test on the briquette was 3000 psi, the density was 1.33 g/cc and the volume increase of the solid product over the original liquid waste was 45% (Table 16). Compositions 11 and 12 (Table 16) are also promising. They have lower strengths, 1250-1350 psi, but also smaller volume increases, 23-28%, and require no sand. The feasibility of using one of these mixtures in waste disposal tests for hydrofracturing will also be evaluated.

Table 16. Composition - Physical Properties
2 in. cube briquettes
(Sulfex declad solution)

Composition	Weight Ratio	Density, g/cc	Volume Increase, %	Compression Test, psi	Curing Time, Days
1. Declad solution	1.0	1.33	45	3000	27
$Ca(OH)_2$	0.26				
sand	0.26				
cement	0.55				
2. Declad solution	1.0	1.38	53	2500	33
$Ca(OH)_2$	0.26				
sand	0.53				
cement	0.43				
3. Declad solution	1.0	1.44	59	2000	23
$Ca(OH)_2$	0.26				
sand	0.79				
cement	0.39				
4. Declad solution	1.0	1.34	44	1750	13
$Ca(OH)_2$	0.20				
sand	0.22				
cement	0.67				
5. Declad solution	1.0	1.42	54	1750	7
$Ca(OH)_2$	0.20				
bentonite	0.03				
sand	0.52				
cement	0.56				
6. Declad solution	1.0	1.25	44	1750	26
$Ca(OH)_2$	0.39				
sand	0.53				
cement	0.23				
7. Declad solution	1.0	1.50	59	1650	7
$Ca(OH)_2$	0.20				
sand	0.53				
cement	0.71				

Table 16 (Cont.)

Composition Weight Ratio		Density, g/cc	Volume Increase, %	Compression Test, psi	Curing Time, Days
8. Declad solution	1.0	1.10	37	1600	26
$Ca(OH)_2$	0.26				
vermiculite	0.41				
cement	0.12				
9. Declad solution	1.0	1.40	54	1550	7
$Ca(OH)_2$	0.20				
fuller's earth	0.03				
sand	0.52				
cement	0.52				
10. Declad solution	1.0	1.29	37	1400	7
$Ca(OH)_2$	0.20				
plaster of Paris	0.16				
sand	0.26				
cement	0.39				
11. Declad solution	1.0	1.26	28	1350	8
$Ca(OH)_2$	0.15				
cement	0.69				
12. Declad solution	1.0	1.06	23	1250	7
$Ca(OH)_2$	0.20				
cement	0.50				
13. Declad solution	1.0	1.32	36	1200	13
$Ca(OH)_2$	0.14				
sand	0.22				
cement	0.68				
14. Declad solution	1.0	1.17	34	1000	7
$Ca(OH)_2$	0.20				
plaster of Paris	0.08				
bentonite	0.08				
sand	0.26				
cement	0.22				
15. Declad solution	1.0	1.30	27	0	7
cement	0.85				
16. Declad solution	1.0	0.96	15	0	7
$Ca(OH)_2$	0.20				
plaster of Paris	0.34				
17. Declad solution	1.0	1.28	11	0	10
$Ca(OH)_2$	0.14				
plaster of Paris	0.41				
18. Declad solution	1.0	1.50	54	0	7
sand	0.45				
cement	0.90				

2.5 Low Level Waste Treatment (R. R. Holcomb)

In the evaluation of ion exchange resins for the treatment of low level process water wastes, 406 volumes of filtered ORNL waste, pH 7.3, containing added mixed fission product tracers, was passed through one volume (123 ml) of hydroxyl-form strong base anion resin (TAD-1) at a flow rate of 0.5 ml/min per milliliter of resin. The gross gamma DF was 3.6 (72% removal). Most of the Ru, Ce-Pr, Ba-La and Zr-Nb were removed. The effluent activity remained essentially constant throughout the run. The OH-resin maintained the pH of the effluent at 11.3 for the first 268 volumes of waste but after that the pH dropped slowly to 9.5. The total effluent from the anion column was then adjusted to pH 11.3, refiltered, and passed through sodium-form sulphonated phenolic cation resin (Duolite C-3) at a flow rate of 0.7 ml/min per milliliter of resin. The cation exchange decontamination factor averaged 24 (96% removal) for 1867 volumes of solution per volume (22.5 ml) of resin. Again, the effluent activity remained constant, indicating no real breakthrough, i.e., the activity in the effluent represents non-sorbing species rather than the gradual breakthrough of sorbing species. The total decontamination resulting from filtration, anion exchange, increased pH and refiltration, and cation exchange amounted to 99.6% removal (d.f. = 224) of gross gamma activity present. An additional 500 volumes of waste, based on the cation resin, was passed through the same filters and resin columns with an average removal of 98.1% (d.f. = 63.7). After this the effluent activity from the cation column gradually rose significantly above background but did not reach the 50% breakthrough point after an additional 2000 volumes.

