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OCTOBER - DECEMBER 1959

**PHILLIPS
PETROLEUM
COMPANY**

ATOMIC ENERGY DIVISION

**NATIONAL REACTOR TESTING STATION
US ATOMIC ENERGY COMMISSION**

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I. SUMMARY

The ICPP successfully processed an experimental core of Organic Moderated Reactor Experiment (OMRE) fuel on a modified, "two cut", stainless steel dissolution flowsheet, achieving 99.63 percent recovery through the first cycle. MTR-ETR aluminum fuel was processed through the dissolution and first cycle extraction system at full rate (500 kg of Al/day) of a newly optimized flowsheet, achieving 99.7 percent recovery.

Laboratory studies on aqueous zirconium fuel processing indicated that increased uranium capacity together with lower waste storage requirements could be achieved with the present process if a system of short-term stability could be tolerated, e.g., in conjunction with some immediate waste treatment scheme such as calcination. If longer stability were required, i.e., 150 days or longer, little improvement could be made over the existing flowsheet. Successful dissolution of Zircaloy-2 with 3 percent uranium has been achieved under various conditions of air sparging and hydrogen peroxide addition using the Zirflex process (ammonium fluoride solution with peroxide oxidation). A pilot plant for study of continuous aqueous dissolution of zirconium fuels using these processes has been completed.

Aqueous stainless steel processing studies, carried out in conjunction with OMRE fuel recovery, disclosed that a surface film on the elements (resulting from decomposition of the terphenyl moderator and coolant in the reactor) which was resistant to sulfuric acid, sodium hydroxide, hydrogen peroxide, and hydrocarbon solvents, could be removed in boiling Turco 4502* solution. The rate of dissolution of stainless steel in sulfuric acid was found to increase in the order, type 318, 347, 304L in the approximate ratio 1 : 2 : 4. In all cases the initial rate of dissolution in 4M, 6M, and 8M acid also varied in the approximate ratio 1 : 2 : 4. Further tests indicated that addition of sufficient nitric acid to achieve a final dissolver solution concentration of 0.7M nitrate, after oxidation of the iron and uranium, was sufficient to assure solution of all the uranium. This was not necessarily established as the lower limit. In a study directed at easing safeguard restrictions in vessels of noncritically safe geometry, it was determined that boron concentration up to 2.7 g/liter could be tolerated in a typical flowsheet, limited by solubility of boric acid in the reagent streams. Use of this has not yet been made in actual plant operations.

Comparison of aluminum dissolution data from the pilot plant and the production plant, for extruded U-Al alloy, discloses that catalyst concentration above 0.01M has no effect on dissolution rate, and that scale-up of continuous dissolvers based on direct cross-sectional area is valid.

In aqueous waste studies the use of a newly designed polarograph cell in conjunction with radioactive tracers will permit measurement of the effect of applied potential on the reduction of fission products in

*Turco 4502 contains high percentages of KOH and KMnO_4 and, presumably, no phenolic materials.

aqueous stainless steel wastes at concentrations several orders of magnitude lower than with conventional polarographic techniques, thus assisting in development of processes for separation of fission products from alloy metal ions. Cesium 137 was removed from acidic radioactive wastes containing gross amounts of aluminum or zirconium by use of the inorganic ion exchange material, ammonium phosphomolybdate, which was found to have an exchange capacity of approximately 0.2 gram of cesium per gram of APM. The distribution coefficient for cesium in synthetic waste was approximately 1000 as compared to less than 1 for cerium and strontium. Interference by other alkali metal ions at concentrations expected in process wastes was negligible.

In a study of solvent stability, the rate of formation of n-butyl nitrate in tributyl phosphate, as a result of contact with various concentrations of nitric acid, has been determined to be a function of the extracted acid concentration, and to be accelerated by the presence of zirconium in the organic phase. A simple potentiometric titration for determination of total nitrate and zirconium in both aqueous and organic media was developed and will be useful in studying solvent performance with high burnup fuels where the increased amounts of zirconium, and resultant n-butyl nitrate, may have serious effects.

Preliminary investigation of electrolytic dissolution of stainless steel in nitric acid suggests flowsheet conditions which might give a metal concentration as high as 150 g/liter in 1M acid, resulting in low column feed rates, low raffinate bulk and very favorable uranium distribution conditions with low percentages of TBP. Stirred tank, continuous dissolution was demonstrated successfully for type 304, 304L, 347 and Carpenter 20 stainless steels; anode residues produced, while fairly bulky at this stage of development, were very fine particulates and contained negligible uranium. Design of an inert anode may hinge on the balance between the lower efficiency but more dependable operability of noble metals, as compared with the higher efficiency but greater difficulty in maintaining electrical contact with niobium.

Since the electrolytic dissolution of zirconium type fuel appears feasible in HCl-methanol, extraction of uranium from this solvent was studied. Extraction was achieved using 24 volume percent TBP in n-hexane; however zirconium also was extracted. In a study of the use of HCl-methanol as a decladding media, it was concluded that the dissolution of uranium dioxide pellets by chemical attack in HCl-methanol was negligible.

A tentative flowsheet for the ARCO process, which employs molten lead chloride as a solvent for zirconium-uranium alloys, is based on demonstration of the quantitative leachability of uranium from a lead chloride product matrix with 8M nitric acid and regeneration of the lead chloride by either aqueous precipitation or direct chlorination. A tentative phase diagram for the lead-rich portion of the UCl_4 - $PbCl_2$ system is presented. Eighteen-day corrosion tests on both welded and unwelded specimens have confirmed that several nickel alloys exhibit corrosion rates of 5 to 7 mils/month, with no intergranular corrosion.

Mechanical equipment development has resulted in a modified Model S Chempump (oversize bearings, welded impeller, dynamic balancing) which has run for one year (9672 hours), recirculating 1.5M aluminum nitrate-1.0M nitric acid solution, with a resulting wear of 1.0 mil or less. The principle of air pulsing is being successfully applied both to extraction column pulsing and to positive displacement pumping without check valves in two development projects which are continuing.

A corrosion evaluation program has indicated excellent resistance of 30 percent iridium-70 percent platinum alloy to boiling mixtures of HF-HNO₃, HCl-HNO₃, and H₂SO₄-HNO₃ in ranges most likely to be considered for fuel element dissolutions.

Notes are included on analytical methods developed for mercury, lead, tin, stainless steel components, and plutonium.

II. ICPP OPERATIONAL SCHEDULE, PERFORMANCE AND PROBLEMS

A. ICPP Processing Schedule, J. R. Bower, Problem Leader

Processing of Organic Moderated Reactor Experiment (OMRE) elements was completed during this quarter. Good uranium recovery and headend decontamination were achieved. Dissolution of MTR-ETR type fuels was started and continued through the end of the period at 75 to 100 percent of flowsheet rate.

Table 1, following, shows the quantities of material dissolved and schedule followed in ICPP operations during this quarter.

Table 1

QUANTITIES OF URANIUM DISSOLVED AT ICPP, OCTOBER-DECEMBER, 1959

<u>Week Ending</u>	<u>OMRE</u>		<u>Other</u>		<u>MTR</u>		<u>ETR</u>		<u>Other</u>	
	<u>Elements</u>		<u>Stainless Steel</u>		<u>Elements</u>		<u>Elements</u>		<u>Aluminum</u>	
	<u>Kg.U</u>	<u>No.</u>	<u>Kg.U</u>	<u>No.</u>	<u>Kg.U</u>	<u>No.</u>	<u>Kg.U</u>	<u>No.</u>	<u>Kg.U</u>	<u>No.</u>
Oct. 3	6.0	7								
Oct. 10	5.9	7								
Oct. 17	0.9	1	5	16						
Oct.24-Nov.28	No dissolution--product recovery underway									
Dec. 5					21.5	104	13.0	48		
Dec. 12					21.6	144	8.5	31	21.0	176
Dec. 19					2.7	16	36.3	224		
Dec. 26					7.2	48	130.0	508		

Four barium 140 product runs were completed. No unusual difficulties or problems were encountered. Product recovery was as follows:

<u>Run No.</u>	<u>Curies</u>	<u>Percent Recovered</u>
034RP	19,695	40.2
035RP	21,620	48.3
036RP	14,075	60.4
037RP	26,137	52.3

B. OMRE (Stainless Steel) Processing, J. R. Bower, Problem Leader; P. N. Kelly

First cycle processing of the first core of the OMRE begun last period⁽¹⁾ was successfully completed this period. The thirty-three elements of the core, each containing an estimated 800 grams of enriched uranium after burn-up (a total of 26.4 kilograms), were processed with low losses and good decontamination. Total loss was 0.37 percent compared to a design loss of 0.9 percent for stainless steel fuels. Log decontamination factors, listed in Table 2, determined from flowing stream samples compare favorably with the design log DF of 4 for stainless steel fuels.

Table 2

OMRE FIRST CYCLE DECONTAMINATION RESULTS

	<u>U</u>	<u>Th</u>	<u>Pu</u>	<u>Ru</u>	<u>Nb</u>	<u>Zr</u>
Log ₁₀ decontamination factor	4.50	4.52	0.85	3.49	4.72	6.14
Material balance (percent)	113	82		58	151	42

Total processing time required was 54 days including 18 days down time for decontamination and maintenance. Exclusive of down time this amounts to 1.1 days processing time per element.

Processing was accomplished in cells designed for Submarine Intermediate Reactor (SIR) fuel reprocessing, without benefit of pilot plant experimentation. Considerable experimentation was done during processing to develop a workable process and optimize the flowsheets.

The resulting flowsheets are shown in Tables 3 and 4, covering dissolution and extraction. The extraction flowsheet is generally similar to that for SIR processing, except for throughput rate, but dissolution varied considerably both in rate and method.

1. Dissolution

Dissolution of the stainless steel cladding and the stainless steel in the matrix alloy was accomplished with boiling 6.5M sulfuric acid using a steel wool trigger to initiate the reaction (Table 3). The trigger is needed because the Carpenter 20 SIR dissolver promotes a passivating effect on the dissolution. The uranium of the matrix was dissolved in a second step in 2M nitric acid, this dissolution also being carried out at reflux temperature. The nitric acid, in addition to dissolving uranium, inhibits action of the sulfate ion and permits the use of stainless steel vessels in the rest of the process.

In detail the metal dissolution steps deviated considerably from the SIR flowsheet. A terphenyl coating had to be removed from the OMRE elements before any metal could be dissolved. Terphenyl is the reactor moderator and is in a partially decomposed state. In this state it forms a tenaceous "tar-like" film resistant to the regular dissolution reagents. However the coating was very effectively removed in the dissolver with a hot (120°C) Turco 4502 (a commercial cleaning agent) solution.

The OMRE elements contain much larger quantities of stainless steel than SIR elements and a simple scale-up of the SIR process scheme was precluded by the limited dissolver operating volume. Dissolution was therefore performed in two "cuts", and this method of operation created a solids problem. Difficulty was experienced in sampling, jetting, and pumping because of solids in the dissolver after the first cut, and shortly after processing commenced one of the pump remote diaphragms ruptured. Processing was therefore interrupted for in-cell maintenance.

Table 3

BATCH FEED PREPARATION FLOWSHEET FOR OMFE FUEL ELEMENTS
Basis: One OMFE Fuel Element Per Batch - 12 Percent Burnup
Two H₂SO₄ and Two HNO₃ Dissolutions Per Element

	Metal ⁽¹⁾ Charged Per Batch	Turco Bath	After Turco H ₂ O Wash	Dissolver ^(1,2) Reagents		Dissolver ⁽⁴⁾ Product (1st cut)	Dissolver ^(1,2) Reagents		Dissolver ⁽⁴⁾ Product (2nd cut)	Dissolver ⁽³⁾ Washes For Two Dissolutions	Coarse Feed Adjustment Solution	Coarse Feed
				H ₂ SO ₄	HNO ₃		H ₂ SO ₄	HNO ₃				
Liters per batch		25	25	40	20	60	40	20	60	180	83	406 ⁽⁵⁾
Sp. G. at 25°C			1.0	1.24	1.19	1.29	1.24	1.19	1.29	1.0	1.367	1.16
Turco (4502), g/l		240										
HNO ₃ , M					6.0			6.0			13.0	
H ₂ SO ₄ , M				6.5								
H ₂ O			Pure									
Stainless steel, gms.	8300											
Stainless steel, g/l						69.2			69.2			20.4
Fission products, gms.	83					0.69			0.69			0.20
Uranium, g/l						6.67			6.67			1.97
Uranium, gms.	800											
H ⁺ , M				13.0	6.0	7.28		6.0	7.28		13.0	4.81
SO ₄ ⁼ , M				6.5		4.33			4.33			1.28
NO ₃ ⁻ , M					6.0	1.83		6.0	1.83		13.0	3.23

(1) Steel wool must be charged each cut to initiate the reaction.

(2) The dissolver must be purged with nitrogen before each H₂SO₄ dissolution.

(3) Includes 4-45 l. H₂O washes, three the first cut and one the second cut. Additional washes as required may be sent to PEW to lower NO₃⁻ for second cut H₂SO₄ dissolution.

(4) Based upon a presumed 50 percent dissolution for both Fe and U on each cut.

(5) Includes 23 liters jet dilution.

Table 4

OMRE FIRST CYCLE EXTRACTION FLOWSHEET
Basis: One Dissolver Batch Per Day

	<u>IAF</u>	<u>IAX</u>	<u>IAR</u>	<u>IAP</u>	<u>IBS</u>	<u>IBX</u>	<u>IBR</u>	<u>IBP</u>	<u>ICX</u>	<u>ICR</u>	<u>ICP</u>	<u>IDS and IDR</u>	<u>IDP</u>	<u>Evap. Boilup</u>	<u>Evap. Product</u>
Liters/day	435	249	436	249	125	50	125	299	74.8	299	74.8	7.5	74.8	71.4	3.4
Liters/hour	18.2	10.4	18.2	10.4	5.2	2.1	5.2	12.5	3.1	12.5	3.1	0.3	3.1	3.0	0.14
Sp.Gr., 25°C	1.16	0.781	1.15	0.791	1.109	0.781	1.117	0.786	1.002	0.781	1.002	0.757	1.145	1.0	1.334
HNO ₃ , M				0.23			0.41	0.003	0.01		0.022		0.022		0.48
Al(NO ₃) ₃ , M					0.70		0.70								
NH ₄ OH, M					0.04										
NH ₄ NO ₃ , M							0.04								
Stainless steel, g/l	19.0		19.0												
Fission Prod., g/l	0.19		0.19												
Uranium, g/l	1.84		0.002	3.22			0.006	2.68		0.003	10.73		10.73		235
H ⁺ , M	4.48		4.35	0.23			0.41	0.003			0.022		0.022		0.48
SO ₄ ²⁻ , M	1.19		1.19												
NO ₃ ⁻ , M	3.00		2.87	0.23			0.41	0.003			0.022		0.022		0.48
TBP, %		10				10				10					
Diluent, Amsco												Pure			

MIXER SETTLER SCRUB STREAMS

	<u>I</u>	<u>II</u>	<u>III</u>	<u>IV</u>
Liters/hr	3.3	3.3	3.3	3.3
Sp.Gr., 25°C	1.050	1.002	1.004	1.002
HNO ₃ , M		0.01		0.01
NaOH, M			0.01	
Na ₂ CO ₃	0.50			

Decontamination of equipment was accomplished with relative ease, using caustic-tartaric acid flushes, the cell radiation being reduced to workable levels in 5 days. This duplicated previous experience for the cell.

In addition to replacement of the ruptured diaphragm and a parallel pump diaphragm, several renovations aimed at alleviating solids problems were made. The pump diaphragm heads were reclined at a 15° angle to the horizontal to reduce the possibility of solids collecting and working against the diaphragm. Also, the tolerance on the ball check valve seats was increased. Both of these latter changes have been tried in other remote head pumps at this plant with good results. In addition to these changes an air lift was placed in parallel with the feed pumps. In order to provide submergence for the lift a recycle tank located at the top of cell was used as a feed tank. Transfer to the recycle tank from former feed tanks was via jet. The lift line chosen to provide desired rates (10 to 30 liters per hour) was 1/8-inch schedule 30 pipe, and is smaller than any lift line previously used in the plant. The lift was used during the balance of processing and performed well.

An additional change made at the same time was installation of a valve in the jet discharge line from the dissolver to the process equipment waste (PEW) system. This permitted vigorous sparging of the dissolver, without loss of solution to the PEW system, and helped alleviate dissolver jet and sample line plugging by keeping solids in suspension. This deficiency had been recognized during previous processing, but correction had been delayed until access to the cell was allowed.

The last mentioned renovation also permitted dissolver operation at a higher level and made a "one cut" dissolution look feasible. Besides being desirable to further alleviate the solids problem, a "one cut" dissolution would increase throughput by shortening heating, cooling, transfer and sampling times which occupy an appreciable portion of the dissolver batch cycle. After processing was resumed several "one cut" dissolutions were tried. None of these were successful as heel dissolutions were required after each attempt. However, correlation of dissolution data since the completion of the processing indicate that "one cut" dissolution may still be possible for any future OMRE processing.

2. Extraction

The extraction process utilizes three perforated plate pulse columns and one packed column, respectively, in the chain, extraction (A), scrub (B), strip (C), and scrub (D) (Table 4). The solvent used for OMRE extraction was 10 percent TBP in Amsco while 3M nitric acid was used for salting strength.

The extraction flowsheet for OMRE processing was similar to that used in SIR processing except for different volumes and throughput rates. Dissolution capacity was limited during this run with the columns operating on whatever feed was made available. As indicated in the introduction, the recovery and decontamination were satisfactory.

C. MTR-ETR Processing, J. R. Bower, Problem Leader; G. J. Raab

Processing of MTR and ETR fuels was underway in the CPM continuous dissolver headend system at the end of the quarter using newly optimized flowsheets (Tables 5, 6, 7 and 8). Both types of elements were processed on the same flowsheets because their aluminum-to-uranium ratios are approximately the same.

Because of a limited operating crew the first cycle product was held up in storage banks before being sent into the second cycle. The same crew alternately operated the headend system and the second and third cycles as required. Desired dissolution was obtained in one dissolver, for the most part, at about 75 percent of flowsheet rate. Extraction column rates ranged from 75 percent to full flowsheet. Full rate was not attained at all times because of a restriction in the first cycle feed control pot.

