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DAREX PROCESS:
PROCESSING OF STAINLESS STEEL-CONTAINING REACTOR FUELS WITH DILUTE AQUA REGIA

F. G. Kitts
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OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

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ABSTRACT

The Darex process developed for the recovery of uranium from stainless steel-containing reactor fuels consists of three steps: (1) dissolution of the fuel material in dilute aqua regia, (2) removal of chloride from the solution to prevent corrosion of downstream stainless steel process equipment, and (3) adjustment of the nitrate solution to solvent extraction feed conditions. Each step can be either continuous, semicontinuous, or batch with continuous operation showing much higher throughput for comparable equipment. The preferred dissolvent is 5 M HNO_3-2 M HCl, since dissolution rates and metal loadings are near maximum. Nitric acid from 60 to 95 wt % can be used in decreasing the chloride concentration to < 350 ppm; the higher strength acids have process advantages. Excess nitric acid is recovered and recycled during production of a concentrated metal-salt solution, which is diluted to Purex solvent extraction feed acidity, 2-3 M HNO_3. Titanium is a satisfactory material of construction, with corrosion rates < 1 mil/mo in all process environments and overall heat transfer coefficients comparable to those of stainless steel.

CONTENTS

1.0 INTRODUCTION

Studies on the Darex head-end process for recovering uranium from irradiated stainless steel-containing fuel elements are reported here. By this process fuel elements that will not dissolve in nitric acid are dissolved in dilute aqua regia, and the chloride is removed from the solution to produce a nitrate solution which, after adjustment of concentrations, can be fed to a standard solvent extraction process operating in stainless steel equipment. Each of the three steps——dissolution, chloride removal, and feed adjustment——was investigated as a continuous, semicontinuous, and batch process with unirradiated prototypes in both laboratory and engineering-scale equipment. Reagents containing 61-95 wt % HNO_3 were used in chloride volatilization. Limited laboratory tests were made with irradiated material to determine fission product distribution. A thorough investigation showed titanium to be a wholly satisfactory material of construction.

Since the recent trend in power reactor fuels has been toward slightly enriched ceramic cores clad in stainless steel, the importance of Darex as a process for recovering uranium from such fuels has increased markedly, especially since Darex is in a more advanced state of development than any of the other processes proposed for the processing of stainless steel-containing fuels. Darex is applicable to the total dissolution of highly enriched uranium dioxide-stainless steel sintered fuels, such as APPR, as well as the low-enrichment fuels consisting of uranium dioxide pellets clad in stainless steel tubing, such as Yankee Atomic. It can also be used for the dejacketing, and with fluoride addition for total dissolution, of stainless steel-clad mixed oxide (UO_2-ThO_2) fuels such as Consolidated Edison.

Acknowledgment. Grateful acknowledgment is made of the work of B. C. Finney, who assisted materially in all phases of the engineering development; J. J. Perona, for his analysis of continuous dissolution; and H. F. Johnson (University of Tennessee), who acted as consultant throughout the investigations. Recognition is also given to J. R. Flanary, J. H. Goode, A. H. Kibbey, and J. E. Savolainen, who carried out laboratory investigations, including the work with irradiated materials. Also greatly appreciated are the efforts of the many technicians who participated in the various endeavors, especially F. L. Rogers, G. B. Dinsmore, and J. F. Talley, who contributed materially to the success of many facets of the program. Much credit also is due the various groups of the Analytical Chemistry Division for their services and especially to the group headed by W. R. Laing whose close cooperation and prompt service allowed the development effort to proceed unimpeded. Corrosion data were obtained by members of the Corrosion Research Division of Battelle Memorial Institute.

2.0 FLOWSHEETS

Several Darex head-end flowsheets were developed for stainless steel-containing uranium fuels, the two currently considered the best being the continuous Darex flowsheet (90 wt % HNO_3 for makeup) and the ORNL Darex "reference" flowsheet for batch processing (61 wt % HNO_3).