The cation-exchange resin column from these runs was subjected to regeneration with 5 M Na_2NO_3-0.5 M HNO_3 solution. As shown in Fig. 12, the bulk of the activity was eluted with 130 ml, corresponding to ~ 5 resin volumes of regenerant. Additional studies of regeneration will be made to see if the amount of regenerant required can be reduced further.

3.0 ION EXCHANGE
(J. T. Roberts)

3.1 Fission Product Recovery by Ion Exchange (W. C. Yee)

In an effort to improve the recovery of rare earths and strontium from diluted Purex 1WW waste, two column runs were made in which the iron in the feed solution was complexed prior to pumping it through the resin bed. In the first run, 0.124 M oxalic acid was used as the complexing agent in 10X diluted 1WW feed to a column containing Dowex 50W X-8 resin. This solution contained approximately 1 mc/liter each of Sr^{85} and Ce^{144}-Pr^{144}. A significantly larger sorption capacity for both strontium and rare earths was observed than when oxalic acid was not used. No significant Sr^{85} activity appeared in the effluent until after about 14 volumes of feed per volume of resin. This is an improvement over a previous run in which Sr^{85} activity in the effluent was first observed after six

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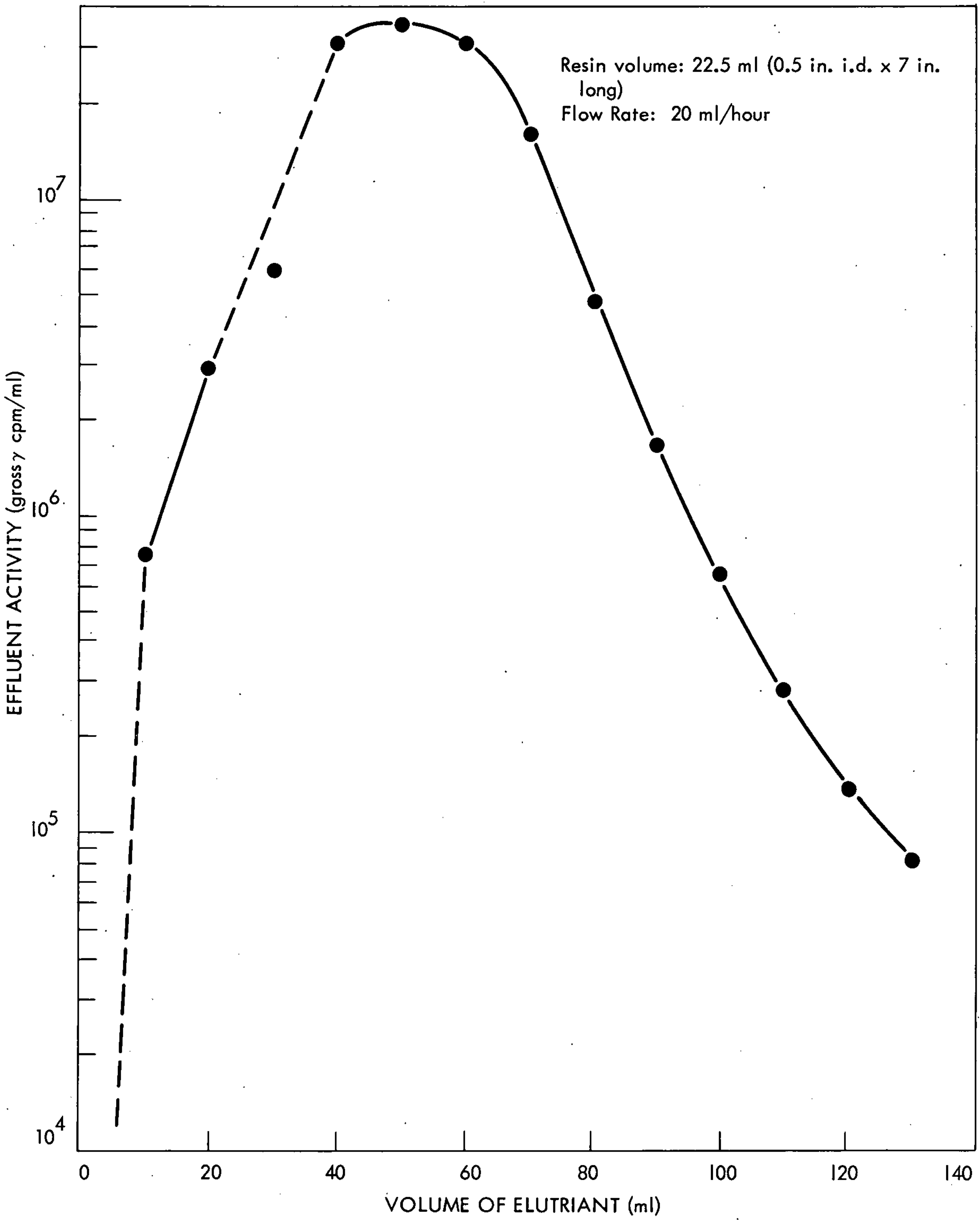