1. Dissolution

The dissolution flowsheet (Table 5) was calculated to apply to MTR elements at 30 percent burnup (the average for elements in storage) since some basis had to be picked to arrive at an accurate balance in terms of uranium, acid, specific gravity, etc. Actually the same flowsheet is suitable for ETR elements since they have very close to the same aluminum-to-uranium ratio. The unirradiated MTR aluminum-to-uranium ratio is approximately 19.5 while that for ETR is approximately 18.6. The flowsheet based on MTR fuel at 30 percent burnup results in a first cycle product (i.e., IIAF) which contains 162 grams per liter of uranium and 1.36M nitric acid at a specific gravity of 1.263. The resulting product from ETR at the same burnup would be approximately the same uranium concentration and slightly lower acid molarity when carried to the same specific gravity in the first cycle product evaporator. Thus any reasonably expected fuel from MTR or ETR should yield a satisfactory second cycle feed using this flowsheet.

The mercury catalyst concentration given in the flowsheet is a suggested value since dissolving characteristics of the fuels vary greatly with irradiation history. A number of unirradiated ETR elements, used for various mechanical tests during pre-startup testing, were processed during the same CPP run with irradiated MTR elements. The dissolution rate for the cold ETR elements was higher than for irradiated MTR fuel and the catalyst concentrations had to be adjusted accordingly.

2. Extraction

A mixture of irradiated MTR, ETR and damaged unirradiated ETR elements was processed, filling the N cell banks with first cycle product near the end of this quarter and making it necessary to shift the operation to the second and third Hexone cycles. The first cycle waste loss was 0.30 percent for this period of operation, based on waste batches sent to storage and metal charged. The decontamination performance for this portion of the run cannot yet be completely evaluated due to lack of analytical information. However, ruthenium was not detectable in the

Table 5

CONTINUOUS DISSOLUTION AND FIRST CYCLE EXTRACTION FLOWSHEET FOR MTR-ETR ELEMENTS

Basis: MTR Elements; 30% Burnup; 500 kg. of Aluminum Dissolved Per Day⁽¹⁾

	Dissolver Reagent	Dissolver Product	IAF	IAx	IAR	IAP	IBS ⁽³⁾	IBR	IBP	ICX	ICP (IDP)	ICR	IDS (IDR)	IIAF	IARm
Flow, liters/hr	500	482	516	380	512	380	58	58	380	200	201	380	20	5.0	
Density, at 25°C	1.199	1.296	1.286	0.77	1.292	0.78	1.159	1.166	0.78	1.001	1.014	0.77	0.76	1.263 ⁽⁴⁾	1.350 ⁽⁵⁾
Al(NO ₃) ₃ , M		1.60	1.60		1.61		1.0	1.0							1.95
HNO ₃ , N	6.3 ⁽²⁾	1.3	1.23		1.18	0.08		0.13	0.013	0.01	0.034			1.36	1.41
Hg(NO ₃) ₂ , M	0.007	0.007	0.007		0.007										0.008
NH ₄ OH, N							0.30								
NH ₄ NO ₃ , M			0.03		0.03			0.30							0.04
Uranium, g/l (irr.)		1.69 ⁽¹⁾	1.62		1.6x10 ⁻⁴	2.20		0.4	2.14		4.04	2.1x10 ⁻⁴		162	1.9x10 ⁻⁴
Uranium, g/l (unirr.)		2.21	2.12			2.86		0.4	2.80		5.28			162	
Solvent				3.25% TBP		3.25% TBP			3.25% TBP			3.25% TBP	Amsco		

(1) Aluminum/uranium ratios for MTR and ETR elements are so close (MTR-4.20 kg. Al., 0.215 kg U; ETR-5.07 kg. Al., 0.272 kg. U) that the same flowsheet serves for both. 500 kg/day of aluminum is equivalent to approximately 4.95 MTR or 4.1 ETR elements per hour.

(2) Assumes oxygen addition for conversion of oxides of nitrogen to HNO₃. (6.8 scfm air and 2.4 scfm O₂ as given in S.O.P. 3.11).

(3) Consists of all available II and IIIAR adjusted to specifications and recycled, together with fresh IBS as required to make up balance.

(4) Density at E. P. = 1.200.

(5) Density at E. P. = 1.302.

SECOND AND THIRD CYCLE EXTRACTION FLOWSHEET FOR MTR-ETR ELEMENTS
(from Storage in N Cell, 35 kg U/day)

	<u>IIAF*</u>	<u>IIAX</u>	<u>IIAS</u>	<u>IIAR</u>	<u>IIAP</u>	<u>IIBX</u>	<u>IIBP</u>	<u>IIBR</u>	II Cycle Evap.. Boilup
Flow, l/hr	9.0	34.6	25.6	34.4	34.9	9.2	9.7	34.6	5.6
Density at 25°C	1.263	0.80	1.320	1.242	0.86	1.002	1.200	0.80	1.00
Al(NO ₃) ₃ , <u>M</u>			2.0	1.49					
HNO ₃ , <u>N</u>	1.36					0.04	0.04		
NH ₄ OH, <u>N</u>			0.75	0.20					
NH ₄ NO ₃ , <u>M</u>				0.36					
U (irradiated) g/l	162			4.3x10 ⁻³	41.8		151	4.2x10 ⁻³	
Solvent		Hexone			Hexone			Hexone	
Fe(NH ₄) ₂ (SO ₄) ₂ , <u>M</u>			0.05	0.04					
HSO ₃ NH ₂ , <u>M</u>			0.10	0.07					

	<u>IIIAF</u>	<u>IIIX</u>	<u>IIIAS</u>	<u>IIIR</u>	<u>IIIP</u>	<u>IIIBX</u>	<u>IIIBP</u>	<u>IIIBR</u>	<u>III Cycle</u> Evap. Boilup	<u>Final</u> Product
Flow, l/hr	4.15	15.9	11.7	15.3	16.2	5.65	6.1	15.9	1.98	4.14
Density at 25°C	1.480	0.80	1.314	1.245	0.933	1.002	1.317	0.80	1.0	1.479
Al(NO ₃) ₃ , <u>M</u>			2.0	1.53						
HNO ₃ , <u>N</u>	0.09					0.04	0.04			0.06
NH ₄ OH, <u>N</u>			0.30	0.21						
NH ₄ NO ₃ , <u>M</u>				0.02						
U (irradiated) g/l	353			9.5x10 ⁻³	90.6		237	9.2x10 ⁻³		353
Solvent		Hexone			Hexone			Hexone		

*The IIAF flow is not defined by product flow from the first cycle; rather, it is based on demonstrated capacity operation of the second cycle.

Table 7
MIXER SETTLER FLOWSHEET

	<u>Mixer Settler Scrub Streams</u>		
	<u>I</u>	<u>II</u>	<u>III</u>
Relative Flow	38	38	38
Density at 25°C	1.002	1.050	1.002
HNO ₃ , <u>N</u>	0.04		0.04
Na ₂ CO ₃ , <u>M</u>		0.50	

Table 8
SOLUTION SPECIFICATIONS FOR MTR-ETR FLOWSHEETS
Cycle I

Dissolver Acid	6.4 ± 0.20M HNO ₃
Catalyst Stock Solution	0.29 ± 0.03M Hg(NO ₃) ₂
IAX	3.25 ± 0.25% TBP by volume
IBS	1.0 ± 0.05M Al(NO ₃) ₃ 0.3 ± 0.06N NH ₃
ICX	0.01 ± 0.001N HNO ₃
First Stage Solvent Wash	0.04 ± 0.01N HNO ₃
Second Stage Solvent Wash	0.5 ± 0.10M Na ₂ CO ₃
Third Stage Solvent Wash	0.04 ± 0.01N HNO ₃

Cycles II and III

IIAS	2.0 ± 0.06M Al(NO ₃) ₃ 0.75 ± 0.06N NH ₃ 0.05 ± 0.01 reducing N
IIBX	0.04 ± 0.004N HNO ₃
IIIAS	2.0 ± 0.06M Al(NO ₃) ₃ 0.30 ± 0.06N NH ₃
IIIBX	0.04 ± 0.004N HNO ₃

first cycle product. Specification product should be produced by the second and third Hexone cycles since ruthenium is the most difficult to remove in these cycles. This processing will continue into the next quarter with each cycle being operated at least twice more. Actual performance will be reported after completion of the campaign.

The second and third cycle (Hexone) flowsheets are common since all IIAF will be essentially of constant composition, within the usual range of plant operation. The volume throughput for the second and third cycles is based on capacity operation as demonstrated in recent processing. The IIAF flow is not defined by product flow from the first cycle since the first cycle product will be held up in N cell storage; therefore, the throughput is greater (kg uranium/day) than for the first cycle operation.

D. Plutonium Contamination of Waste Solvent, J. R. Bower, Problem Leader;
G. K. Cederberg

Plutonium, amounting to about 150 micrograms per liter, was identified in the waste solvent following the end-of-run clean up of the first cycle extraction equipment in July 1959. This concentration was a potential health hazard because the solvent is burned and the combustion products are discharged to the atmosphere via the 250-foot plant stack. Poor atmospheric diffusion conditions could cause above tolerance concentrations of plutonium at ground level. Burning was stopped until the solvent could be decontaminated to a "safe level" which was set at 1.5 micrograms per liter by the Site Survey Branch of the IDO Health and Safety Division.

Studies on solvent samples in the laboratory showed that 0.05M ferrous ammonium sulfate and 0.1M sulfamic acid in 0.2M nitric acid would strip the plutonium from the solvent. However, the test data did not clearly indicate what mechanism caused the plutonium to appear in the stream in the first place. The waste solvent stored in the plant vessels was decontaminated by contacting it with the prescribed aqueous mixture in the plant mixer settlers and in tanks using pumps and jets for recirculation where the solvent could not be processed in the mixer settlers. These results were reported in greater detail last quarter(1)

Subsequent scrutiny of the test data has not revealed what chemical or physical mechanism caused the plutonium to appear in the waste solvent. Apparently it was a unique problem which had not previously occurred at ICPP. This was deduced from a review of the daily alpha emission through the plant stack using the stack gas monitor record. Prior to this time, routine alpha analyses of stack gas monitor solutions showed only one-tenth to one-hundredth the alpha count as compared with stack monitor concentrations while some of the contaminated solvent was being burned.

Adequate Health Physics protection of personnel in the vicinity of the burner required the initiation of a new procedure to routinely sample the waste solvent at the storage tank (LE-102) and analyze it for plutonium. The batches of solvent which exceed 1.5 micrograms of plutonium per liter are contacted with an aqueous strip solution of ferrous ammonium sulfate, sulfamic acid and nitric acid.

Samples of solvent taken from the burner waste solvent storage tank (LE-102) frequently indicate that the plutonium concentration increases when the solvent is transferred from the temporary waste solvent storage tank (H-108). This suggests that the plutonium behaves erratically because it is present in both soluble and solid states. Possibly the agitation effected by transfer redistributes some of the solid plutonium which may be concentrated on surfaces and at solution interfaces. This could cause a fine dispersion which is observed in the sample as an increase in plutonium concentration. It is also possible that the pump and pipeline (several hundred feet) from H-108 to LE-102 have been contaminated and that the transfers erode the plutonium into the uncontaminated stream.

During a plant test the burner was operated using clean solvent to determine if plutonium activity already in the burner was being eroded in hazardous quantities. The test result was negative; however, preheating of the fire box with clean solvent proved beneficial in eliminating fire blowouts, which usually occur on startup, while burning contaminated solvent. Preheating equipment was installed for permanent use. Intermittent burner operation was suspected of blowing contaminated gas out of the blow holes around the burner. Hinged flappers were installed to decrease the volume of gas blown out the holes.

Additional experimental work is planned to define the equilibrium plutonium concentration in the waste solvent during normal plant operation. Plant tests will scope the effectiveness of various other methods for removing the plutonium from the waste solvent.

E. Activity in ICPP Raw Water, J. R. Bower, Problem Leader; V. D. Sullivan

Ruthenium 106 activity in the raw water supply has fallen to approximately 2.5×10^{-7} $\mu\text{c/ml}$, near the pre-May, 1959, level. As previously reported,⁽¹⁾ a peak of activity was reached during May, 1959, when 70×10^{-7} $\mu\text{c/ml}$ ruthenium 106 was detected. The maximum permissible content for ruthenium 106 in drinking water is 4×10^{-3} $\mu\text{c/ml}$.

New vitrified tile service waste lines from the service building to the monitoring building and from the monitoring building to the disposal well are in the process of being installed to replace the leaking concrete lines reported previously. At the same time that the ground was opened for this change, a badly leaking fire water loop, running parallel for several hundred feet, was replaced. This was adding a sub-surface flow of water which may have helped transport activity leaking from the service waste line.

Drilling of a new monitoring well, No. 52, 1,400 feet east of the disposal well and 1,800 feet south (downstream) of the supply wells was started in November, 1959. Water was encountered at about 161 feet (normal water table is at a depth of approximately 450 feet). Samples from depths of 166 feet and 220 feet contained 76 and 320×10^{-7} $\mu\text{c/cc}$ respectively of ruthenium 106 activity. Samples from this well were analyzed for nitrates and found to contain approximately 15 ppm nitrates which is close to the mean average for streams in the area. In the event the nitrate content had been high the permanent storage tanks would have been suspect. The source of this activity is at present unknown.

III. AQUEOUS PROCESSING STUDIES

A. Aqueous Zirconium Fuel Processing

In an effort to improve the present zirconium processing methods, exploration of the boundaries of the stability regions of the zirconium, aluminum and fluoride containing extraction column streams has continued. In connection with barium fluozirconate precipitation to remove zirconium and fluoride from STR process solution, the problem of handling the resulting high nitric acid solutions is being pursued. Continued studies on the Zirflex process have resulted in definition of conditions for dissolution of fuel containing 3 percent uranium. A pilot plant for continuous dissolution of zirconium fuel has been completed and is to be used for study of modifications to the existing process and the Zirflex process as discussed herein.

1. Interim Zirconium Flowsheet Modifications

a. The Stability of the Extraction Column Feed, K. L. Rohde, Problem Leader; O. W. Parrett

One method of improving the original STR process flowsheet is to obtain a more concentrated and yet stable extraction feed which would in turn increase the uranium capacity of the process and reduce the waste volume.

Existing stability data^(2,3,4) were obtained from extraction feeds which were aged for a four-day period. The extreme boundaries of the stability regions of the system were not clearly defined by this short-term data and no data have been available for a system that had aged for a period of greater than four days.

In previous studies,⁽⁵⁾ utilizing raffinate solutions that were produced from hydrofluoric acid dissolutions, it was found that increasing the hydrogen ion concentration did enhance the short-term, ten-day, stability and it was indicated that a reduction in the aluminum concentration could improve the long-term, 150-day, stability.

The purpose of this current study was (1) to utilize the above information and determine the effect of variation in the composition of the system upon the stability of the extraction process feeds, (2) to more completely define the boundaries of the stability regions as affected by **aging**, and (3) determine the position of the existing flowsheet in these stable regions.

Experimental

The initial compositions of a series of extraction process feed solutions are shown in Table 9. These feeds were obtained from actual zirconium fuel dissolutions with hydrofluoric acid and adjustments to the compositions desired. The initial aluminum nitrate concentrations were held constant at three levels, namely, 1.0M, 0.75M, and 0.5M. The initial fluoride ion concentrations were varied in each

Table 9
STR FEED STABILITY
Initial and Equilibrium Solution Composition

Sample No.	Initial Composition					Final Equilibrium Comp.		
	Zr <u>M</u>	F <u>M</u>	Al <u>M</u>	H <u>M</u>	NO ₃ <u>M</u>	Zr <u>M</u>	F <u>M</u>	Al <u>M</u>
11	0.75	3.75	0.75	1.05	2.55	0.603	3.2	0.75
12	0.75	4.00	0.75	1.30	2.55	0.514	3.4	0.75
13	0.75	4.25	0.75	1.55	2.55	0.453	3.4	0.75
14	0.75	4.50	0.75	1.80	2.55	0.462	3.5	0.70
15	0.75	4.75	0.75	2.05	2.55	0.488	3.5	0.52
16	0.75	5.00	0.75	2.30	2.55	0.513	3.2	0.39
17	0.75	5.25	0.75	2.55	2.55	0.544	2.9	0.25
18	0.8	3.2	0.75	0.51	2.56	0.476	2.61	0.74
19	0.8	3.7	0.75	1.01	2.56	0.595	3.31	0.75
20	0.8	4.2	0.75	1.51	2.56	0.467	3.34	0.73
21	0.8	4.7	0.75	2.01	2.56	0.473	3.19	0.46
22	0.8	5.2	0.75	2.51	2.56	0.526	3.16	0.19
23	0.8	5.7	0.75	3.01	2.56	0.79	4.76	0.18
24	0.8	6.2	0.75	3.51	2.56	0.79	5.13	0.12
25	0.8	3.2	0.5	0.51	1.81	0.60	3.07	0.471
26	0.8	4.2	0.5	1.51	1.81	0.666	4.17	0.422
27	0.8	5.2	0.5	2.51	1.81	0.777	4.82	0.182
28	0.8	6.2	0.5	3.51	1.81	0.785	5.85	0.130
29	0.8	3.2	1.0	0.51	3.31	0.433	2.52	1.04
30	0.8	4.2	1.0	1.51	3.31	0.408	3.14	0.99
31	0.8	5.2	1.0	2.51	3.31	0.319	2.34	0.53
32	0.8	6.2	1.0	3.51	3.31	0.550	3.31	0.15
78	0.75	3.2	0.75	0.51	2.56	0.478	2.51	0.74
79	0.75	3.7	0.75	1.01	2.56	0.600	3.25	0.76
80	0.75	4.2	0.75	1.51	2.56	0.470	3.40	0.72
81	0.75	4.7	0.75	2.01	2.56	0.468	3.26	0.42
82	0.75	5.2	0.75	2.51	2.56	0.550	3.51	0.20
83	0.75	5.7	0.75	3.01	2.56	0.715	4.62	0.20
84	0.75	6.2	0.75	3.51	2.56	0.722	5.22	0.12

level of aluminum nitrate from 3.2M to 6.2M and the hydrogen ion concentrations were varied correspondingly from 0.5M to 3.5M. The zirconium concentrations were initially constant at around 0.8M. These samples were allowed to reach equilibrium at room temperature. Periodic samples of the supernate were taken for analysis of the zirconium concentration. Emission spectroscopy analysis of the solids showed them to be compounds of aluminum and zirconium, however, x-ray diffraction patterns obtained from these solids disclosed that the only crystalline compounds present were the zirconium tetrafluoride trihydrate and another

as yet unclassified zirconium compound. (6) In seven sets of samples, numbers 11 through 17, material balances were made for fluoride, aluminum, and zirconium between the initial solutions and the final solutions plus the precipitates. The material balance for the zirconium was found to be 101.1 percent with a standard deviation of ± 2.8 percent; for the aluminum the material balance was found to be 97.0 ± 12.0 percent; and for the fluoride the material balance was found to be 84.3 ± 8.0 percent. Further examination of the data indicated that the low fluoride material balance must be due to the solid analysis and not an error inherent in the solution fluoride analysis.