In the continuous Darex flowsheet (Fig. 2.1), dissolution product generated continuously is fed to the top of a chloride stripper where the chloride is removed by countercurrent contact with a stream of concentrated HNO_3 vapor from the HNO_3 boiler. The metals-containing stream flows from the bottom of the stripper to the feed adjustment tank where excess HNO_3 is recovered, resulting in concentration of the solution of metallic salts. This concentrated stream requires only H_2O dilution to produce solvent extraction feed. The HNO_3 taken overhead in the feed adjustment tank is upgraded by addition of 90% HNO_3 (~21 $\underline{M}$) and recycled to the HNO_3 boiler along with an external makeup stream of the same composition. This HNO_3 loop portion of the flowsheet could be operated at HNO_3 concentrations higher than the ~15 $\underline{M}$ shown. The HNO_3-HCl mixed acid stream leaving the top of the stripper is condensed and fed to a surge tank, whose contents are maintained at dissolvent composition by the addition of concentration HCl and HNO_3. From this surge tank aqua regia flows to the dissolver and back to the stripper, completing the chloride loop. An alternative system with an HNO_3 rectifier fed by the feed adjustment tank overhead was envisioned to operate on HNO_3 less than the azeotropic composition (15.3 $\underline{M}$) but no advantage was seen if 95% HNO_3 was available.

In the batch chloride removal flowsheet (Fig. 2.2) batches of fuel are dissolved in continuously flowing 5 $\underline{M}$ HNO_3-2 $\underline{M}$ HCl. The dissolution product is accumulated, and a batch of solution is distilled to remove dilute mixed nitric-hydrochloric acid which is sent to waste. Then 12 $\underline{M}$ HNO_3-trace chloride recycle acid is added continuously to the fuel solution and mixed acid is distilled off at the same rate. The HCl concentration in the mixed acid quickly reaches a maximum and then declines, while the nitric acid concentration continues to increase. The nitric acid concentration of the metals-bearing solution also increases and approaches an equilibrium value determined by the concentration of metallic nitrates in solution. When a volume of mixed acid ~87% the initial dissolution product charge volume has been collected, the recycle acid addition is stopped, a batch of fresh 61% (13.3 $\underline{M}$) HNO_3 is added, and the solution is refluxed with air sparging to volatilize the remaining chloride. True countercurrent action is achieved in that fresh 61% HNO_3 is added before the last chloride removal step. After refluxing until the chloride concentration is < 0.015 $\underline{M}$, recycle acid (~12 $\underline{M}$ HNO_3 with trace chloride) is distilled off and collected for use in the next run. The nitrate product is diluted with water to adjust the nitric acid and metal concentrations to the levels desired for solvent extraction. A greatly simplified procedure results if 90% HNO_3 can be tolerated.