Fig. 12. Elution of activity from Duolite C-3 with 5 $\underline{M}$ $NaNO_3$-0.5 $\underline{M}$ HNO_3.

volumes of feed. The 50% breakthrough for Sr^{85} occurred at about 22 resin volumes, compared with 8.5 in the previous run. Resin capacity for rare earths was much greater also since less than 1% breakthrough of the Ce^{144}-Pr^{144} activity was detected after 33 resin volumes, compared with 50% breakthrough after 17 volumes in a previous run without oxalic acid. Fig. 13 shows the effluent activity during the oxalic acid run.

In the elution cycle, 10 resin volumes of 0.2 M diammonium citrate, pH 4.7, and 7 resin volumes of 0.13 M trisodium versenate, pH 7.9, were used to strip off rare earths and strontium (Fig. 13). Although only a rough separation of strontium from the rare earths was intended, cross-contamination was excessive. Actually, more strontium was eluted with the rare earths during the citrate elution than in the succeeding versenate elution. The first 3 or 4 resin volumes of versenate removed most of the activity remaining after the citrate elution. At the conclusion of the versenate elution, there was some evidence of precipitation on the resin bed in that the top half of the resin bed had turned dark, perhaps indicating hydrolysis of iron in the resin.

For the second run, rare earth and strontium recovery from 3X diluted 1WW concentrate was studied using Dowex chelating resin A-1. Iron in the 1WW concentrate was complexed with sodium tartrate (effective concentration in the diluted solution -0.33 M) and the resulting solution adjusted to a pH of 7.5 with 5 M NaOH. The feed solution also contained 0.1 mc/liter of Ce^{144}-Pr^{144} and 0.5 mc/liter of Sr^{85}. The resin bed was preconditioned with 0.33 M sodium tartrate, pH 7.7. The 50% breakthrough point for Ce-Pr occurred after about two resin volumes and was approached but not reached after five resin volumes for Sr. Three volumes of 2 M HNO_3 eluted about 75% of the activity sorbed on the resin bed, which was primarily Sr with only a trace of Ce-Pr. Thus strontium recovery from 3X diluted 1WW was improved by adjusting the feed solution to pH 7.5, compared to pH 5.5 as reported previously.[23]

Another stock solution of synthetic Purex 1WW concentrate was prepared as reported previously[24] with the following exceptions: (1) instead of the chloride forms of rubidium, ruthenium and rhodium, equivalent amounts of $RbNO_3$, $RuNO(OH)_3 \cdot H_2O$ and $Rh(NO_3)_3$ were used; (2) a solution of $ZrO(NO_3)_2$ was substituted for $Zr(OH)_4 \cdot 2H_2O$. Tables 17 and 18 give the revised composition. The mixture was refluxed for 4 hr. After filtration, the specific gravity of the filtrate was 1.295.