The Effect of Composition Variation Upon Long-Term Stability

The final equilibrium compositions are tabulated in Table 9. From these data it was found that in a system in which a dissolver solution was adjusted with hydrofluoric acid and aluminum nitrate, the hydrogen ion concentration must not exceed $1.5M$ if the aluminum is to be soluble, be it at the 0.5 , 0.75 , or $1.00M$ level of aluminum concentration. At all these levels when the hydrogen ion concentration exceeds $1.5M$ precipitation of aluminum occurred, whereas, at lower hydrogen ion concentrations only the zirconium compounds precipitated.

Other conclusions can also be made in the three levels of aluminum concentration that were studied:

- (1) At the $0.75M$ aluminum nitrate concentration, the highest zirconium concentration obtained was about $0.6M$ in a system composed of $3.2M$ fluoride, $1.05M$ hydrogen and $2.56M$ nitrate. See samples numbered 11, 19 and 79 of Table 9.
- (2) At the $1.00M$ aluminum nitrate concentration level, the highest zirconium concentration obtained was about $0.4M$ in a system composed of $2.5M$ fluoride, $0.51M$ hydrogen and $3.31M$ nitrate. See sample numbered 29 of Table 9. Sample number 30 also retained this aluminum concentration in solution with a slightly different composition.
- (3) At the $0.5M$ aluminum nitrate concentration level, the highest zirconium concentration obtained was about $0.67N$ in a system composed of $4.17M$ fluoride, $1.51M$ hydrogen and $1.81M$ nitrate. See sample numbered 26 on Table 9. Sample numbered 25 also retained this aluminum concentration with a slightly lower zirconium concentration.

The standard deviation obtained from control data on the fluoride analysis was such that several more analyses were needed to increase the confidence limits of the data. With these additional analyses a much more precise picture of the stable regions will be presented in a topical report now being prepared.

The Effect of Composition Variation Upon Short-Term Stability

If a plot is made of the zirconium concentration in solution against the aging time (Figures 1 and 2), the 0.5M aluminum nitrate concentration level appears to be most promising in that a system was obtained containing about 0.8M zirconium which was stable after aging for 24 days throughout the total range of fluoride and hydrogen ion concentrations studied (see Figure 2). Calculations showed that an increase from 10 to 12.5 percent in tributyl phosphate concentration compensated for the reduction in salting strength resulting in the decrease from 0.75M to 0.5M aluminum nitrate indicating that uranium recovery from this latter system was entirely feasible.

CPP-S-1310

Fig. 1 - STR extraction feed stability curves at the 0.75M aluminum nitrate level. Curve numbers refer to data from Table 9 for the corresponding sample numbers. Solid curves (o—o) indicate solution from which only zirconium compounds precipitated. Dotted curves (□---□) indicate solutions from which both aluminum and zirconium compounds precipitated.

Conclusions

From this study it was concluded that variation of the concentrations of aluminum, hydrogen and fluoride will not produce a system that is stable for 150 days and yet appreciably more concentrated than that which was designed for the existing flowsheet.

However, if a system of short-term stability can be utilized in conjunction with some immediate waste treatment, such as calcination, then a more concentrated extraction feed could be flow-sheeted which would increase the uranium capacity of existing equipment by 35 percent and reduce the waste volume to be calcined.

CPP-S-1311

Fig. 2 - STR extraction feed stability curves at the 0.5M aluminum nitrate level. Curve numbers refer to data from Table 9 for the corresponding sample numbers. Solid curves (o—o) indicate solution from which only zirconium compounds precipitated. Dotted curves (□--□) indicate solution from which both aluminum and zirconium compounds precipitated.

b. Barium Fluozirconate Precipitation Process, K. L. Rohde,
Problem Leader; B. E. Paige

Barium fluozirconate precipitation has been studied as a possible means for simultaneously removing both the zirconium and fluoride from STR process solutions. Scoping studies have been made to determine the feasibility of such a precipitation either as a tail-end process to separate bulk zirconium from fission products or as a head-end process to allow a decrease of column feed volumes by evaporation without jeopardizing the stability of the process solutions. Waste volume gains would also be made by such a head-end process. A complete resume of the experimental data for these scoping studies will be published.

A process for the barium fluozirconate precipitation from the STR dissolver solution has continued to be of primary interest and attention has been focused on the neutralization of the excess acid in the solution. Data on the solubility of barium fluozirconate in aluminum nitrate which have now been obtained have confirmed previous indications that a tail-end process, or any process for barium fluozirconate precipitation from an aluminum nitrate solution, could not produce a high degree of zirconium removal. Solubility values as high as 10 grams of zirconium per liter in 0.3M aluminum nitrate and 40 grams of zirconium per liter in 1.2M aluminum nitrate were obtained. Nitric acid solubility data presented in the last quarterly report⁽¹⁾ showed that the solubility of two species of barium fluozirconate increased from about 1 or 2 grams of zirconium per liter in 0.1N nitric acid to 5 or 7 grams of zirconium per liter in 3N nitric acid. Precipitation of barium fluozirconate from STR dissolver solutions with barium nitrate produces nitric acid concentrations which not only limit the zirconium removal because of this solubility, but are also too high for a purex extraction system after they have been evaporated to the limit of zirconium stability. Two methods of eliminating the high nitric acid concentration have been studied.

Precipitation with Solid Alkaline Barium Compounds

Barium carbonate, barium hydroxide, barium oxide, and barium peroxide were studied as possible solid precipitants for barium fluozirconate which could neutralize the excess acid during precipitation. Stoichiometric amounts of these compounds which were added to partially neutralize the excess acid did not decrease the acidity to 0.2N as expected. The solution acidity could not be lowered by the addition of more alkaline precipitant. This was probably due to the hydrolysis of the zirconium species in solution which also prevented the further formation and precipitation of barium fluozirconate. These precipitants decreased zirconium concentration in the supernate from 1.6M to 0.5M which is not as low as has been obtained with solid barium nitrate. The final acidity of the supernate ranged from 0.5 to 0.9N. A second precipitation step using barium nitrate further reduced the zirconium to about 0.1M, the usual concentration obtained with barium nitrate precipitations.

The alkaline barium compounds have an advantage over barium nitrate as solid precipitants because of their rapid and complete reaction with the acid solution. In the case of the barium carbonate, the zirconium removal and acid neutralization were complete in less than 10 minutes

after the last carbonate addition. X-ray analysis showed that there was no residual solid precipitant left in the barium fluozirconate precipitate after a one hour reaction period at 85°C with any of the alkaline precipitants. Although barium carbonate precipitation is accompanied by effervescence, this precipitant reacts rapidly and thus has only one solid phase present during the barium fluozirconate precipitation and therefore, may be more desirable from a process standpoint. Uranium losses for these precipitations were comparable to other barium fluozirconate precipitation techniques, and multiple washing with dilute nitric acid will be necessary to decrease the uranium losses to as low as 0.2 percent.

Denitration with Formaldehyde

Following a solid barium nitrate precipitation, formaldehyde was added continuously to the slurry at 85°C to decompose excess nitric acid. In order to achieve maximum nitric acid removal sufficient formaldehyde was added for a decomposition efficiency of only 1.8 moles of nitric acid per mole of formaldehyde. After the continuous addition of formaldehyde was completed, digestion at 85°C for 3 hours did not produce further decomposition. The nitrate ion was decreased from about 3M to 0.1M, but the hydrogen ion was decreased only to about 1M. This was probably due to residual formic acid. Zirconium concentration was reduced 90 percent by the combined barium nitrate precipitation and formaldehyde denitration steps. A final barium nitrate precipitation produced a likely process solution containing only 0.03M barium fluozirconate, which is the solubility limit, and having a nitric acid concentration slightly less than 1M. Uranium losses to the precipitate were not increased by the denitration.

- c. Homogeneous Dissolution of Three Percent Uranium-Zirconium Alloys Using the Zirflex Process, K. L. Rohde, Problem Leader; B. J. Newby

Studies directed toward the development of a process for the continuous, homogeneous dissolution of uranium-Zircaloy-2 (STR fuel) in ammonium fluoride with peroxide oxidation have continued. The conditions for the successful batch dissolution of fuel 3 weight percent* in uranium have been defined during the current quarter and work will proceed on continuous dissolution studies with the objective of preparing a flowsheet for pilot plant testing.

Experimental

Part of the batch dissolution studies attempting to dissolve 3 percent uranium-Zircaloy-2 in ammonium fluoride-hydrogen peroxide were performed under conditions resulting in the removal of ammonia produced during the reaction. The procedure, technique, and apparatus for performing such experiments have been described in the immediately

*With the present methods of STR type fuel disassembly, the 3 percent uranium segment used here would be representative of a full fuel element.

preceding quarterly progress report⁽¹⁾ with the exception that some of these experiments were carried out without air sparging. The fluoride-zirconium mole ratio was held constant from experiment to experiment while the hydrogen peroxide concentration in the dissolver solution (assuming no decomposition) and the manner of adding hydrogen peroxide during the dissolution were varied.

The remainder of the batch dissolutions were performed under conditions of total reflux making no special attempt to remove ammonia. Hydrogen peroxide was injected a drop at a time into the bottom of the dissolver while the fuel was held just beneath the surface of the dissolver solution. Since the rate of Zircaloy-2 dissolution increased as the fluoride-zirconium mole ratio was increased, hydrogen peroxide was added more rapidly as this ratio was increased. Fluoride-zirconium mole ratios were varied from 6.6 to 7.7 : 1. Other experimental conditions were identical to those used for the dissolutions described in the previous paragraph.

Results and Conclusions

The results of the various ammonium fluoride-hydrogen peroxide dissolutions described in the experimental section of this report are recorded in Table 10. Findings may be summarized as follows:

(1) no advantage could be seen in using dissolutions under conditions that purposely result in the removal of the ammonia produced during the reaction (sweeping ammonia out with air and allowing free evaporation while replacing the loss) over dissolutions performed under total reflux, (2) air sparging does not appear to oxidize uranium (IV) under the experimental conditions described, (3) it was not clear whether or not more successful homogeneous dissolutions resulted when hydrogen peroxide (which is thought to form an oxygen supported film on the fuel resulting in decreased Zircaloy dissolution rate) was added to the dissolver solution at a point distant from the fuel position rather than in the vicinity of the fuel, (4) adding a given amount of hydrogen peroxide slowly as a concentrated solution did not appear to offer advantages over adding the same amount of hydrogen peroxide more rapidly as a more dilute solution, (5) increasing the fluoride-zirconium mole ratio from 6.6 to 7.7 : 1 markedly increases the amount of 3 percent uranium-Zircaloy-2 that could be dissolved homogeneously and, (6) no short time stability differences could be discerned between the dissolver solutions resulting from dissolution using fluoride-zirconium mole ratios ranging from 6.6 to 7.7 : 1.

2. Continuous Dissolution Pilot Plant Status, J. A. Buckham, Problem Leader; M. D. Martin and E. D. Howell

Construction and calibration of a pilot plant facility for development of improved aqueous processing schemes for zirconium-bearing fuels are essentially complete. Experimental studies will be initiated in the near future. These facilities will be used to study continuous aqueous reprocessing applicable to a wide variety of zirconium fuels ranging from those power reactor fuels containing only a few percent zirconium to the Navy-type fuels containing over 98 percent zirconium. It is intended that these studies will make available high capacity, low cost processes for zirconium fuels which can utilize proven technology and therefore

Table 10

CONDITIONS AND RESULTS OF ZIRFLEX DISSOLUTION OF 3 PERCENT URANIUM-ZIRCALOY-2 FUEL
(6 Hr. Batch Dissolution of 10 g. Fuel Pieces)

Type of Dissoln.	Composition of Soln. Used to Replace Liquid Loss	Method of H ₂ O ₂ Addition	Mole Ratio of Fluoride to Zr. in Coupon	Mole Ratio of H ₂ O ₂ to U in Final Dissolv. Soln. (Assuming No H ₂ O ₂ Decomp.)		Zircaloy-2 Dissoln. Rate Mg/(sq.cm)(min)	Dissolver Solution		Equivalent Fuel Dissolved Homogeneously
							Zirconium M	Uranium g/l	
A	Water	None Added	6.6			9.8	0.75	0.02	0.03
A	0.01M H ₂ O ₂	D	6.6	8		3.4	0.75	0.10	0.1
A	0.05M H ₂ O ₂	D	6.6	41		3.6	0.66	1.49	2.1
A	0.05M H ₂ O ₂	D	6.6	41		3.4	0.49	0.94	1.8
A	Water	E	6.6	5		3.5	0.63	0.34	0.5
B	Water	E	6.6	5		3.5	0.59	0.50	0.8
A	Water	E	6.6	10		3.5	0.49	0.34	0.6
B	Water	F	6.6	7		3.6	0.55	0.46	0.8
C		G	6.6	10		3.8	0.61	0.55	1.0
C		H	7.0	13		3.8	0.61	1.28	2.3
C		I	7.0	13		3.8	0.67	1.60	2.7
C		J	7.7	16		3.8	0.59	1.78	3.1
C		K	7.7	16		3.8	0.66	1.92	3.0

- (A) The dissolution was performed allowing evaporation loss to take place and replacing the loss; also, 117 c.c./min of air (at 70°F and 14.7 psia) was bubbled through the dissolver solution.
- (B) This dissolution was performed allowing evaporation loss to take place and replacing the loss; no air was bubbled through the dissolver solution.
- (C) The dissolution was performed under total reflux; no air was bubbled through the dissolver solution.
- (D) H₂O₂ was added as a dilute solution to replace evaporation loss.
- (E) A drop of 1.5M H₂O₂ was added at the bottom of the dissolver about every 4 minutes.
- (F) Same as (E) with the exception that the H₂O₂ was added over the surface of the dissolver solution.
- (G) 0.1 ml of 1.5M H₂O₂ was added at the bottom of the dissolver every 3 minutes for 4 hours, every 15 minutes for 2 hours; fuel was held at the dissolver solution surface.
- (H) Same as (G) with the exception that the 1.5M H₂O₂ was added every 2 minutes for the first 4 hours.
- (I) 0.1 ml of 3.0M H₂O₂ was added at the bottom of the dissolver every 4 minutes for 4 hours, every 15 minutes for 2 hours; fuel was held at the dissolver solution surface.
- (J) 0.1 ml of 1.5M H₂O₂ was added at the bottom of the dissolver every 1.5 minutes for 40 minutes, every 2 minutes for 3 hours and 50 minutes, every 15 minutes for 1.5 hours; fuel was held at the dissolver solution surface.
- (K) 0.1 ml of 3M H₂O₂ was added at the bottom of the dissolver every 3 minutes for 40 minutes, every 4 minutes for 3 hours and 50 minutes, every 15 minutes for 1.5 hours; fuel was held at the dissolver solution surface.

can be applied on a production scale much sooner than many of the more futuristic processes. If suitable advances are made in processing of the waste solutions from these processes, aqueous processes may be the most economical manner of reprocessing zirconium fuels for many years.

Initial studies will be made on the continuous dissolution of 2 percent zirconium fuels in nitric acid containing sufficient aluminum fluoride so that the effluent fluoride-zirconium mole ratio always exceeds four. Most of the studies with Navy-type high zirconium content fuels will involve adaptations of the STR and Zirflex batch flowsheets. Whenever possible, development will be directed towards integral continuous dissolution of the entire fuel. The use of processes under current laboratory development involving oxidation of uranium to the hexavalent state with nitric acid, hydrogen peroxide, or aluminum nitrate for tolerance of increasing quantities of uranium in Navy fuels will be investigated.

Dissolver effluents which contain free fluoride ion will be complexed with aluminum nitrate so that they will be compatible with existing stainless steel and glass extraction equipment. Precomplexing by introduction of the aluminum nitrate into the feed will also be investigated. Some studies in the extraction equipment will be made concurrently with the dissolution studies.

a. Pilot Plant Details

A pilot plant facility for study of continuous aqueous dissolution of zirconium fuels using processes such as described above has been completed. The equipment is enclosed in a Transite cubicle equipped with an exhaust fan discharging through the roof of the laboratory building to provide protection from any fumes or vapors which might be released. The operating panel is mounted on a wall of the cubicle in the laboratory operating area. Figure 3 is a simplified diagram of the equipment and facilities provided.

Annealed Carpenter-20 alloy was used for most of the vessels and process piping although equipment which does not come into contact with hydrofluoric acid was constructed of stainless steel. Corrosion studies indicate that Carpenter-20 is the best compromise alloy for service with nitric acid-hydrofluoric acid mixtures; however, the corrosion rates may be severe with some of the flowsheets to be investigated.

The fuel elements will be charged to the continuous dissolver through a special slide valve and charging tube, the latter passing through an annulus in the tube sheet of the off-gas condenser into the dissolver. This tube is purged with nitrogen to prevent explosions due to sparking of fuel elements when they are dropped and to keep the reacting solution from rising in the tube. An excess of fuel will be maintained in the tube with the fuel level in the dissolver being controlled by the position of the lower end of the charging tube. Three interchangeable charging tubes have been provided to allow investigation of fuel bed heights of 3, 6 and 12 feet.