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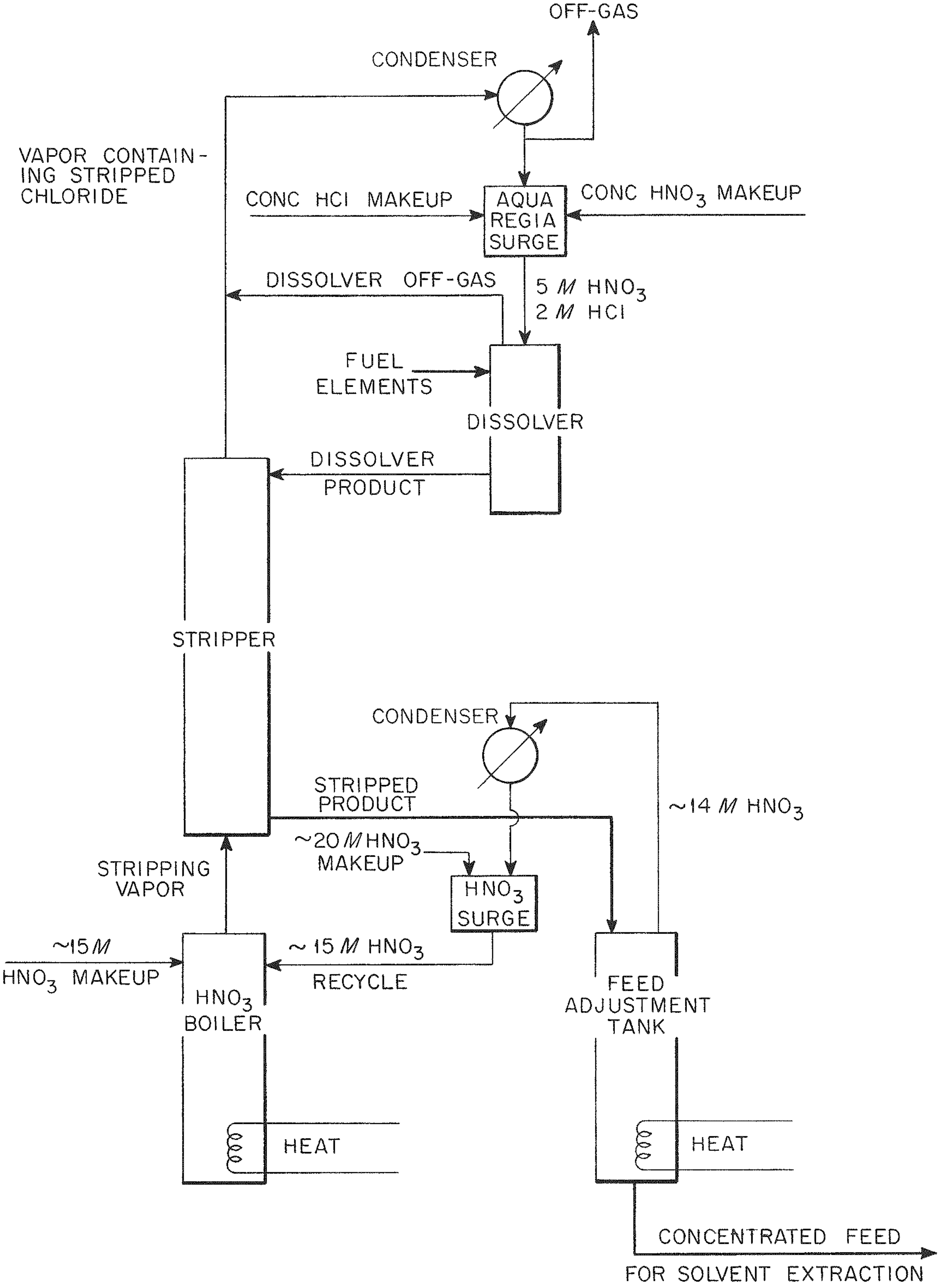

Fig. 2.1. Continuous Darex flowsheet for stainless steel–uranium fuels.

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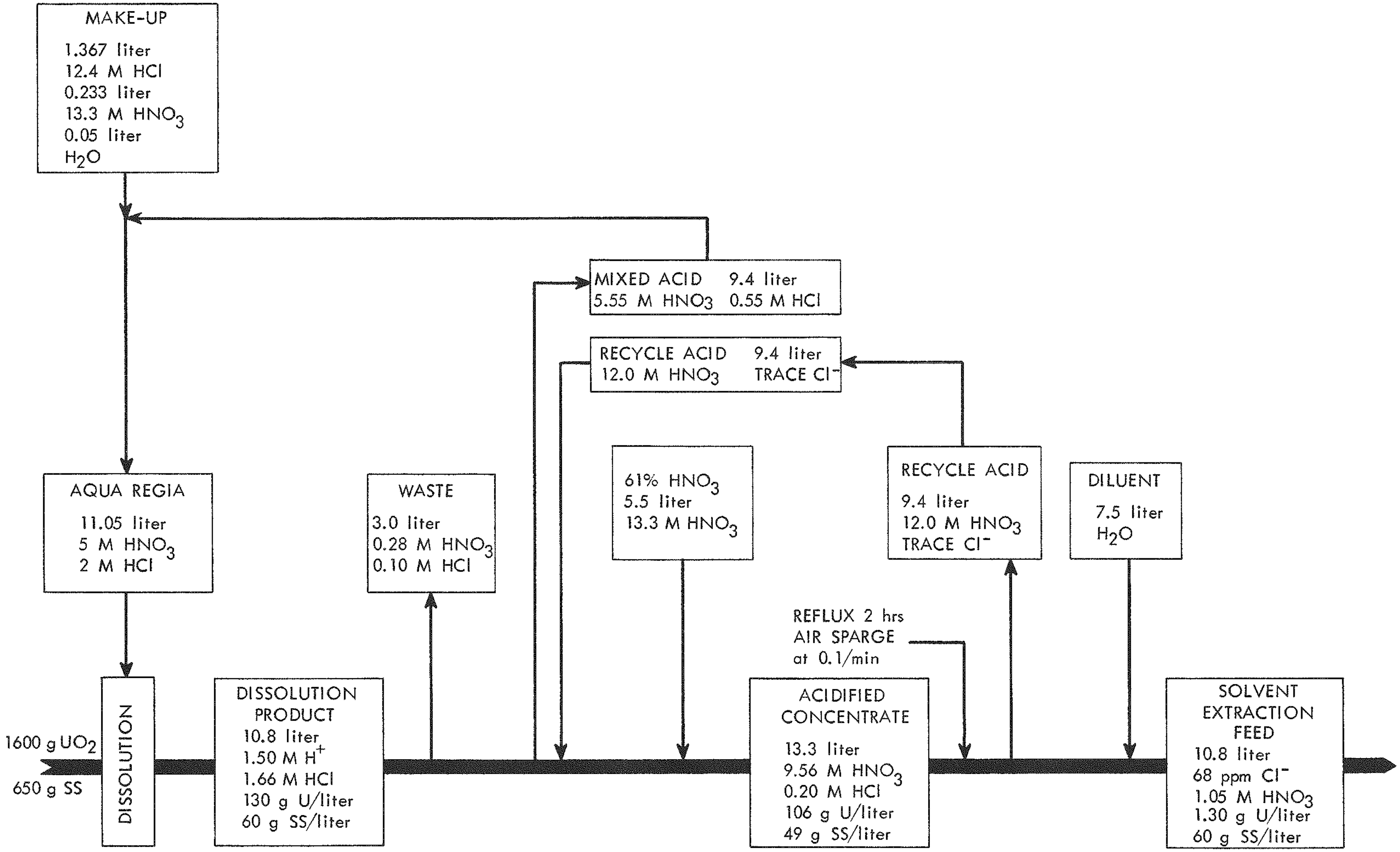