3.2 Radiation Damage to Ion Exchange Resin (W. C. Yee)

In the previous monthly report,[25] it was stated that there was an apparent discrepancy between results of the irradiated resin capacity as determined by titration and that by total sulfur analysis (Paar bomb method). Analysis of the Na^+ form of the "cleaned" resin for impurities gave no indication of the presence of any elements in significant quantity to explain this discrepancy. A sample of the "oven-dried" resin used in the sulfur determination was found to have only about 1% moisture, which is insufficient

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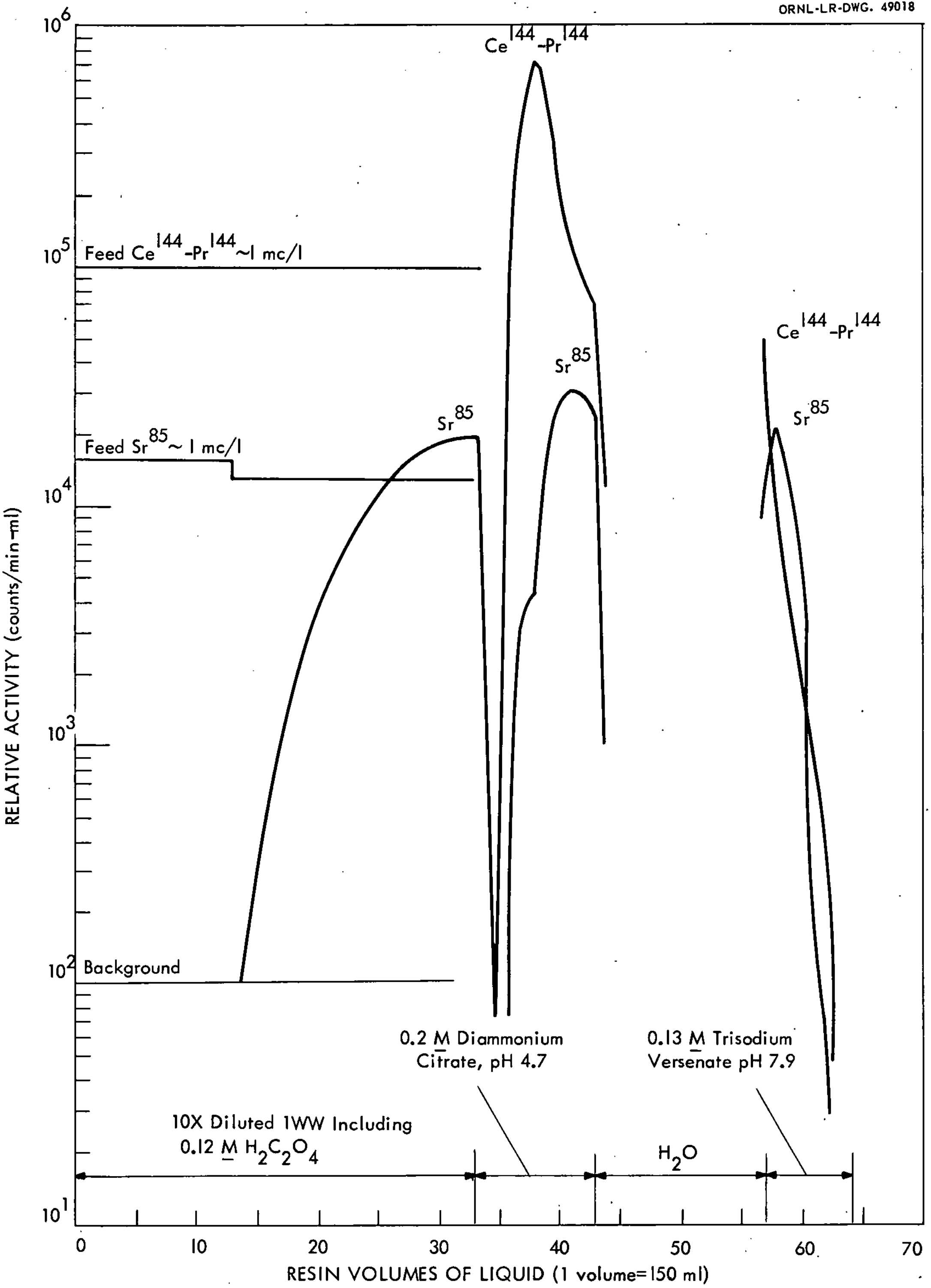

Fig. 13. Strontium and rare earth recovery from 10X Diluted Purex 1WW with 0.12 M oxalic acid added as iron complexing agent.