FIGURE 3
CONTINUOUS ZIRCONIUM DISSOLUTION SYSTEM

CPP-S-1312

Extensive control instrumentation is used to reduce required entrance into the process cubicle during operation. The liquid feed rate is automatically controlled (and recorded) over a range of approximately 4 to 60 liters per hour.

Sampling is performed at a centralized, remote sampling station using glove box techniques. Sample streams are recirculated from the process vessels, through sample pots, and back to the process by use of air lifts.

B. Aqueous Stainless Steel Fuel Processing

Stainless steel fuels are processed at the ICPP by dissolution of the steel in 6M sulfuric acid followed by dissolution of the uranium in 2M nitric acid added to the sulfuric acid-stainless steel "cut". This solution is adjusted with 13M nitric acid in preparation for TBP extraction.

The OMRE (Organic Moderated Reactor Experiment) fuel processed during this period resisted dissolution due to the presence of a carbonaceous surface film resulting from degradation of the organic moderator in the reactor. Removal of this film, to permit dissolution of the fuel to proceed normally, was the subject of laboratory investigation. Other plant assistance type activities involved dissolution rate studies, nitrate requirements to assure complete uranium dissolution, stability of dissolver solutions, and possible use of boron containing solutions to extend criticality safeguard limits.

1. Plant Assistance Flowsheet Studies, K. L. Rohde, Problem Leader;
R. D. Cannon

a. OMRE Fuel Cleanup

OMRE fuel elements, as removed from the reactor for reprocessing, are coated with a carbonaceous degradation product of the terphenyl moderator-coolant used in the reactor. This protective layer must be removed, exposing the element to the dissolving reagent, if the dissolution is to proceed at a satisfactory rate. Tests on coupons cut from a fully irradiated, unfueled, fuel element have shown this coating to resist attack of boiling concentrated sulfuric acid, 6M sulfuric acid, 8M sodium hydroxide, 1M hydrogen peroxide with or without 6M sulfuric acid, and organic solvents i.e., Amsco 125-90W. The film can be removed by a two hour contacting with Turco 4502 (hot, 2 lb/gal). This treatment does not create a passive film on the steel nor destroy steel wool, which may be added to trigger the dissolution. Heating the element in air at 500°C for two hours also removes the residue layer.

The Turco 4502 treatment was successfully verified on fully irradiated fuel-plate coupons which subsequently showed no passivation toward 6M sulfuric acid dissolution.

b. Dissolution Rate Data

A series of dissolution rates for various stainless steels in sulfuric acid were measured. These data were taken to facilitate process planning for some GCRE scrap and to provide a foundation for extending the range of applicability of the existing stainless steel equipment. Dissolution rates for 304L, 347 and 318 stainless steels in boiling 4, 6, and 8M sulfuric acid were measured (Table 11). Only the 318 in 4M acid showed an initial rate less than 2 mg cm⁻² min⁻¹. At 50 g/l dissolved stainless steel and 4M sulfate ion, the rate for 318 was 0.2 mg cm⁻² min⁻¹ but the rates for 347 and 304L were still above 2 mg cm⁻² min⁻¹. In 6 and 8M sulfuric acid the initial rates were appreciably higher than in 4M acid but ferrous sulfate precipitated in the presence of 50 g/l dissolved steel.

c. Stainless Steel Dissolver Solution Stability

Solution samples from a number of laboratory dissolutions of typical stainless steel fuel in 6M sulfuric acid were held at room temperature to determine the short-term stability of these solutions over the range of possible process interest (Table 12). The equilibrium solubility of ferrous sulfate as reported in the literature⁽⁷⁾ is also shown in the table. This value may be used with the assumption that all the components of the system behave as sulfuric acid with respect to the solubility of the iron. The 66 g/liter value has been run in the plant with no detectable precipitation.

It appears that practical, intermediate dissolution product solutions which may contain up to 100 g of stainless steel in sulfuric acid, are not necessarily stable for long periods of time. The dilution with nitric acid leads to corresponding solutions of far greater stability.

Table 11

DISSOLUTION RATES OF STAINLESS STEELS IN SULFURIC ACID

Stainless Steel (Type)	Dissolution Rates ⁽¹⁾ , (mg cm ⁻² min ⁻¹)		
	<u>No Initial Dissolved Salt</u>		
	<u>4M H₂SO₄</u>	<u>6M H₂SO₄</u>	<u>8M H₂SO₄</u>
318	1.63 ± 0.09	3.2 ± 0.7	8.5 ± 1.5
347	3.1 ± 0.1	6.7 ± 1.4	15.3 ± 2.6
304L	5.8 ± 0.5	13.3 ± 0.5	26.1 ± 6.7
<u>50 g/l Dissolved Steel</u>			
318	0.25 ± 0.2	Ferrous Sulfate ppt. ⁽²⁾	
347	1.9 ± 0.9		
304L	3.5 ± 0.3		

(1) At the boiling point at 650 mm. Hg.

(2) In these dissolution rate studies precipitation occurred at a stainless steel concentration below that noted as short-term stable in the following section.

Table 12

STABILITY OF STAINLESS STEEL DISSOLVER SOLUTIONS

Concentration of Stainless Steel ⁽¹⁾ in Dissolver Solution (g/l)		Precipitate Formed, (days)
<u>H₂SO₄</u>	<u>H₂SO₄+HNO₃</u>	<u>Precipitate Formed, (days)</u>
30		Equilibrium solubility
66		No precipitate detected in plant runs
70		9
	61.5	>25
92		8
	76	>26
117		~2 hours (formed on cooling)
	79	>16

(1) The first column represents the dissolver solution after the sulfuric acid phase of the dissolution; the second column shows the same solution after the addition of the nitric acid necessary for the dissolution of the UO₂ which is not soluble in sulfuric acid.

d. Stability of Excess Nitrate Containing Solutions

As a basis for the development of future sulfuric acid process flowsheets, the stability of the dissolver product and adjusted feed system-ferric iron (chromium and nickel), hydrogen ion, and sulfate and nitrate ions was investigated.

A study was made in which three portions, each, of three 6M sulfuric acid solutions containing 1, 2, or 3 moles of ferrous iron per liter were titrated with nitric acid to oxidize the iron present in the first case, plus one molar added nitric acid in the second and two molar added nitric in the third. These samples were allowed to stand for three weeks to come to equilibrium and the supernatant liquids analyzed for iron, nitrate, sulfate and hydrogen ions. Figure 4 shows the stable solution composition, as determined by analysis, for each of the samples.

e. Nitrate Requirement for Uranium Dioxide Oxidation

The stoichiometry for the oxidation of the iron and the dissolution of the uranium dioxide is not clear cut due to the effects of air oxidation and radiation induced oxidation reactions during the first dissolution step. It is assumed therefore, that an empirically determined terminal level of nitric acid associated with complete uranium dissolution can be used for flowsheet design.

Fig. 4 - Stability of Nitrate-Containing Iron Sulfate Solutions

For the experiments, 37 ml aliquots of a 91 gram per liter stainless steel solution, prepared in 6M sulfuric acid, were mixed with appropriate amounts of water and nitric acid to give initial nitrate ion concentrations ranging from 1.01 to 1.97M (in increments of 0.24M) in 52 ml of solution. Uranium dioxide (70-100 mesh) was added to each solution to give a terminal uranium concentration of 6.96 grams per liter. The solutions were boiled for one hour under reflux, cooled rapidly, and analyzed for uranium and nitrate. There were no observed residues. In each case, the uranium was completely in solution and terminal nitrate concentrations ranging from 0.68 to 1.61M were observed. The observed change in nitrate concentration amounted to 0.41M or a stoichiometry of $\text{NO}_3^- \rightarrow \text{NO}$. Flowsheets resulting in a terminal level of at least 0.7M nitrate were recommended as safely assuring oxidation of the uranium although this level was not established as a lower limit for completion of the reaction.

f. Boron Poisoning

The introduction of neutron absorbers into the stainless steel headend equipment has been considered as a solution criticality control measure. The use of boron or some other material with a high neutron-capture cross section could lead to production rate advantages in the processing of high uranium fuels or act as a secondary safety measure when unsafe-geometry vessels are used.

To study the solubility of boric acid in the coarse feed, a simulated dissolution and coarse feed adjustment was made according to a typical high-uranium flowsheet (Design and Operations Manual for 3IR-STR Fuel Processing, IDO-18002, p. 72, Secret). The dissolver product solution analyzed 15.1 g/l uranium, 0.69M nitrate ion, 2.67M sulfate ion, and 3.70N hydrogen ion. Coarse feed specimens were set up at flow-sheet composition at 25°C with calculated boron concentrations, from boric acid, of 0.46, 2.98, and 5.5 g/l. The first two analyzed 0.47 and 2.81 g/l respectively. The third sample began to precipitate boric acid after about 16 hours but apparently came to equilibrium after a 15 day period. It analyzed 4.88 g/l boron, which may be taken as saturation for the system.

The addition of boron to plant streams is limited by the solubility of boric acid in the various reagent streams going into the process. The solubility of boric acid in sulfuric acid⁽⁸⁾ ranges from approximately 9.5 g/l (as boron) at 0M sulfuric acid to a minimum of about 3 g/l at 8M sulfuric acid, at which point the solubility rises sharply to a maximum of 42 g/l at 11-12M sulfuric acid. The addition of boron to a 6M sulfuric acid stream would be limited to slightly more than 3 g/l.

The solubility of boric acid in nitric acid⁽⁹⁾ drops from about 9.5 g/l (as boron) in 0M nitric acid through about 4 g/l in 6M nitric acid down to 2.2 g/l at 14M HNO_3 .

The limited solubility of boron in the reagent streams, rather than the final solution stability, limits the amount of boron in the

system. In a typical flowsheet, the boron concentration possible is of the order of 1.24-2.70 g/l depending on the amount of wash water needed to flush the dissolver prior to subsequent dissolution cycles.

C. Continuous Aluminum Dissolution Studies, J. A. Buckham, Problem Leader; C. R. Ford

1. Comparison of Plant and Pilot Plant Data

A comparison of ICPP (7 $\frac{1}{2}$ -inch diameter) and pilot plant (2-inch diameter) continuous dissolver data has been completed for extruded aluminum-fuel processing. This comparison has resulted in the following conclusions:

- (1) Dissolution rate varies with the 0.95 power of the acid-feed rate in both the ICPP and the pilot plant continuous dissolvers.
- (2) A change in catalyst concentration above 0.01 molar mercuric nitrate has no effect on dissolution rate in either the ICPP or the pilot plant continuous dissolvers.
- (3) The ratio of the cross-sectional areas of the ICPP dissolver to the pilot plant dissolver (14.1 : 1) is a valid scale-up factor.
- (4) The difference between dissolution rates for irradiated and unirradiated extruded aluminum materials is negligible.

2. Effect of Feed Acid Concentration on Dissolution Rate

Considerable uncertainty has always existed regarding the effect of feed acid concentration on the performance of a continuous aluminum dissolver. The considerable amount of available previous data has been supplemented by a small amount of new data where gaps existed; these data are now being empirically correlated for the preparation of a report. It is hoped that this report will allow prediction of dissolver performance at any acid feed concentration from 2 to 11 molar at all practical values of feed rate and catalyst concentration.

D. Solvent Stability Studies, H. T. Hahn, Problem Leader; A. J. Moffat

It was reported previously⁽¹⁾ that the so-called nitric acid catalyzed hydrolysis of tributylphosphate (TBP) is not primarily an hydrolysis reaction, but a dealkylation reaction in which the major volatile product is n-butyl nitrate. It has also been suggested that the presence of zirconium in process solutions may result in a much greater decomposition of TBP than is experienced with nitric acid alone.⁽¹⁾ Thus, it was felt that the TBP-HNO₃-zirconium studies are very important to present and future nuclear fuel processing.

In this report the rate of butyl nitrate formation was determined chromatographically in a series of experiments in which equal volumes of aqueous solution were equilibrated with equal volumes of carbonate-washed, distilled TBP. Each sample was run in duplicate and a standard was

analyzed before and after each unknown. A method is also described for determination of zirconium and total nitrate in both aqueous and organic media.

1. Acid Catalyzed Dealkylation

The nitric acid concentration in the organic phase was determined by titration with base. Table 13 lists the nitric acid concentration in the organic phase as a function of the initial aqueous nitric acid concentration.

Table 13

HNO₃ DISTRIBUTION BETWEEN AQUEOUS PHASE AND TRIBUTYL PHOSPHATE

<u>Initial Aqueous HNO₃, M</u>	<u>Organic HNO₃, M</u>
2.0	0.89
5.0	2.02
8.0	2.92
16.0	5.01

TBP equilibrated with 16.0M HNO₃ is degraded via oxidation (i.e., NO₂ is formed) and the rate of dealkylation under these conditions was not investigated.

The net rate of production of n-butyl nitrate is a function of the extracted acid concentration (Figure 5). The rate possibly parallels the hydrogen ion activity since it certainly does not parallel an acid concentration of first or higher order. Long and Paul⁽¹⁰⁾ have recently reviewed the two major types of acid catalysis and on the basis of their discussion, a likely mechanism for the first steps of the acid catalyzed dealkylation of TBP is:

The rate of formation of n-butyl nitrate according to equations (1) and (2) should be proportional to the hydrogen ion activity⁽¹⁰⁾. This mechanism may be contrasted to one with a different 2nd step:

In the latter, the rate of production of n-butyl nitrate would be a function of the Hammett H₀ acidity function (i.e., the reaction rate would be proportional to the acid concentration raised to some power >1).⁽¹⁰⁾

Experiments are being started to determine the role which dibutyl phosphoric acid plays in the step-wise dealkylation of TBP.

2. The TBP-Zirconium Tetranitrate Reaction

The influence of extracted zirconium $[\text{Zr}(\text{NO}_3)_4 \cdot 2\text{TBP}]$ (11) upon the degradation of TBP is depicted in curves 1 and 2 of Figure 5. Curve 2 (TBP phase reaction) demonstrates the rapid initial decomposition of $\text{Zr}(\text{NO}_3)_4 \cdot 2\text{TBP}$ followed by the much slower reaction between TBP and HNO_3 . It has not been established whether the complex undergoes rearrangement or whether an additional free tributyl phosphate molecule is involved. The point where the zirconium reaction ends and the nitric acid reaction becomes the predominant reaction indicates that approximately two moles of n-butyl nitrate are formed per mole of zirconium extracted. The crystalline zirconium compound which precipitates as the reaction nears completion was found to be $\text{Zr}(\text{NO}_3)_2(\text{DBP})_2$. An analysis is given in

Fig. 5 - Rate of Formation of n-Butyl Nitrate in Tributyl Phosphate at 50°C.

- (1) Organic phase, after equilibration with and remaining in contact with 5.5M NO_3^- , 0.255M Zr .
- (2) Organic phase only, after equilibration with 5.5M NO_3^- , 0.255M Zr .
- (3) Organic phase only, after equilibration with 8M NO_3^- .
- (4) Organic phase only, after equilibration with 5M NO_3^- .
- (5) Organic phase only, after equilibration with 2M NO_3^- .

Table 14. X-ray data for $\text{Zr}(\text{NO}_3)_2(\text{DBP})_2$ is listed in Table 15. Thus, the net reaction is:

Curve 1 (Figure 5) indicates that as the zirconium in the organic phase reacts, more zirconium is extracted from the aqueous phase. Eventually the rate of production of n-butyl nitrate approaches that of the TBP- HNO_3 reaction as the extractable zirconium from the aqueous phase is exhausted.

Table 14

COMPOSITION OF THE CRYSTALLINE Zr-TBP DECOMPOSITION PRODUCT

<u>Element</u>	<u>Wt. % Found(12)</u>	<u>Wt. % Calc'd as $\text{Zr}(\text{NO}_3)_2(\text{DBP})_2$</u>
C	31.0	30.3
H	6.0	5.7
P	9.7	9.8
N	4.1	4.4
Zr	13.3	14.4
Total %	64.1	64.6

Table 15(13)

X-RAY DATA FOR $\text{Zr}(\text{NO}_3)_2(\text{DBP})_2$

<u>d, Å</u>	<u>I/I₁</u>
11.2	100
10.7	55
6.54	15
6.34	15
5.65	15
5.42	15
4.75	20
4.43	20
4.11	25
3.84	20
3.34	20

One experiment was designed to determine the effect of water upon the zirconium-TBP reaction. The organic phase (after equilibration with 0.255M Zr-5.50M NO_3) was divided into two equal samples. One sample was placed in the 50°C bath while the other sample was evacuated for approximately $\frac{1}{2}$ hour at 50°C (approximately 1 mm of Hg) to remove most of the water present. The rate of formation of butyl nitrate is sufficiently slow to be neglected for this brief a period. The sample from which most of the water had been removed produced n-butyl nitrate at a rate slightly greater than the sample with water. Thus, the rates were not appreciably different since the evacuated sample would have a slightly higher zirconium concentration due to removal of water.

3. Potentiometric Behavior of Zirconium in Nitrate and/or Fluoride Systems

Total nitrate⁽¹⁴⁾ and zirconium in aqueous or organic media be determined by potentiometric titration with base. The general equation for the determination of total $\text{NO}_3^\ominus$ is:

When a zirconium-nitrate solution is treated with excess fluoride, the following reaction occurs:

Thus, the zirconium is converted to a fluozirconate ($\text{ZrF}_7^\ominus$ for example). Titration of the fluozirconate and acid to a phenolphthalein end point results in:

From equations (5) and (7) the zirconium concentration may be calculated by:

$$\text{Zr} = \frac{\text{IV} (\text{ml}_o - \text{ml}_f)N}{4(\text{ml}_s)} \quad (8)$$

where ml_o and ml_f are the volumes of base required for the titration of ml_s milliliters of sample in the absence of and in the presence of fluoride, respectively. N is the normality of the base.

IV. NEW WASTE TREATMENT METHODS

A. Aqueous Waste Treatment

Study of the separation of alloy metals from the fission products in stainless steel wastes has continued, making use of a newly designed polarograph cell which is described. Use of ammonium phosphomolybdate to adsorb cesium 137 from acid wastes is discussed.