Fig. 2.2. ORNL Darex reference flowsheet (Nuclear Ship Savannah prototype, Run NSS-69). Batch chloride removal.

3.0 DISSOLUTION STUDIES

3.1 Batch Dissolution

In selecting the optimum dissolvent for dissolution of both core and cladding of stainless steel-containing fuel elements, the following factors were considered: (a) the dissolution rate should be relatively high, though controllable, and relatively uniform throughout the dissolution; (b) passivation must not be encountered in the range selected; (c) the final solution should contain a maximum loading of the dissolved material; and (d) the dissolvent should be as low in chloride as is practicable. Tests were made with stainless steel samples, prototype APPR fuel specimens (type 302B stainless steel-UO_2 sinter clad in type 304L stainless steel), and prototype Yankee Atomic fuel (type 304L-clad natural UO_2). All work reported in this section was done in laboratory glassware.

3.1.1 Dissolution Rates

Cladding. Dissolution rates of unirradiated type 304L stainless steel were maximum, varying from 80 to 96 mg/cm^2·min, in 5 to 6 M HNO_3-1.5 to 2.0 M HCl (Fig. 3.1a) and changed abruptly with change in the nitric acid concentration at a given HCl concentration. Rates did not drop off nearly so rapidly with increase in the HCl concentration. The general shapes of the dissolution curves are quite similar to those for nickel-chromium alloys.

In 1- to 3-min dissolution experiments at 90-100°C, during active dissolution type 347 stainless steel dissolved at rates in the same general range as type 304L but became passivated more rapidly:

HNO_3, M	HCl, M	Dissolution Rate, mg/cm^2·min
1	3	19.7
1	4	Passivated
1	5	Negligible
1	6	159
1.5	3	26.1
1.5	4	78.0
1.5	5	Passivated
2	5	120

Fuel types from prototype Army Package Power Reactor (APPR) elements dissolved in 5 M HNO_3-2 M HCl at 90°C, in 1- to 6-in. lengths, at a rate of 86 mg/cm^2·min:

HNO_3, M	HCl, M	Dissolution Rate, mg/cm^2.min
5	1	0.015
5	1	0.0017
5	1.5	0.0061
5	2	85.9