Table 17. Make-up of Synthetic Purex Waste-Concentrate

	Molarity	Chemical Used	Molecular Weight	Amount per Liter
H^+	5.6	-	-	-
NO_3^-	6.1	HNO_3	63	268 ml, 15.9 M
$SO_4^=$	1	H_2SO_4	98	38.7 ml, 18.1 M
Na^+	0.6	$Na_2SO_4 \cdot 10H_2O$	322	96.6 g
Al^{+++}	0.1	$Al(NO_3)_3 \cdot 9H_2O$	375	37.5 g
Fe^{+++}	0.5	$Fe(NO_3)_3 \cdot 9H_2O$	404	202 g
Cr^{+++}	0.01	$Cr(NO_3)_3 \cdot 9H_2O$	400	4.00 g
Ni^{+++}	0.01	$Ni(NO_3)_2 \cdot 6H_2O$	291	2.91 g
UO_2^{++}	0.01	UO_3	286	2.86 g
$PO_4^{\equiv}$	0.02	H_2SiO_3	78	1.56 g

Table 18. Fission Products in Purex Waste Concentrate for Low Burn-up Reactor

	Concentration g/l	Chemical Used	Formula Weight	Amount per liter
Pb	0.054	$RbNO_3$	148	0.0932 g
Sr	0.137	$Sr(OH)_2 \cdot 8H_2O$	266	.416 g
Zr	0.462	$ZrO(NO_3)_2$	1 M soln, 81 g Zr/l	5.7 ml
Nb	0.007	Nb(metal)	92.9	.007 g
Mo	0.371	Mo(metal)	95.9	.371 g
Ru	0.184	$RuNO(OH_3 \cdot H_2O)$	200	.364 g
Rh	0.046	$Rh(NO_3)_3$	10% soln, Sp G, 1.05	1.23 ml
Pd	0.024	$Pd(NO_3)_2$	231	.052 g
Cs	0.318	$CsNO_3$	195	.466 g
Ba	0.130	$Ba(OH)_2 \cdot 8H_2O$	316	.299 g
La	0.133			
Ce	0.345			
Pr	0.130	Re_2O_2 Mixture	309 (avg)	2.626 g
Nd	0.443	Lindsay Mixture[a]	1110	
Sm	0.064			
Y	0.069			

[a] Rare earth mixture produced by Lindsay Chemical Co., West Chicago, Ill.

La	20-25%	Nd	15-20%
Ce	25-30%	Sm	7-10%
Pr	7-10%	Y	6-12.5%

to afford an explanation of the difference. A wet analytical method for sulfur analysis involving nitric and perchloric acid oxidation of the resin is being attempted to compare with the Paar bomb sulfur results. Both of these methods involve the complete oxidation of the sulfur to the sulfate form.

4.0 CHEMICAL APPLICATIONS OF NUCLEAR EXPLOSIVES (CANE)

(W. E. Clark)

Thermogravimetric Studies (W. D. Bond)

The apparatus and method used for the study have been described elsewhere.[26,27] The results of two separate runs showed that the measured weight loss - time curves were different for the same weight of initial sample, when the measurements were made under the same conditions of H_2 flow and temperature (Table 19). The reason for such behavior is apparently bed diffusion. The sample occupied more than half the volume in the sample pail and thus it is unlikely that one could get the same bed thickness and porosity every time.

Static Studies (W. D. Bond)

Studies were made in conventional vacuum equipment where the rate of consumption of hydrogen was measured by a manometer and the reduction product, water, trapped on a bed of $CaSO_4$. The dead volume varied between determinations and will be determined at a later time so that absolute reaction rates can be calculated. The pressure-time curves were essentially linear over the 200-600 mm range (Fig. 14). The departure from linearity near the ends of the curves is probably due to decrease in surface area as a result of sample consumption. The linearity of the curves suggests that the reaction is not adsorption controlled with the surface essentially saturated with adsorbed hydrogen at high pressures. Further work must be performed before a complete interpretation can be made.