In zirconium waste studies, electrodialysis was investigated as a method of preparing acid-deficient zirconium nitrate and fluoride solutions. Studies have continued on the extraction of zirconium from fluoride containing solutions, and experiments have been performed on nitrate reduction in STR wastes by use of paraformaldehyde as well as neutralization of STR wastes with sodium hydroxide.

1. Mercury Cathode Electrolysis, D. W. Rhodes, Problem Leader;
K. T. Faler, M. E. McLain and D. R. Anderson

Work continued to study the separation of alloy metals from the fission products in stainless steel wastes.

a. Effect of Cathode Potential

Laboratory experiments were conducted using the Eberback "Dyna Cath" equipment in an attempt to measure the effect of cathode potential on the transfer of iron, nickel, chromium and tracer cesium 137 from a synthetic stainless steel waste solution to the mercury cathode. The cathode potential was varied from -1.75 to -3.00 volts vs the saturated calomel electrode, and samples of the aqueous solution and the mercury were removed periodically to measure the concentration of cesium 137 and alloy metals.

The amount of cesium transferred to the mercury in these experiments was on the order of 0.01 percent of the total cesium with no apparent effect attributable to change in the applied potential. Measurements of the cesium concentration in the mercury were probably no better than ± 50 percent. This may have been due, in part, to the fact that the counting technique did not discriminate between cesium 137 and barium 137. Additional experiments under more closely controlled conditions are planned to better define the effect of potential on the transfer of fission products to the mercury.

No consistent change in the rate of removal of iron, nickel and chromium with change in applied potential was observed between -1.75 and -2.75 volts. However, at 3.00 volts all three metals were essentially completely removed within about 40 ampere hours or less vs 120 to 140 ampere hours at the lower voltages. Work is also continuing on this problem to obtain more accurate and more reproducible data using polarographic techniques.

b. Development of Polarograph Equipment

Recent experiments with several different polarographic cell arrangements resulted in the use of the cell shown in Figure 6. The mercury drop, which is formed at the cathode, falls through the sample solution into a layer of carbon tetrachloride, which washes off any aqueous material adhering to the surface of the mercury. The mercury drops are removed through the stopcock and placed in a sodium iodide well crystal counter to measure the amount of fission product contained in the mercury. Voltage from the polarograph is applied between the saturated calomel anode and the dropping mercury cathode. This cell makes it possible to obtain simultaneously the polarographic curve of a metal being electrolyzed and the amount of radioactive tracer carried down in the mercury drop. A study of the relationship between the amount of fission product in the mercury and the voltage and current is expected to give some indication of the mechanism of the transfer of the fission product into the mercury.

c. Polarographic Data

Preliminary experiments using the polarograph and the aqueous system iron, nickel and chromium in sulfuric acid indicated that only the

CPP-S-1315

Fig. 6 - Polarograph Cell For Studying Inclusion of Fission Products in Mercury During Electrolysis of Stainless Steel Wastes

reactions $\text{Ni(II)} \rightarrow \text{Ni}$ and $\text{Cr(III)} \rightarrow \text{Cr(II)}$ could be clearly observed on a polarogram due to interferences caused by reduction of the hydrogen ion in the acid system. Half wave potentials for the reactions were obtained, however, in a potassium chloride system and a potassium sulfate-sulfuric acid system as shown in Table 16.

Table 16

HALF WAVE POTENTIALS FOR IRON ($1 \times 10^{-3}\text{M}$), NICKEL ($2 \times 10^{-3}\text{M}$),
AND CHROMIUM ($1 \times 10^{-3}\text{M}$), IN A CHLORIDE AND A SULFATE SYSTEM

Temperature = 25°C

Reaction	Half Wave Potential	
	0.5M KCl	0.05M K_2SO_4 , $5 \times 10^{-4}\text{M}$ H_2SO_4
$\text{Fe(II)} \rightarrow \text{Fe}$	-1.58	-1.49
$\text{Cr(III)} \rightarrow \text{Cr(II)}$	-0.90	-0.92
$\text{Cr(II)} \rightarrow \text{Cr}$	-1.47	-1.49
$\text{Ni(II)} \rightarrow \text{Ni}$	-1.09	-1.03
$\text{H}^+ \rightarrow \frac{1}{2}\text{H}_2$		-1.57

These data will be used as a basis for studying the relationship between the transfer of fission products into the mercury and reduction of the alloy metals.

2. Removal of Long-Lived Fission Products, D. W. Rhodes, Problem Leader; M. W. Wilding

Experimental work was begun to find methods for the removal of long-lived fission products, particularly cesium 137 and strontium 90, from highly radioactive wastes. Methods which would require little or no pretreatment of the acid wastes were to be given first consideration. First attempts to remove cesium-137 from acid wastes, by adsorption on the heteropoly salt ammonium phosphomolybdate (APM), were reasonably successful, so the major effort in this program to date has been directed toward obtaining data for cesium removal.

a. Adsorption of Various Fission Products

Batch equilibrium experiments were conducted using tracer concentrations of cesium 137, strontium 90 and cerium 144 in a solution of 1.5M aluminum nitrate and 1.5N nitric acid. The results of these experiments indicated a distribution coefficient (grams of fission product per gram of solid/grams of fission product per ml of solution) for cesium 137 of about 1200. Distribution coefficients for strontium 90 and cerium 144 were less than 1. Further experiments were limited to defining the characteristics of the cesium reaction with APM.

b. Effect of Acidity

Increasing the nitric acid concentration from 1.5N to 12N decreased the distribution coefficient for cesium 137 from about 1200 to 390. Batch equilibrium experiments using tracer cesium 137 in synthetic STR waste (hydrofluoric acid waste) and in 3 N sulfuric acid solution gave

distribution coefficients of 2400 and 900 respectively. These data suggested that (APM) may be used to remove cesium from a variety of acid wastes.

c. Effect of Alkali Metal Ions

Batch equilibrium experiments in 1.5M aluminum nitrate -1.5N nitric acid solutions containing sodium nitrate indicated little if any effect of the sodium on the adsorption of cesium. The maximum concentration of sodium used was 10.5 grams per liter of sodium vs 60 milligrams per liter of cesium. Presumably, the larger hydrated radius of the sodium ion prevented any appreciable amount of sodium from occupying the exchange sites on the APM in preference to cesium.

The use of potassium, an ion having a hydrated radius similar to cesium, in similar batch type experiments indicated a decrease in the distribution coefficient for cesium by a factor of 0.5 when the concentration of potassium was 2.6 grams per liter vs 60 mg per liter of cesium. Apparently ions having a similar hydrated ionic radius do interfere but a fairly large ratio of interfering ion/cesium is required. Little interference from the alkali metal ions is expected in the acidic wastes.

d. Characteristics of Ammonium Phosphomolybdate

The exchange capacity of APM for cesium in nitric acid solution was determined using cesium 137 as a tracer. The exchange capacity based on the average of three experiments was 1.6 milliequivalents (~0.2 gram) of cesium per gram of APM. Approximately 80 percent of the cesium was readily eluted from the APM by washing with ammonium nitrate.

Thermal decomposition experiments were made by heating APM (crystalline to X-ray diffraction) in a combustion tube furnace. The APM compound was stable to about 450°C. Above 450°C ammonia and phosphate were volatilized leaving MoO₃ as the only crystalline material. Above 750°C the MoO₃ sublimed.

e. Effect of Time and Temperature

Rate studies using batch equilibrium experiments indicated that approximately 99 percent of the cesium was adsorbed on the APM in one minute of contact.

Similar experiments in which the temperature was varied from 2°C to 83°C indicated no effect of temperature on the adsorption of cesium. Column experiments are planned in which flow rates sufficiently rapid to permit operation at less than equilibrium conditions may show an effect of temperature.

3. Zirconium Wastes, D. W. Rhodes, Problem Leader; R. L. Hickok and D. A. Hanson

a. Preparation of Acid Deficient Zirconium Solutions

Preliminary experiments were carried out to investigate the use of electrodialysis as a method for preparing acid deficient zirconium nitrate and fluoride solutions. A three-compartment cell was used in which the anolyte and catholyte were both 1M nitric acid. The zirconium nitrate solution was placed in the center compartment, which was separated from the anode compartment by an anion exchange membrane and from the cathode compartment by a cation exchange membrane. This method was not satisfactory because of loss of zirconium to the cation exchange membrane. A smaller apparatus having two chambers separated by an anion exchange membrane, which had a relatively small membrane area, was tried. The zirconium solution was placed in the cathode chamber and 1M nitric acid in the anode chamber. Initial data showed that the small membrane resulted in current densities too high for membrane stability. Present efforts are directed toward use of the larger equipment using an anion exchange membrane to isolate the cathode instead of a cation exchange membrane. Sodium hydroxide solution will be used as the catholyte instead of nitric acid and nitric acid as the anolyte. Data are not yet available for this system.

b. Theoretical Studies of Zirconium Extraction From Fluoride Containing Solutions

Additional studies of extraction data together with calculations of the concentrations of the various zirconium fluoride complexes existing in solutions of nitric and hydrofluoric acids indicated that three zirconium species may be extracted into TBP. Equilibrium constants have been calculated for the extraction reactions, and although these constants are not exact due chiefly to a lack of knowledge concerning activity coefficients, they are believed to be at least in the right order of magnitude for the reaction conditions, 0.01M zirconium, 6-7M nitric acid and 0-0.02M fluoride. The proposed reactions with their constants are as follows:

c. Nitrate Reduction in STR Process Waste

A number of experiments have been carried out to investigate the possibility of removing nitrate from simulated STR raffinate solutions by reduction of the nitrate with paraformaldehyde. These experiments demonstrated that if the solution remains acidic, up to 90-95 percent of the nitrate can be removed, simultaneously precipitating 90-95 percent of the zirconium and none of the aluminum. Formic acid was added to maintain the acidity during the reaction.

d. Neutralization of STR Waste

Laboratory experiments were conducted in which synthetic STR waste was neutralized with sodium hydroxide to about pH7. The precipitate, although bulky, was easily filterable, settled, leaving a clear supernatant liquid, in 2 to 4 hours and was easily slurried by agitation after standing for several days. Chemical analysis indicated that the supernatant liquid contained $<0.038M$ aluminum, $<0.001M$ zirconium and $<0.03M$ fluoride. Radiochemical analysis indicated that approximately 50 percent of the cesium and greater than 90 percent of the cerium, strontium and ruthenium precipitated or carried with the precipitate.

B. Calcination of Wastes, J. I. Stevens, Problem Leader

The progress of the research and development work on waste disposal by calcination is the subject of a separate progress report.* However, an abstract of the salient features of the work for this reporting period is presented.

Laboratory investigations of the volatility of strontium oxide at elevated temperatures showed less than 0.001 percent volatile at $1100^{\circ}C$. Preliminary calcination experiments of zirconium wastes (which contain fluorides) admixed with silica showed silicon tetrafluoride to be the major gaseous fluoride compound. Fluidized bed calcination of a simulated aluminum type waste which had been spiked with radioactive ruthenium showed over sixty-five percent of the ruthenium to be retained in the solid product when calcining at $400^{\circ}C$ with return of venturi scrub liquid. The efficiency of an electrostatic precipitator for removing alumina particles was found to be greater than 99 percent for the size range 0.3 to 2.40 micron, and 76 percent between 0.01 and 0.3 micron at voltages of from 20 to 25 kilovolts.

The attrition rate of calcined alumina was studied in a six-inch diameter calciner in an attempt to establish a base for attrition resulting from conditions other than nozzle atomization but interpretation of results is still under study. Tests were made to determine the limits of operability of the two-foot square calciner; however, operational difficulties prevented definition of these limits to the desired degree. Metallographic examination of a stainless steel type 316 bellows which failed in NaK service indicated the failure was mechanical and not attributable to corrosion.

A microscopic method for determining the growth rate of particles in a fluidized bed is proposed as an aid to determine the fundamental mechanisms that occur in a fluidized bed when calcining simulated radioactive wastes. Shakedown runs were made on a pulsed-plate liquid-solids contactor and observations on operability of the equipment are recorded.

Overall completion of a Demonstrational Waste Calcining Facility was estimated as 65 percent. The results of short-term corrosion tests with various alloys in contact with sand and calcined alumina, the latter

* J. I. Stevens, to be published.

spiked with cesium and sodium nitrates, indicated Inconel to be the preferred material of construction for temperatures in excess of 1200°F. The latest conceptual design of a High Temperature Solids Storage Facility includes provisions for controlling the temperature of the containment vessel in a range that will be compatible with available materials of construction.

V. ELECTROLYTIC DISSOLUTION STUDIES

A. Electrolytic Dissolution of Stainless Steel in Nitric Acid

The early work of Pitzer⁽¹⁵⁾ and the more recent efforts of Martin and Waterman⁽¹⁶⁾ and Henry⁽¹⁷⁾ have established the overall chemical feasibility of the electrolytic dissolution of stainless steel clad irradiated fuel elements in nitric acid. Several important chemical questions and many equipment design problems which could vitally affect the successful application of the process remained to be answered for specific fuels.

Preliminary investigation of electrolytic dissolution of stainless steel in nitric acid suggests flowsheet conditions which might give a metal concentration as high as 150 g/liter in 1M acid, resulting in low column feed rates, low raffinate bulk, and very favorable uranium distribution conditions with low percentages of TBP. Stirred tank continuous dissolution was demonstrated successfully for type 304, 304L, 347 and Carpenter 20 stainless steels; anode residues produced, while fairly bulky at this stage of development, were very fine particulate and contained negligible uranium. Design of an inert anode may hinge on the balance between the lower efficiency but more dependable operability of noble metals as compared with the higher efficiency but greater difficulty in maintaining electrical contact with niobium.

Some preliminary experiments to measure the rates of the overall anodic and cathodic reactions as a function of electrode potential, and also to determine if and what gaseous products were liberated at each electrode, are reported. Corrosion information on electrode materials and raffinate storage vessels is also reported.

1. Preliminary Chemical Flowsheet and Equipment Development, K. L. Rohde, Problem Leader; C. E. May

The Army Package Power Reactor fuel was selected as typical of the stainless steel clad, uranium dioxide-stainless core fuels which might be encountered. The objectives of the current study included the examination of the dissolver residue (anode sludge) associated with electrolytic dissolution as to amount, particle size, uranium content and composition, so that, if required, developments could be initiated to minimize the bulk of this residue or designs perfected to handle it. It was also intended that the dissolution stoichiometry be observed as well as cathodic corrosion and the current-voltage relationships of the cell.

a. Experimental

In order to obtain data on the properties of the dissolution system which would be readily interpretable in terms of the dissolver solution composition and the dissolver operating conditions, and readily extrapolative to continuous dissolver design, the laboratory dissolution experiment was designed to operate at essentially steady state conditions. To attain this objective without resorting to the elaborate

auxiliary equipment associated with true continuous dissolution, a simple batch dissolution was arranged with a strip anode which could be advanced into the electrolysis zone.

The dissolution was initiated with acid slightly above, and iron, chromium and nickel nitrates slightly below, the dissolver product composition. Samples were withdrawn periodically in such volume as to keep the average dissolver solution composition on flowsheet. The volume of the samples was replaced with nitric acid of the dissolver reagent concentration. The design flowsheet value and deviations were, for example, $3.0 \pm 0.27M$ nitric acid and 48.7 ± 2 g/liter iron. The period of the sawtooth fluctuation was 20 or 30 minutes in a four-hour experiment. The electrodes were plane and parallel, and spaced $1/4$ inch face to face. The cathode area was 20 cm^2 and it was assumed that the active anode area was the same. Both electrodes undoubtedly had areas of much lower current density at the edges and back. The presence of these regions of low anodic current density is unfortunate from the point of view of basic measurements, but is entirely realistic since any fuel element, or the fragments thereof, will have areas of current density lower than average which may have different dissolution characteristics. Constant current was maintained during the course of a dissolution by adjustment of a rheostat in series with the cell. The cell voltage fluctuations were observed and are reported. Most dissolutions were done at the boiling point with the IR drop of the electrolysis providing considerable vertical agitation in the area between the electrodes and producing vigorous stirring of the whole vessel.

Design calculations for this laboratory dissolver indicated that at the dissolution and flow rates planned, and with the dissolver reservoir volume anticipated, the dissolver product solution would not reach more than about 50 percent of the steady state value for the concentration of any component building up in the solution. Therefore, the dissolutions were initiated with steady state values of acid and iron, chromium and nickel nitrates present. This resulted in essentially uniform current-voltage characteristics right from the start of the run. For components not initially present, soluble uranium from the fuel and ammonium ion as a decomposition product of nitric acid, the steady state composition was calculated assuming uniform input and overflow in a stirred tank.

- Thus where
- (1) the continuous dissolver operated with a solution holdup of v (liters),
 - (2) reagent inflow and product removal rates are f (liters per hour),
 - (3) the component of interest has an initial concentration, C_0 (M , g/l , etc.),
 - (4) at time, t (hours), after observation of C_0 , a new concentration, C , is observed, and
 - (5) C_{ss} is the concentration obtainable by dividing the production rate of a substance produced in the reaction by the flow rate, f , and is the concentration at steady state, $t = \infty$,

then the expression

$$\ln \frac{C_{ss} - C_o}{C_{ss} - C} = (f/v)t$$

can be used to calculate the steady state concentration.

b. Dissolver Operating Conditions

The four-hour operating period was arbitrarily selected as adequate to give a minimum of eight samples of dissolver effluent and to yield periodic data on the dissolution while a typical fuel coupon was completely penetrated. Residue quantities were large enough for accurate weighing and analysis. The current densities selected, 0.5, 1.0, and 1.5 amperes/cm² covered the range that had been found reasonable in the early work and avoided excessively high potentials. The electrode geometry and current density determined the cell current and coulombs per run.

The solution compositions and the detailed run data are given in Table 17. The observed cell voltage range generally reflects the current density variations, but in the three experiments at 1.5 amps/cm² current density (Numbers 3, 4, and 7 of Table 17) the increase in cell potential at lower solution hydrogen ion concentrations also suggests increasing cathodic concentration polarization.

c. Anode Behavior

The anode current efficiencies for the electrolytic dissolution process were greater than 96 percent assuming chromium dissolution as chromium VI. This is to be expected at the higher cell potentials. Experiment 5, 0.5 amps/cm² and 2.8 volts cell potential, would give a current efficiency of 86 percent with chromium(IV) as a product and greater than 100 percent with chromium(VI), suggesting that chromium(VI) might not be produced exclusively at lower cell and electrode potentials.

d. Anode Sludge

The weight of anode residue or sludge was high, varying randomly from 1 to 7 percent of the anode weight loss. In this experimental arrangement, the anode sludge had no opportunity to recontact an anode surface and, therefore, these values are not indicative of overall process experience with more elaborate designs.