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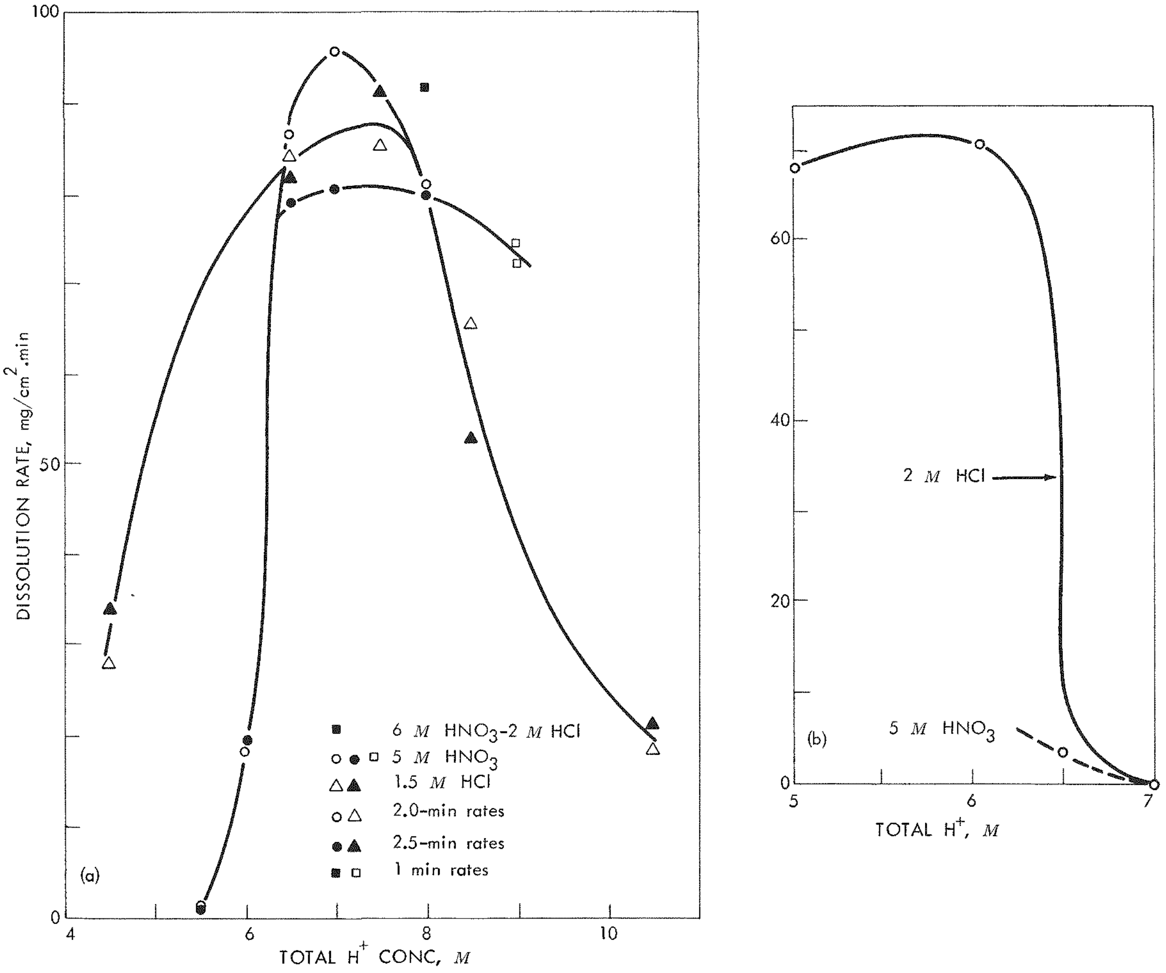

Fig. 3.1. Dissolution rates of type 304L stainless steel in (a) dilute aqua regia at 90–100°C and (b) dilute aqua regia containing 71 g of dissolved stainless steel per liter. Rates calculated from weight loss of specimens.

HNO_3, M	HCl, M	Dissolution Rate, mg/cm^2·min
6	2	95.3
6	2	97.0

As expected, the dissolution behavior of this heterogeneous material was somewhat less predictable than that of type 304L stainless steel alone, with core and cladding dissolving at unequal rates. Dissolution rates with less than 2 M HCl in the aqua regia (5 M HNO_3) were too low to be practical.

Core Alloys. Dissolution rates of various core alloys in boiling 5 M HNO_3-2 M HCl were high enough, > 5 mg/cm^2·min (Table 3.1), that dissolution in this reagent is practical. However, uranium losses to residual solids were prohibitively high when the percentage of niobium in the alloy was appreciable. The possibility of explosions with these alloys in HNO_3-HCl should be studied further.