Table 19. Summary of Thermogravimetric Studies of the Reaction of $CaSO_4$ and H_2

H_2 Flow Rate = 1370 cc/min: surface area = 2.9 m^2/gm

Run # 1			Run # 2		
Time, min	Temp., °C	Total Wt Loss mg	Time, min	Temp., °C	Total Wt Loss mg
30	800°C	10	74	850	45
10	840°C	20	90	865	235.2
110	850°C	235.9			

Initial Sample Weight = 0.5038 gm. Initial Sample Weight = 0.5052 gm.

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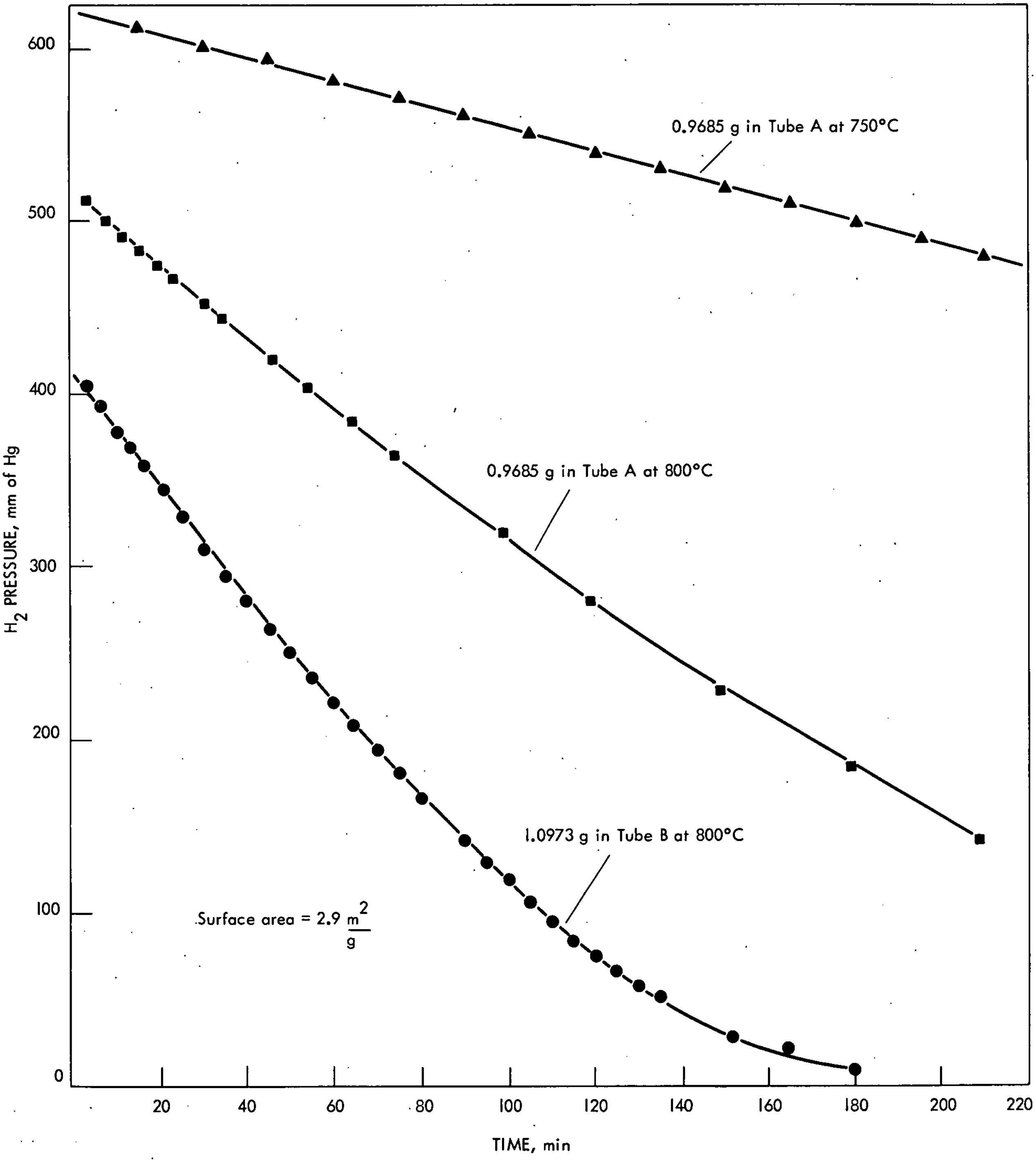

Fig. 14. Consumption of hydrogen by $CaSO_4$ in a static system.

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