For examination of the sludge, the final dissolver reservoir contents were filtered through 0.45 micron Millipore filters, dried at 100°C and weighed. Particle size estimation by direct microscopic measurement gave diameters of 9 to 13 microns with particles of considerable symmetry. Aggregates of these small particles were present, but platelets or other shapes of grossly unequal dimensions were absent. Spectrographic analysis of the particulate showed molybdenum, niobium, and silicon as anticipated from the compositions of the several steels and also much greater proportions of iron, chromium and nickel indicating that intergranular attack and the detachment of individual grains from the matrix might have been the sludge producing mechanism.

Table 17

ELECTROLYTIC DISSOLUTION OF STAINLESS STEEL IN NITRIC ACID
20 cm² Plane Electrodes, 0.63 cm Apart, Carpenter-20 Cathode

Anode Material		APPR Plate				304		304L		347	Carp. 20	
Experiment	Flowsheet	1	2	3	4	5	6	7	8	9	10	11
Current density(1), amps/cm ²		1.0	1.0(8)	1.5	1.5	0.5	1.0	1.5	1.0	1.0(8)	1.0	1.0
Cell voltage(2) volts		+0.6 4.2-0.4	+0.7 4.1-0.1	+0.9 7.1-0.6	+0.5 6.4-0.9	2.8±0.0	+0.2 3.9-0.1	+0.7 8.1-0.4	+0.3 4.2-0.2	+1.0 4.0-0.2	+0.3 4.1-0.2	4.0±0.2
Steel dissolved(3) g/amp.hr.		0.57	0.57	0.57	0.57	0.62	0.57	0.57	0.58	0.57	0.57	0.60(4)
Cathode corrosion mg/amp.hr.			0.40	3.05	0.23	0.21	0.33	4.66			0.66	1.43
Product solution												
Fe ⁺⁺⁺ , g/l	48.7	45	45	49	48	54	46	54	47	46	44	35(4)
H ⁺ , M	1.0	1.13	1.35	0.90	2.8(5)	0.50	1.48	0.54	1.17	1.36	1.11	1.25
U, g/l	6.0	7.5	5.4	12(6)	10(6)							
NH ₄ ⁺ , M	0.0	<0.5	<0.5	0.01	<0.01	<0.05	<0.02	<0.04	<0.5	<0.1	<0.05	<0.02
Nitric acid consumption moles/equiv.(7)	1.2	1.22	1.29	1.41	1.45	1.36	1.25	1.37	1.22	1.17	1.24	1.39
Residue												
Portion of anode wt. loss, %		2.0	1.5	3.8	2.7	5.2	7.5	2.1	0.9	2.2	2.1	5.3
Uranium content mg/g		0.07	0.07	0.6	0.2							
Uranium loss %		0.001	0.001	0.02	0.005							

(1) Amp-hrs/experiment = 80 x current density.

(2) Average and extreme values are indicated.

(3) The equivalent anode current efficiencies assuming $\text{Cr} \rightarrow \text{Cr}^{\text{VI}}$ are 96 percent for 0.57 gms/amp-hr.

(4) With Carpenter-20 the total weight of steel dissolved was normal but the solution composition reflected the deviation from normal 18-8 steel proportions.

(5) Planned acidity for this single experiment was 3.0N.

(6) Anode here was a strip from the center of a plate.

(7) Moles H⁺ lost per equivalent of metal dissolved. Allowance was made for uranium oxidation.

(8) Experiments 2 and 9 were run at 85°C, all others at 101°C (the boiling point).

The uranium content of the sludge from APPR dissolution ranged from 0.07 to 0.6 mg/g; the uranium loss to the sludge from 0.001 to 0.02 percent. This favorable result may reflect either the easy disintegration of the meat portion of the fuel, or the origin of the residue in the steel. The particles are too small to include appreciable uranium dioxide.

e. Cathode Corrosion

The corrosion rates observed for the Carpenter-20 cathode here are in good agreement with the longer exposure observations of other studies. Although no single electrode potentials were measured here, the variations in corrosion rates with cell voltage and dissolver solution composition are readily interpretable in terms of the polarization curves for the cathode reactions. (Ref. (1) Sec. IV-B). Thus in experiments 2, 6, 10, and 11 at 1 amp/cm², and especially in experiment 5 at 0.5 amp/cm², the cathode is apparently operating in a relatively passive region on the polarization diagram and is only slightly corroded. In experiments 3 and 7, at 1.5 amp/cm² and higher cell voltages, the cathode is no longer passive. Passivity is regained in experiment 4, due probably to the change in solution composition.

f. Product Solution Compositions

The analyses of the continuous electrolytic dissolution products are shown in Table 17. Variations from flowsheet were due to improper flow of reagent and product samples rather than any lack of control of the dissolution rate. Under these conditions the production of ammonium ion appears to be limited to 0.01M or less at steady state.

The nitric acid stoichiometry associated with the electrolytic dissolution varied from 1.17 to 1.45 moles nitric acid consumed per equivalent of metal dissolved (based on chromium(III) which is apparently the final product of dissolution). The average value of 1.3 moles nitric acid per equivalent suggests an average valence state of the nitrogen reduction product of two, considering other evidences that hydrogen is not a prominent reaction product.

g. Chemical Dissolution of Uranium Dioxide

A series of chemical (non-electrolytic) dissolutions of reactor type uranium dioxide powder, 70-100 mesh, were made to outline the conditions required for homogeneous dissolution of stainless steel-uranium dioxide fuels in nitric acid. The results indicate that with one-half hour contact times, complete oxidation is only achieved at the boiling point of the nitric acid-metal nitrate mixture (Table 18). A tentative flowsheet composition for the dissolver product is 1.0 + 0.4M nitric acid. Since the mechanism of the dissolution may involve decomposition of nitric acid, the oxidation may be facilitated by the electrolytic conditions and require less free acid or a lower temperature. Incidentally, one experiment was prepared where the solution contained chromic oxide simulating the anodic oxidation product of chromium. The uranium dissolution was not catalyzed.

Other chemical oxidants may be considered if the reaction conditions outlined here are incompatible with optimum electrolytic results.

Table 18

CHEMICAL DISSOLUTION OF URANIUM DIOXIDE

75 g/l stainless steel nitrates,
342 mg UO_2 /50 ml, 1/2 hour contact time

<u>Temp.</u>	<u>Nominal Nitric Acid Level</u>			
	<u>0.3M</u>	<u>0.6M</u>	<u>1.0M</u>	<u>2.0M</u>
	<u>Uranium Oxide Dissolved (percent)</u>			
25°C	21	14	30	38
50°C	60	69	63	76
75°C	92	92	93	95
100°C	96	99	97	99
50°C		44*		

* 580 mg CrO_3 added

h. Process Flowsheets for APPR Fuel

The flowsheet of Table 19 appears to be an operable chemical flowsheet in view of the experimental work just described. With about 1M nitric acid established as adequate to insure the chemical dissolution of the uranium oxide, the selection of salt concentrations and higher free acidities will be dependent on the salt solubility data and electrochemical effects which were not studied here. A flowsheet in which the total metal concentration of the dissolver product is 150 grams/liter at about 1M acid might be achieved. This would give tremendous real advantage in column feed and raffinate bulk. Because of the high ratio of metal nitrate to nitric acid in the dissolver product solution very favorable uranium distribution conditions can be obtained with relatively low percentages of tributyl phosphate. This suggests flowsheet advantages in decontamination and criticality control over aqua regia derived feed.

Table 19

FLWSHEET FOR ELECTROLYTIC DISSOLUTION OF
APPR FUEL AND SOLVENT EXTRACTION

		<u>Fuel</u> <u>(kg)</u>	<u>Dissol.</u> <u>Reagent</u>	<u>Dissolver</u> <u>Product*</u> <u>IAF</u>	<u>IAX</u>	<u>IAR</u>	<u>IAP</u>
Volume	1		166	166	166	166	166
U	g/l	1.0		6.0		1x10 ⁻³	6.0
Fe	g/l	8.11		48.7		48.7	
Ni	g/l	1.16		7.0		7.0	
Cr	g/l	2.21		13.3		13.3	
H ⁺	<u>N</u>		5.4	1.0		0.9	0.1
NO ₃ ⁻	<u>N</u>		5.4	4.7		4.6	0.15
TBP	Vol. %				5		5

*Dissolver off-gas contains 125 equivalents of nitrogen as lower oxides of nitrogen or nitrogen.

1. Conclusions

(1) The investigation of the flowsheet parameters for electrolytic dissolution reported here reaffirms the impression gained from the literature that there are numerous flowsheet advantages to be gained from electrolytic integral dissolution of stainless steel fuels in nitric acid.

(2) The anode residues produced, while apparently large in bulk at this stage of developments, are very fine particulate and include only negligible uranium.

(3) Stirred tank, continuous dissolution was demonstrated successfully for several different metals with no chemical flowsheet problems evidenced.

2. Laboratory Studies of Electrolytic Dissolution in Nitric Acid

a. Electrode Kinetic Studies, H. T. Hahn, Problem Leader;
J. R. Aylward, R. E. Ohlin

The electrolytic dissolution of stainless steel fuel elements in nitric acid involves a multitude of reactions at the electrodes as well as in the bulk of the solution itself. To arrive at an overall

reaction stoichiometry it is necessary to determine the rate of each individual reaction as a function of the electrode potential. In the case of the anodic reactions, this is relatively simple but still requires a great deal of experimental work. On the other hand, the reduction of nitric acid at the cathode is complex in that a number of different reduction products are formed, and the individual reactions leading to these various reduction products cannot be isolated for separate study. However, a potential versus rate study of the overall cathodic reaction along with chemical analysis can result in an approximate stoichiometry.

Some preliminary experiments have been carried out to measure the rates of the overall anodic and cathodic reactions as a function of electrode potential, and also to determine if and what gaseous products were liberated at each electrode.

The cell consisted of separate anode and cathode compartments with provisions for collecting gaseous products formed at the working electrode. The potential of the working electrode (at 80°C) was measured against a saturated calomel electrode at room temperature by means of a Luggin capillary. No provision was made for stirring the solution.

Figure 7 shows the anodic and cathodic potential versus current density curves (the average of two runs) for 304 stainless steel electrodes in a solution containing 49 g/l of Fe^{+3} , 7.0 g/l of Ni^{+2} , 13 g/l of Cr^{+3} , 1N H^{+} , and 5N NO_3^- . The temperature of the solution was $80 \pm 1^\circ\text{C}$. The potentials shown in Figure 7 have been converted to the standard hydrogen electrode scale but include the liquid junction and thermal emf. The lower section of the anodic curve ($< 20 \text{ ma/cm}^2$) has the expected Tafel slope of 0.08 volts/decade. No gas was given off at the anode even at current densities as high as 2 amps/ cm^2 ($= + 1.7$ volts). Therefore, the exchange current for oxygen evolution must be very small in this system. It was obvious in observing the solution in the anode compartment after electrolysis that Cr III was oxidized to Cr VI.

The slope of the cathodic curve below 10^{-2} amps/ cm^2 was much greater than expected (0.20 volts/decade). A limiting current density, predicted theoretically, was observed at 350 milliamps/ cm^2 . This can easily be increased a factor of ten by stirring the solution. At the higher cathodic current densities, a small amount of gas evolution took place. This gas, most of which was collected at currents higher than the limiting current density, consisted mainly of H_2 and N_2O with small amounts of NO and N_2 . Hydrogen evolution is to be expected in the potential range encountered near and beyond the limiting current density. The amount of hydrogen formed could be decreased considerably by stirring the solution, since this would result in less negative potentials at the higher current densities.

Fig. 7 - Overvoltage in a Simulated Nitrate Dissolver Solution

Although it is premature to identify a particular mechanism with the cathodic overvoltage curve obtained from this single experiment, it is interesting to speculate on the change in slope observed at 10⁻² amps/cm² with the mechanism proposed by Vetter⁽¹⁸⁾ for the cathodic reduction of medium and strong HNO₃ solutions. This is as follows:

Step (a) is rate determining at high current densities and step (c) at low. The change in slope found at 10⁻² amp/cm² may be associated with the change in the rate determining step from step (c) to step (a). It will be noted that the overall reaction involves no gaseous products. This is consistent with the results found in the above experiment at

current densities less than the limiting. At high nitrate and hydrogen ion concentrations, the nitrous acid is unstable and decomposes as follows:

The overall cathodic reaction under these conditions is

Therefore, it is to be expected that in starting up a dissolver with a high initial nitric acid concentration, evolution of N_2O_4 and its equilibrium product NO_2 will result.

b. Electrolytic Dissolver Anode Material

A major requirement of an electrolytic dissolution system is a means of making and maintaining anodic contact with fuel pieces until dissolution is complete. The device which shows the greatest potential value for this function is a perforated anode cylinder made from a metal which exhibits the electrolytic valve effect. Fuel pieces in the cylinder are forced to maintain physical contact with the cylinder until they become small enough to escape from it. The most promising materials of construction for the anode cylinder are tantalum and niobium and alloys of these metals with tungsten.

One problem associated with the use of a valve metal anode cylinder, however, is that although physical contact with fuel pieces is easily maintained electrical contact is rather difficult to maintain. Dissolution of stainless steel pieces in a niobium anode begins easily, but as the dissolution proceeds, resistance increases and eventually halts the dissolution. Pitzer,⁽¹⁵⁾ in early work on electrolytic dissolution, attributed this increase in resistance to the interposition of a layer of non-conducting, insoluble sludge between the fuel pieces and the anode container. The increase of resistance, however, is also encountered with fuel materials, such as pure chromium, which produce no sludge.

Pitzer solved the problem of high contact resistance by agitation of the container to break up the sludge layer and restore contact. This agitation also serves to break the insulating oxide layer on the anode. Pressure on the fuel pieces, applied by a piston, restores electrical contact by penetrating the insulation between fuel pieces and the anode.

- (1) Contact Resistance on Niobium, H. T. Hahn, Problem Leader;
J. R. Aylward, R. E. Ohlin

The use of niobium as an inert electrical contact for the anode of an electrolysis cell depends upon the valve action properties of its oxide. When this metal is made anodic in nitric acid solution, an oxide film forms on its surface and the thickness of the film is directly proportional to the voltage of formation. Once the oxide film

is formed, the current decreases to a very small value; in other words, the film has a high resistance to the passage of anodic current to the solution. The conductivity through the oxide film to another metal, however, is high, but with a very large current and small contact area an appreciable voltage drop could occur at this point. For this reason it was decided to measure the contact resistance of niobium oxide films as a function of film thickness and contact pressure.

A simulated dissolver solution containing 48.7 g/l of Fe^{+3} , 7.0 g/l of Ni^{+2} , and 13.3 g/l of Cr^{+3} in 1N HNO_3 was used as an anodizing bath. Coupons of niobium sheet $\frac{1}{2}$ " x 2" were anodized in this solution at voltages ranging from 1 to 20 volts measured with respect to a saturated calomel electrode.

An attempt was made to measure the resistance of these films by placing a 2-mm diameter probe against the niobium coupon which rested on the pan of a solution balance. A current of 10 milliamps was passed through the oxide film and the voltage drop measured at different pressures and probe positions. The results of these measurements were so erratic and irreproducible as to be worthless. Difficulty in lining up the surface of the probe parallel to the niobium surface was thought to be responsible for this behavior.

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Fig. 8 - Resistance of Niobium Oxide Film as a function of film thickness (voltage of formation) and contact pressure

A new probe with a much larger surface area (7.8 x 6 mm diameter) was constructed, along with a leveling table for lining up the sample with the probe. Reproducibility with this setup was better but still left much to be desired. The results of measurements for oxide films formed at 10, 5 and 2 volts are shown in Figure 8. Measurements were made at two different positions on the surface for each pressure.

Since measurements with two different probe sizes yielded results which were indistinguishable (within a rather wide experimental error) there is still some hope that resistance measurements may be used as a crude measure of contact area.

(2) Use of Noble Metals, K. L. Rohde, Problem Leader;
M. W. Roberts

Both agitation and pressure, though effective in maintaining good electrical contact for the fuel pieces, are undesirable for full scale use because each requires a separate, moving mechanism in conjunction with the dissolver and is capable of causing damage to the anode cylinder. The problem may be obviated by the use of a noble metal liner in the valve metal container. Platinum and related metals, though they do not exhibit the valve effect, are not corroded when used as anodes in nitric acid and do not form an insulating film on the surface which interferes with the flow of current to a dissolving fuel piece. The principal difficulty introduced by the use of a noble metal in the anode is that the absence of an insulating layer allows oxygen liberation which competes with the dissolution reaction. Two undesirable effects result: oxygen appears in the off-gas and the dissolution efficiency is reduced. By proper design, oxygen production and current losses may be kept at acceptable levels.

A dissolver capable of using a variety of anode materials was constructed to evaluate the use of noble metals as anode materials. The dissolver, made of Teflon, has a two-inch inside diameter and is ten inches long. It is fitted with inlet and outlet tubes so that reagent (8M HNO_3) may be passed through the dissolver. The cathode is a water cooled stainless steel coil in the upper part of the dissolver; anodes are flat circular disks, two inches in diameter, which cover the bottom of the dissolver. Fuel pieces, simulated by stainless steel raschig rings, rest on the anode under their own weight. Current is provided by a six-volt storage battery and recorded by a Brown recorder. Total current passed is determined by integration of the current. Results of dissolutions with various anodes are shown in Table 20.

The niobium anode which was completely covered by stainless steel pieces was never exposed to high potentials and did not develop a heavy protective coating. The dissolution proceeded continuously. A second niobium anode which was not completely covered by stainless steel pieces was exposed to high potentials and rapidly became inoperable. Noble metal anodes, though less efficient, were not subject to interruption of operation. The dissolution of stainless steel in preference to oxygen liberation at a noble metal anode is probably caused by the reduction

of potential at the anode near a stainless steel piece. These data indicate that a platinum or platinum alloy may be incorporated into the design of an electrolytic dissolver to make agitation or pressure on the fuel unnecessary.

Table 20

PERFORMANCE OF ANODE MATERIALS

<u>Anode Material</u>	<u>Duration of Experiment (Minutes)</u>	<u>Dissolution Current Utilization (gm/amp. hr.)</u>	<u>Dissolution Efficiency* (Fraction)</u>	<u>Fraction of Anode Covered by Stainless Steel</u>	<u>Note</u>
Nb	15	0.651	1.10	1.00	1
Pt	15	0.47	0.794	0.716	2
Nb	Inoperable after 6 min.	0.421	0.711	0.716	3
Au	15	0.454	0.767	0.716	4
Au	26	0.54	0.912	0.716	4
Pt-Rh wire	27	0.42	0.710	0.51	5

- (1) Surface coating removed from anode before use. Dissolution continued without interruption.
- (2) Little gas evolution in vicinity of stainless steel pieces.
- (3) Surface coating removed from anode before use. Dissolution stopped in about 6 minutes.
- (4) Little gas evolution near stainless steel pieces; metallic gold found in dissolution product.
- (5) Platinum-rhodium wire coil was used to simulate the use of noble metal strips in the anode instead of a continuous liner.

* Assuming Cr^{+6}

3. Corrosion Resistance of Possible Materials of Construction

The promise of suitable construction materials is required prior to the establishment of the desirability for scale-up or pilot plant studies for the proposed electrolytic method. Accordingly, bench-scale accelerated scoping corrosion experiments were started.

In the electrolytic dissolution method, most process vessels would be required to handle various concentrations of iron-chromium-nickel nitrate salts at or near ambient temperatures. The head-end dissolver vessel, under certain dissolution conditions, could operate at near boiling. The uranium nitrate thermosyphon evaporator usually would operate at 35 psig in the steam chest (136°C).

a. Corrosion of Dissolver Electrode Materials, N. D. Stolica,
Problem Leader; M. R. Bomar

Tests were run to determine possible materials of construction for dissolver service in the proposed electrolytic dissolution process for stainless steel. Of primary interest was the cathode because it would be desirable for the container to serve as the cathode.

Room temperature tests in 4M nitric acid and boiling temperature tests in 35 percent and 70 percent nitric acid solutions were carried out. The corrosion coupons were made cathodic and a current of one ampere per square centimeter was maintained. The results of these tests are shown in Table 21.

Table 21

CORROSION RATES OF POSSIBLE CATHODE MATERIALS FOR ELECTROLYTIC
DISSOLUTION OF STAINLESS STEEL IN NITRIC ACID

Tests at Current of One Ampere per Cm^2

<u>Material</u>	<u>Nitric Acid Concentration</u>	<u>Temp.</u>	<u>Corrosion (In./Month)</u>
C-20	4M	20°C	0.13
SS-347	"	"	0.20
Nb	"	"	Nil
Ta	"	"	Nil
Ti	"	"	0.0014
Cr	"	"	Nil
Zr	"	"	Nil
Nionel	"	"	0.14
Inconel	"	"	0.14
C-20	35%	Boiling	Nil
C-20 Welded	"	"	0.00005
SS-347	"	"	0.0007
Nb	"	"	Nil
Ti	"	"	"
C-20	70%	"	"
SS-347	"	"	"

A niobium anode bus bar showed a corrosion rate of 0.000005 inches per month.

b. Corrosion in Raffinate Storage Vessels, N. D. Stolica,
Problem Leader; T. L. Hoffman

The alloy used in these accelerated corrosion experiments was type 304L stainless steel. Each specimen was surface finished by machining. The alloy was in the as-received annealed metallurgical condition except for stress risers associated with the machining operations.

Test solution was prepared by dissolving austenitic stainless steel in 4M nitric acid at 20°C under an impressed current density of one ampere per square centimeter of cathode area. Under these dissolution conditions, the total iron, chromium, and nickel concentration should be near 69 grams per liter. Table 22 lists the composition of the stainless steel electrolytic dissolver solution obtained, compared with the theoretical flowsheet raffinate composition. The total iron, chromium and nickel concentrations from this particular dissolution were about 17 grams per liter lower than desired. This concentration; however, was considered adequate for the assessment of the corrosiveness of an iron-chromium-nickel nitrate raffinate.

Bench-type studies were conducted for five 48 hour exposure periods to determine the corrosive effects of the iron-chromium-nickel nitrate waste stream upon type 304L stainless steel. Each specimen was placed in a separate glass cold fingered reflux flask containing the iron-chromium-nickel nitrate raffinate.

A possibility exists that localized heating may be caused by the concentration of fission products; therefore, studies were conducted which reflect the effect of elevated temperatures upon the corrosion rate of 304L stainless steel immersed in the waste stream. Two different test conditions were chosen; three type 304L specimens were exposed at 57°C, and four at the boiling reflux temperature of 104°C.

Table 22

COMPOSITION OF STAINLESS STEEL TEST SOLUTION

<u>Element</u>	<u>Test SS Dissolver Solution</u>	<u>Flowsheet (Table 19) Raffinate Composition</u>
Fe	37.25 g/l	48.7 g/l
Ni	4.32 g/l	7.0 g/l
Cr	10.63 g/l	13.3 g/l
H ⁺	1.85N	0.9N
NO ₃ ⁻		4.6N
Sp. Gr.	1.246	
B. P.	104 ± 1°C	

Table 23 lists the rate of penetration in inches per month for five successive 48-hour test periods. In addition, the cumulative and average IPM rates are listed.

All specimens which were immersed in the flasks containing the boiling iron-chromium-nickel nitrate raffinate suffered severe grainboundary attack, while those immersed in the 57°C temperature raffinate completely resisted the corrodent. At the lower temperature the original machine marks were evident on each specimen.

Table 23

HUEY TYPE TESTING OF TYPE 304L STAINLESS STEEL IN
ELECTROLYTIC DISSOLUTION RAFFINATE SOLUTION

Specimen No.	Corrosion Rate-Inches Penetration Per Month						240 Hour Cumulative
	1st Period ⁽³⁾	2nd Period	3rd Period	4th Period	5th Period	5 Period Average	
V-297 ⁽¹⁾	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
V-298	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
V-299	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
V-419 ⁽²⁾	0.0020	0.0039	0.0035	0.0046	0.0053	0.0039	0.0038
V-420	0.0024	0.0035	0.0037	0.0056	0.0056	0.0042	0.0042
V-421	0.0022	0.0024	0.0033	0.0040	0.0046	0.0033	0.0033
V-422	0.0020	0.0024	0.0037	0.0044	0.0050	0.0035	0.0035

(1) Specimens V-297-V-299 INCL were exposed at 57°C.

(2) Specimens V-419-V-422 INCL were exposed at 104°C.

(3) Exposure periods were 48 hours each.

Promise does exist that an alloy can be chosen which fulfills the demanding requirements for permanent storage of the electrolytic dissolution raffinate.

B. Electrolytic Dissolution of Zirconium Alloys in HCl-Methanol

Previous work⁽¹⁹⁾ has demonstrated that zirconium alloys may be dissolved electrolytically in HCl-methanol solution. The amount of particulate residue is reduced to less than 0.5 percent of the dissolved zirconium by the use of relatively high current densities (>1.2 amps/cm²). The proposed process would include three steps: electrolytic dissolution, solvent extraction of the uranium, and concentration of the waste by distillation of the methanol.⁽¹⁾

Currently reported work includes potential-current density relationships for both zirconium and stainless steel in HCl-methanol. Rates of dissolution of uranium dioxide pellets in HCl-methanol were also measured. Extraction of uranium(IV) by 24 percent tributyl phosphate in n-hexane was accomplished; however, the presence of zirconium was found to vitiate the extraction.

1. Preliminary Dissolution Experiments, H. T. Hahn, Problem Leader; J. R. Aylward, R. E. Ohlin

A preliminary investigation was made of the potential-current density relationships for 304 stainless steel and zirconium in methanol saturated with hydrogen chloride at 25°C. The study was undertaken with the new potentiostat. The behavior of both materials was similar in that both showed a region of electro-polishing. In this region a large increase in potential results in a small current density change. The current densities corresponding to the electropolishing region are 100-250 ma/cm² (2 - 4 mg/cm²/min) for stainless steel and 800 ma/cm² (> 11 mg/cm²/min) for zirconium. Stirring the solution increases the current density of the electropolishing region by a factor of 2 - 3. This is small compared to the change produced by stirring when the limiting current density is due to concentration polarization. The 304 stainless shows a hysteresis effect in the electropolishing region, with increasing potentials giving higher current densities than decreasing potentials. The potential-current density curves for both metals have regions in which the current density is time dependent at constant potential temperature, and bulk solution composition. Future experiments will be designed to elucidate the details of the potential-current density curves in regard to changes with time and hysteresis.

2. Solvent Extraction, H. T. Hahn, Problem Leader; E. M. Whitener

As the electrolytic dissolution of zirconium-type fuel elements appears feasible in HCl-methanol, a study was initiated to determine if uranium could be extracted from this solvent. From scoping experiments it appears that tributyl phosphate in n-hexane would be a satisfactory extractant system.⁽¹⁾ A more complete study was undertaken to determine distribution coefficients for uranium in this system as well as separation coefficients for zirconium and uranium.

Extraction of uranium from methanol-HCl was achieved using 24 volume percent tributyl phosphate in n-hexane. The concentration of uranium was varied from 0.25M to 1.7M. On the basis of analytical results, it appeared that greater than 40 grams of uranium per liter could be extracted from HCl-methanol with an extraction coefficient of 1.5. Experiments to extract zirconium from HCl-methanol using 24 volume percent tributyl phosphate in n-hexane resulted in extraction coefficients of 0.3-0.6.

However, upon extraction of an HCl-methanol solution containing zirconium (0.56M) and uranium IV (0.01-0.5M), it was noted there was an increase in alcohol phase volume with a decrease in the hexane phase volume, the total volumes of the two phases remaining the same. Zirconium was preferentially extracted into the hexane while the distribution coefficients for uranium were considerably less than in the case of separate extraction. Apparently the zirconium competes successfully with the uranium for the tributyl phosphate, and the zirconium-tributyl phosphate complex is more soluble in methanol than in hexane, hence the volume change. Further work is in progress to study complexing agents for zirconium which will not adversely affect the extraction of uranium.

3. Solubility of Uranium Dioxide, H. T. Hahn, Problem Leader;
E. M. Whitener

The possible use of HCl-methanol as a decladding media for Dresden-type fuel elements raised the question of uranium dioxide solubility in HCl-methanol. Previous work indicated the oxide to be insoluble.⁽²⁰⁾ Tests were carried out at various temperatures from 13 to 40°C on uranium dioxide pellets approximately 0.5 mm in diameter. No chemical dissolution occurred at 13°C and at 40°C the rate was less than 1×10^{-4} mg/cm²/min⁻¹, based on weight loss. The latter rate corresponded to a uranium loss of less than 0.01 percent per hour. Chemical analysis of the solution showed the uranium concentration to be even less than that calculated from the weight loss. An analysis of the solution by emission spectrophotometry showed the presence of zirconium and calcium in sufficient quantity to account for the uranium discrepancy between the weight loss value and the determined value. It was concluded that the dissolution of uranium dioxide pellets by chemical attack in HCl-methanol was negligible.

VI. THE ARCO PROCESS - DISSOLUTION OF FUEL ALLOYS IN MOLTEN CHLORIDES

The ARCO process employs molten lead chloride as a solvent for zirconium-uranium alloys.⁽²¹⁾ The product salt contains the uranium together with excess lead chloride and the alkali, alkaline earth and rare earth fission products. Ruthenium tended to remain with the lead. Zirconium is removed during dissolution as the volatile zirconium tetrachloride. When Zircaloy cladding is used, tin is found principally in the lead phase.

Dissolutions were extended to the 100-gram scale⁽¹⁾ with no evidence of the formation of nitric acid-insoluble residues. Other chlorides which have been tested have proved less satisfactory than lead chloride. Aluminum and chromium were dissolved in lead chloride melts. Certain nickel alloys demonstrated relatively good resistance to corrosion (3-8 mils/month) in the lead-lead chloride system.

Current research has been concerned with the definition of a tentative flowsheet for head-end processing, with the gathering of additional corrosion data, and with the determination of basic properties of lead chloride melts. Uranium salts may be quantitatively leached from the lead chloride product matrix with 8M nitric acid. Lead chloride may be regenerated by either aqueous precipitation or direct chlorination. In the former, lead dissolves rapidly in refluxing nitric acid with maximum rate at an initial concentration of 6M nitric acid. A tentative phase diagram has been developed for the $\text{UCl}_4\text{-PbCl}_2$ system. Eighteen-day corrosion tests on both welded and unwelded specimens have confirmed that several nickel alloys exhibit corrosion rates of 5-7 mils/month, with no intergranular corrosion.

A. Salt Matrix Treatment, H. T. Hahn, Problem Leader; E. M. VanderWall, D. L. Bauer

Experiments were conducted which were designed to remove the uranium salts from a synthetic ARCO salt matrix. These matrices were prepared by dissolving uranium metal in molten lead chloride. Upon cooling, the salt mixture was ground and anhydrous stannous chloride added. The compositions were approximately ten mole percent uranium chloride, ten mole percent tin chloride and the remainder lead chloride. These mixtures (13-14 grams) were then refluxed with ten milliliters of nitric acid (in varying concentrations) for one to two hours. The resultant mixture was cooled, filtered and washed with an additional 15 milliliters of nitric acid of the same concentration. The solid was subsequently washed with water and refluxed with concentrated acid.

More than 98 percent of the uranium was removed as a result of refluxing and washing with 8M and 10M acids; only 96 percent removal was effected in 4M HNO_3 . The remaining uranium was removed during either the water wash or the concentrated acid reflux. Spectroscopic examination of the residual solids revealed no uranium in several cases and only traces in the others. However, the limits of detection are sufficiently low that only an upper limit of 0.7 percent can be set for the uranium loss; it is believed that the actual loss is considerably

less than this. Residues will be dissolved to determine this loss more closely. Removal of the tin is almost quantitative during leaching.

B. Reconversion to Lead Chloride, H. T. Hahn, Problem Leader;
E. M. VanderWall, D. L. Bauer

Since reconversion of the lead produced by the ARCO process into lead chloride is economically desirable, a brief survey was made of possible methods. One alternative is the dissolution of lead in nitric acid. Conversion of lead nitrate into lead chloride is a simple metathesis reaction based on the relative insolubility of lead chloride.

Data were not available for the dissolution of lead in refluxing nitric acid of various concentrations. The concentrations selected in this study were based on data obtained at 35°C, in the region where maximum dissolution rates were attained.⁽²²⁾ The dissolution rate of lead at reflux temperatures was found to be highly dependent on the nitric acid concentration. The data are presented in Figure 9. The rates were determined from the tangent to the slope of the dissolution curve at zero time. The maximum dissolution rates occur between 5.5 and 6.0M nitric acid.

Fig. 9 - Initial Rate of Dissolution of Lead in Refluxing Nitric Acid

A prolonged dissolution of lead was performed in 5.89M nitric acid. Initially, the reflux temperature was 103°C; the temperature decreased to 99°C as the acid concentration decreased to 1.10 molar (atmospheric pressure, 640 mm Hg). The stoichiometry, based on five values during the dissolution, indicates that the mole ratio of nitric acid consumed per mole of lead dissolved is 2.29 ± 0.09 in this case. The resultant solution was 2.15M in lead and no precipitate appeared as long as the solution was at reflux temperatures. The average rate of dissolution over a 90-minute period was 43.4 mg/cm²/min.

Preliminary experiments have also demonstrated that lead may be readily converted to lead chloride by passing chlorine through molten lead at temperatures slightly above the melting point of lead chloride.

C. Tentative Flowsheet for Head-End Process, H. T. Hahn

Demonstration of uranium leachability and methods for reconversion of lead permits consideration of a tentative flowsheet for head-end processing. Figure 10 employs an aqueous lead reprocessing step; an alternative could be the direct chlorination of lead.

FIGURE 10
TENTATIVE FLOWSHEET FOR
THE ARCO PROCESS

5 kg/DAY PLANT WITH LEAD
RECOVERY BY AQUEOUS MEANS

CPP-S-1319

Calculations are based upon a fuel composition of two percent uranium. The dissolver product at 520°C is assumed to contain ten mole percent uranium chloride in lead chloride. Phase diagram studies have indicated that this concentration may be raised to increase capacity or the temperature progressively lowered to decrease corrosion.

Storage volume for zirconium tetrachloride is based upon 50 percent of theoretical density or 6.0M zirconium. Greater stability and further concentration (a factor of 2-4) may be achieved by conversion of the tetrachloride to the oxide. The second waste stream consists of insoluble lead salts resulting from the leaching operation, and is of relatively small volume.

Solubility data⁽²³⁾ indicate that at least 0.9M uranium may be attained in the 8M nitric acid leach solution prior to chloride removal. Nitric acid requirement is based upon an acid to lead ratio of 2.6. The volume of the lead dissolution system may be minimized by high acid flow rate.

D. Corrosion Tests of Metals and Alloys, N. D. Stolica, Problem Leader; G. S. Adams, O. R. Klemens

An additional series of static corrosion tests was completed in the lead-lead chloride system at 528°C. The experimental procedure has been previously described.⁽¹⁾ Results are given in Table 24 for both welded and unwelded specimens of three nickel alloys: Hastelloy F, Carpenter-20, and Inconel X.

Table 24

CORROSION OF SELECTED ALLOYS IN THE
LEAD-LEAD CHLORIDE SYSTEM AT 528°C

<u>Alloy</u>	<u>Exposure, Days</u>	<u>Weight Loss, Mils per Month</u>	
		<u>Unwelded</u>	<u>Welded</u>
Hastelloy F	5	8	9
	10	7	6
	18	5	5
Carpenter-20	5	12	6
	10	16	14
	18	11	6
Inconel X	5	-	20
	10	-	10
	18	-	7

Both Hastelloy F and Inconel X display consistently decreasing corrosion rates in general agreement with previous results. Except for unwelded Carpenter-20, all 18-day rates were in the 5-7 mil/month range. Carpenter-20 results were erratic and the unwelded coupon rates were about twice as high as previously reported; these will be rechecked.

Incoloy 804

Inconel X, Showing Grain Boundary Attack

Fig. 11 - Metallographs of samples after 18-day exposure to Pb-PbCl₂ at 528°C (210 x, Aqua Regia Etch).

Metallographic examination of 18-day exposure coupons showed no grain boundary attack or intergranular attack upon Hastelloy F, Incoloy 804 or Carpenter-20. In the case of Inconel X, however, there were some spots where grain boundaries had been attacked beneath the surface. When present this localized condition was observed approximately ten mils beneath the surface. Micrographs are shown in Figure 11.

E. Phase Studies, H. T. Hahn, Problem Leader; E. M. VanderWall,
D. L. Bauer

The system $\text{PbCl}_2\text{-UCl}_4$ has been studied in the PbCl_2 rich region. The data obtained so far are given in Figure 12. A eutectic point is observed at 378°C and 26.5 mole percent UCl_4 . The compounds involved probably are PbCl_2 and PbUCl_6 . Based on only a few observations in the region greater than 26.5 mole percent UCl_4 , and reasonable uranium coordination, it appears that the compound PbUCl_6 exists. Further data are needed to confirm this. There is a polymorphic transition at 336°C . This is probably due to PbUCl_6 polymorphism. Preliminary X-ray analysis shows only the existence of crystalline PbCl_2 and an amorphous compound below 336°C .

Fig. 12 - Tentative Phase Diagram for $\text{UCl}_4\text{-PbCl}_2$ System

VII. MECHANICAL EQUIPMENT DEVELOPMENT

A Model S Chempump has been modified to give one year of trouble-free operation and is recommended for pumping of clear radioactive solutions. A direct operated piston pulser design is being adapted from the Hanford design for possible installation at the ICPP, a direct air pulser has proven feasible on a full-size column at the pilot plant, and life testing of bellows pulsers is under way. Alumina bearings have proven satisfactory in a pump for a slurry of alumina particles but some damage has been indicated at high nitric acid concentration. Development of an impulse type pump is under way in an effort to minimize moving parts in a radioactive area and overcome the disadvantages of current positive displacement pumps.

A. Canned Motor Pump Testing, J. A. Buckham, Problem Leader; F. A. Graf

As part of the continuing, nation-wide effort to develop inexpensive, reliable pumps for radioactive chemical processing, the Model S Chempump was selected a year ago as being worthy of development and testing. After preliminary testing, the basic pump was modified by installation of 100 percent oversized bearings, by welding the impeller to the shaft, and by careful dynamic balancing. This modified pump has now passed the desired requirement of one year (9672 hours) of trouble-free operation. The pump ($3/4$ h.p.) was installed in a special test setup recirculating a 1.5 molar aluminum nitrate, 1.0 molar nitric acid solution. Wear on no part of the pump during this year-long test exceeded 1.0 mil. Testing of this pump has been terminated; it can now be recommended for use in radioactive chemical processing plants as an inexpensive and reliable pump.

A $3/4$ h.p. Melrath canned motor pump has also been under test as an alternate possibility to the modified Chempump. This pump performed satisfactorily for 2470 hours, at which time it was damaged by overheating when the cooling water was accidentally turned off. Testing of this pump has been terminated because the pump does not appear to be as satisfactory as the fully-tested Model S Chempump; it is less efficient, bulkier, heavier, and less easily maintained.

B. Column Pulser Development, J. A. Buckham, Problem Leader; F. A. Graf

Reliability of column pulsing equipment is extremely important to the overall performance of a reprocessing plant using pulsed solvent extraction columns. The ICPP uses remote diaphragm Lapp pulsers which have a high initial cost and have given some trouble in operation. In spite of recent improvements in operating technique which have increased the reliability of the existing pulsers, a concerted effort to develop more economical and more reliable pulsers is indicated. This program is currently proceeding along three parallel paths: piston pulsers, air pulsers, and bellows pulsers.

The piston pulser has a long history of reliable operation at Hanford. Therefore, design of a modified Hanford-type pulser has been undertaken for possible use on a 10-inch diameter ICPP column. This approach was selected because it will make available an alternate pulser for use at ICPP at the earliest possible date.

A longer-range, but ultimately more promising approach is the development of direct air pulsers. A column can be pulsed by intermittent application of air pressure to a jackleg. Such a pulser would not have a single moving part inside the radioactive area and would be much less expensive than a piston or diaphragm pulser. Experimental testing of this concept has been started in a 10-inch diameter pilot plant column. A 1-1/2 inch diameter jackleg is pulsed by alternate application and release of compressed air. The air supply was initially controlled by means of solenoid valves, but improved performance has been obtained by use of rotary valves. The current apparatus uses a three-stage rotary valve which allows for an intermediate air reservoir and thus separates frequency and amplitude control of the pulse wave. The concept appears to be a very promising one and development efforts are continuing.

The third pulser testing effort is on bellows pulsers which are a desirable type for hot pilot plant use where extremely long life is not required. Life testing of two stainless steel bellows has been undertaken. The bellows are 6.8 inches long, 2.875 inches i.d., and 3.625 inches o.d. Neither bellows has failed yet; one has been flexed for 5 million cycles and the other for 11 million.

C. Slurry Pump Testing

Several pumps have been tested during the previous year for possible service in recirculating an acidic alumina slurry in the demonstration calciner. The pump selected for installation, a Johnston 6-AXC deep-well turbine pump, has been given additional testing. Graphite bearings were shown to be unsuitable in alumina slurry service. Alumina bearings exhibited satisfactory performance when pumping a slurry of alumina particles in water; however, they suffered excessive wear when pumping a hot acidic slurry of alumina. Consideration is now being given to the use of boron carbide bearings, a test being planned for the near future.

D. Impulse Pump Development, M. E. Weech

Several types of positive displacement pumps have been used at the CPP as metering and transfer pumps. In a number of applications these pumps have either failed to meet their set delivery rates or stopped pumping altogether. If the pumps are in radioactive areas, repairs after such failures involve slow and costly decontamination prior to actual maintenance. In the large majority of cases, check valve malfunctioning has been the primary cause of pump failure. These valves fail to seat due either to corrosion of the seats and balls or to foreign material plugging the valve apertures.

1. Description of Impulse Pump

In an effort to overcome the disadvantages of current positive displacement pumps and minimize the moving parts in radioactive areas, the pump shown in Figure 13 was developed. Assume that fluid from the feed tank has filled the pressure pot from level B to A (solenoid valve (2) is open and solenoid (1) is closed). At this level, the timer closes valve (2) and opens valve (1) which allows a sudden surge of air pressure from the air reservoir to enter the pressure pot. The fluid in the pressure pot, under this suddenly applied air pressure, can flow either through the delivery line or back through the feed line. Flow in the feed line is limited by the change in direction of flow that has to occur, the inertia of the fluid in the line, and the high fluid friction loss in the small line that arises when moderate to high velocities are approached. Since the delivery line contains little fluid when the pressure pulse is applied, and its friction loss is low relative to the feed line, the flow is preponderantly through the delivery line.

When flowout of the pressure pot reduces the liquid level in the pot from A to B, the timer closes solenoid (1) and opens solenoid (2). This relieves the air pressure from the pressure pot. The fluid in the delivery line falls back into the pot, and fluid from the feed tank begins to run into the pressure pot. When the liquid level in the pressure pot reaches point A, the timer closes valve (2) and opens valve (1) and the process repeats itself.

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Fig. 13 - Schematic of Impulse Pump

2. Impulse Pump Performance

Figure 14 shows the performance curve that was established under the following conditions:

Feed Line	1/4 inch Schedule 40 iron pipe, 6 feet long.
Delivery Line	3/4 inch glass pipe, 25 feet 7 inches long from venturi inlet to overflow.
Air Pressure "On" Time	0.5 seconds.
Air Pressure "Off" Time	Variable over 7 to 20 second interval to allow level in pressure pot to return to point A.

Fluid

Water at 70°F.

Pressure

Variable (that shown on the figure is the pressure after the air in the reservoir has expanded to fill the air line and freeboard in the pressure pot).

The points scatter more widely than would be desired and the reasons for this scatter are being investigated. It is interesting to note that the upper portion of the curve is close to linear, which indicates that some interesting pump control possibilities exist.

Work is continuing to establish the pumping curve for other pressure "on" times up to $1\frac{1}{2}$ seconds. These data will be correlated as described in Section 3, following.

Fig. 14 - Impulse Pump Performance Curve

3. Correlation of Results

The pulse pump operating characteristics can be described by four basic differential equations. These equations fit the flow conditions existing in the delivery line and feed line immediately after the pressure pulse is applied and in the feed line when the pressure is relieved. A satisfactory correlation between these equation solutions and the experimentally established pump performance curve would provide a design basis for any conceivable application of this type of pump.

The solution of these differential equations is difficult and tedious by hand methods so solutions are being obtained on an analog computer. Sufficient parameters will be included in the machine solutions to permit their use for general design purposes.

VIII. MISCELLANEOUS CORROSION STUDIES

An evaluation program aimed at finding a material of construction suitable for a dissolver to handle all types of dissolutions has indicated excellent resistance of 30 percent iridium-70 percent platinum alloy to boiling mixtures of HF-HNO₃, HCl-HNO₃, and H₂SO₄-HNO₃ in ranges most likely to be encountered. For evaluation of existing waste storage tanks, corrosion specimens have been installed and are to be inspected at intervals for a year or more.

A. Universal Head-End Dissolver, N. D. Stolica, Problem Leader; T. L. Hoffman

The search for a universal head-end dissolver vessel for reprocessing nuclear fuels is an objective of ICPP Technical. Promise does exist that an iridium-platinum alloy can be chosen which fulfills the demanding requirements for that service. Accordingly, scoping corrosion tests were conducted on 30 percent iridium-70 percent platinum alloy coupons while immersed in various boiling binary mineral acid mixtures. Table 25 lists the composition of these acid mixtures together with the corrosion data.

Bench-type tests were conducted for five 48-hour exposure periods to determine the corrosive effects of each different boiling acid mixture upon 30 percent iridium-70 percent platinum alloy. All specimens were tested in the as-received highly polished condition. Each specimen was placed into a different cold fingered reflux vessel containing the separate boiling acid mixtures. Glass flasks and water cooled condensers were used for the hydrochloric-nitric and sulfuric-nitric acid studies. Teflon beakers were used for the hydrofluoric-nitric acid mixtures. Water cooled condensers for these beakers were made from round bottom boiling flasks which were covered with sheets of polyethylene paper. The glass flasks were heated on an electric hot plate while the teflon beakers were heated in a 130°C oil bath. Table 25 lists the period and cumulative corrosion rates for these iridium-platinum specimens.

Table 25

CORROSION OF 30 PERCENT IRIIDIUM - 70 PERCENT PLATINUM IN VARIOUS REFLUXED BOILING MINERAL ACID MIXTURES

Corrosion Rate Mils Penetration Per Month

<u>Specimen Number</u>	<u>Acid Mixture</u>	<u>First Period</u>	<u>Second Period</u>	<u>Third Period</u>	<u>Fourth Period</u>	<u>Fifth Period</u>	<u>5-Period Average</u>	<u>Cumu- lative Rate</u>
R-4	2M HF	0.0000	0.0000	0.0000	0.0010	0.0020	0.0004	0.0008
R-5	13M HNO ₃	0.0070	0.0000	0.0000	0.0000	0.0000	0.0014	0.0017
R-6	15M HF	0.0098	0.0020	0.0000	0.0000	0.0000	0.0024	0.0025
R-7	5M HNO ₃	0.0000	0.0042	0.0000	0.0000	0.0000	0.0008	0.0014
R-8	2M HCl	0.0000	0.0056	0.0097	0.0000	0.0154	0.0061	0.0049
R-9	5M HNO ₃	0.0000	0.0126	0.0154	0.0070	0.0112	0.0092	0.0101
R-10	8M H ₂ SO ₄	0.0000	0.0000	0.0097	0.0000	0.0000	0.0019	0.0009
R-11	2M HNO ₃	0.0000	0.0000	0.0056	0.0000	0.0000	0.0011	0.0006

The observed rates indicate almost complete resistance of 30 percent iridium-70 percent platinum alloy to all four acid mixtures at boiling conditions. It could be judged that the 2M hydrochloric-5M nitric acid mixture was the most aggressive of the four corrodents with an observed corrosion rate of 0.01 mils per month.

B. Waste Tank Corrosion Studies , N. D. Stolica, Problem Leader;
O. R. Klemens

Pre-weighed corrosion samples of type 304L stainless steel were installed in permanent waste tanks WM-185, -186, -187, and -188. These samples consist of one-inch hoops cut from schedule 40 pipe. These samples are suspended by cables 18, 48, and 72 inches from the tank bottoms. Twenty-four samples are at each position. By periodic removal of some samples and replacement of these samples at the next withdrawal, corrosion data over extended time periods can be obtained.

C. Neutralized Waste Studies, N. D. Stolica, Problem Leader; G. S. Adams

Specimens of type 347 columbium stabilized and type 304L stainless steels were immersed in dibasic aluminum nitrate, neutralized with para-formaldehyde, for a one-year study at 60°C. Specimens were to be withdrawn after three months, six months, and twelve months of exposure. The corrosion rate for both stainless steels after six months' exposure time was less than 4×10^{-7} inches per month.

IX. ANALYTICAL DEVELOPMENT STUDIES

J. E. Rein, Group Leader; G. L.
Booman, Assistant Group Leader

Notes are included on analytical methods developed for mercury, lead, tin, stainless steel components and plutonium.

A. Determination of Mercury, S. S. Yamamura

A modified method, based on the dithizone colorimetric method of Friedeberg,⁽²⁴⁾ was developed for microgram quantities of mercury. Milligram quantities of aluminum and high ratios to mercury of such normally dithizone reacting elements as copper are tolerated. Two extractions are involved. The first is a preliminary separation of the mercury as the dithizonate complex from a citrate--EDTA medium into xylene. The mercury is stripped from the xylene phase with strong hydrochloric acid, pH is adjusted, and a second (and final) extraction of the dithizonate complex of mercury is made into carbon tetrachloride. The first extraction separates the mercury from the bulk of the impurities. The method has been successfully tested on several different types of CPP Technical samples.

B. Determination of Lead, S. F. Marsh and S. S. Yamamura

A method, superior to the EDTA titrant-mercury electrode end point method, was developed for ARCO type samples containing large amounts of zirconium, tin, and uranium. Lead is separated from these three metals by cation exchange in the presence of fluoride and nitrate. Lead retains on the column (Dowex 50 x 8) while the other metals pass through as neutral or negatively charged complexes. A small amount of uranium accompanies the lead upon elution with 8M nitric acid. The eluted lead phase is evaporated to near dryness and the lead is determined by an indirect EDTA titration method involving excess EDTA and back titration with zinc to an Eriochrome Black T indication end point. The small amount of uranium is masked with carbonate.

C. Determination of Tin, S. S. Yamamura and R. E. Foster

A spectrophotometric and a polarographic method were developed for the determination of tin in ARCO type samples. In both methods, tin is first separated by bromide distillation.

In the polarographic method, the distilled free bromine is destroyed with hydroxylamine and the tin (II) to tin metal reduction wave is followed. This method has a lower limit corresponding to 0.2 mg of tin per ml of submitted sample.

The colorimetric method using pyrocatechol violet as the chromogenic agent is about 100 times more sensitive.

D. Determination of Stainless Steel Major Components

Titrimetric methods were developed for iron, chromium, and nickel applicable to stainless steel-uranium fuel dissolver samples.

1. Iron, F. W. Dykes

The sample is first fumed with perchloric acid to oxidize chromium (III) to chromate. Iron is precipitated with ammonia in the presence of carbonate (to prevent precipitation of uranium). The iron hydroxide precipitate is dissolved with hydrochloric acid, reduced with excess tin (II), the excess tin(II) is oxidized with mercury(II), and the iron(II) is titrated with standard chromium(VI) to the diphenylamine sulfonate indicator end point.

2. Chromium, R. W. Henry

The sample is first treated with hydrogen peroxide in a sulfuric acid media and evaporated to fumes of sulfur trioxide. The hydrogen peroxide reduces any chromium(VI) to prevent loss of volatile chromyl chloride and the evaporation removes chloride and nitrate, both of which would interfere in subsequent steps. The resulting chromium(III) solution is oxidized to chromium(VI) by boiling with ammonium persulfate and silver (I) catalyst. After cooling, the chromium(VI) is titrated with standard iron(II) to a ferroin internal indicator end point.

3. Nickel, K. W. Puphal and S. S. Yamamura

This element is separated as the dimethylglyoxime precipitate from ammoniacal solution with tartrate masking to prevent precipitation of iron, chromium, and uranium. The precipitate is dissolved with nitric acid and evaporated to fumes of perchloric acid to remove organic residue. A measured excess of EDTA is added and a back titration is made with standard zinc solution at pH 8.7 to a zincon indicator end point.

E. Radiochemical Development Program, M. C. Elliott and W. J. Maeck

Plutonium

A two-cycle extraction procedure was developed. After oxidation with potassium permanganate, plutonium(VI) is extracted as the tetrapropylammonium trinitrate complex from acid deficient aluminum nitrate salting solution into Hexone. Plutonium is simultaneously stripped and reduced to plutonium(III) by contact with ferrous chloride and hydroxylamine. It is then preferentially oxidized to the +4 valence state with nitrite and extracted into thenoyltrifluoroacetone-xylene. An aliquot of this organic phase is mounted, evaporated, ignited and counted for plutonium alpha activity on a Frisch grid chamber. Plutonium recovery is 98.7 percent $\pm$ 0.7 coefficient of variation. Ruthenium and zirconium, the only 80-day cooled fission products which follow the plutonium, are decontaminated to better than 1×10^{-4} . Uranium decontamination is greater than 99 percent. Neptunium follows the plutonium but in irradiated highly enriched uranium fuel, the quantity of neptunium produced is insignificant compared to plutonium.

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