Table 3.1. Dissolution Rates on Uranium Losses to Insoluble Residues on Dissolution of Core Alloys in Boiling 2 M HCl-5 M HNO_3

Alloy Composition, %					Dissolution Rate, mg/cm^2·min	Uranium Retained by Insoluble Residue, % of total
U	Nb	Zr	Mo	Si		
98	2	-	-	-	10.95	0.16
95	5	-	-	-	9.06	0.98
90.3	9.7	-	-	-	13.58	0.05
85	15	-	-	-	6.51	0.57
95	0.5	4.5	-	-	12.33	1.40
93.4	1.33	5.27	-	-	14.68	1.07
99.25	0.12	0.41	0.22	-	32.70	0.02
98	-	-	2	-	12.56	No residue
99.5	-	-	-	0.5	7.60	0.002
97.9	-	2.1	-	-	7.61	1.39
92.5	-	7.5	-	-	9.33	5.97
90	-	10.0	-	-	17.88	9.60
85	-	15.0	-	-	9.46	10.08
80	-	20.0	-	-	6.80	15.27

3.1.2 Passivation

Passivation never occurred initially in 5 M HNO_3-2 M HCl but was observed occasionally with buildup of dissolution products (Fig. 3.1b), accompanied by acid depletion, and with fresh specimens.

With prototype APPR fuel plate, cooling during dissolution resulted in passivation, which was broken by copper. When a 15-g specimen of such plate was immersed at 100°C in 125 ml of 5 M HNO_3-2 M HCl, half the volume required to completely dissolve it, dissolution was vigorous for 15 min but then ceased because of the depleted HCl concentration. When the solution and residual plate were cooled to 80°C for 15 min and the other half of the dissolvent was added and reheated to 97°C, dissolution was complete in another 20 min. However, cooling to 25°C for 4 hr resulted in passivation of the stainless steel surfaces of the specimen, and the plate did not dissolve when the remaining half of the dissolvent was added and heated to boiling (103°C). The passivation in this latter case was broken by addition of 0.5 g of metallic copper.

Passivation depends largely on the previous history of the metal but is most likely to occur under oxidizing conditions. Increasing the nitric acid concentration above a certain value may be expected to cause passivation, while increasing the hydrochloric acid concentration tends to prevent it. Dissolved stainless steel tends to cause passivation, particularly if the iron is in the tripositive state. Chromate, which may also cause passivation, is not stable in hot acid containing appreciable chloride.

Once passivation has occurred, conditions considerably more severe than those required to initiate dissolution must be applied to break it, and the reinitiation may be sudden and somewhat violent. For breaking passivation the recommended procedure is to drain the dissolver and refill with hot (90°C) 5 M HNO_3-2 M HCl.

3.1.3 Change in Dissolution Rate with Time

When the HCl concentration in the aqua regia was 1.5 M, dissolution rates of type 304L stainless steel increased to 32-40 $mg/cm^2 \cdot min$ and the amount of dissolved stainless steel reached 35-43 g/liter in the first 2 min (Fig. 3.2, Table 3.2), but after this there was a plateau or decrease in the rate curve. With acid mixtures only 1 M in HCl, rates were fairly uniform, 5 $mg/cm^2 \cdot min$. With the lowest acid concentration investigated, 3 M HNO_3-1 M HCl, hydrolysis occurred after 7 min, as shown by a decrease in iron and increase in hydrogen ion concentration of the solution. With acid mixtures 2 M in HCl, dissolution rates were so high that sampling and complete off-gas scrubbing were not possible.

The dissolution vessel was swept with oxygen to ensure absorption of the NO. Samples of dissolver solution were taken periodically and the amount of steel dissolved was determined by analyzing for iron. The dissolvent solution was heated to 90°C before the stainless steel was added; when the reaction became very rapid the temperature rose to the boiling point.

3.1.4 Solution Saturation

The "solubility" of APPR elements in aqua regia was higher (Fig. 3.3, Table 3.3) than that of stainless steel alone due to the greater surface area presented by the sinter. With stainless steel alone, as the nitric

Table 3.2. Change in Dissolution Rate of Type 304L Stainless Steel with Time in Dilute Aqua Regia

Temperature: 90-100°C
Initial dissolvent vol: 50 ml

Dissol'n Time, min	Solution Composition SS, g/l	H$^+$, M	Cl$^-$, M	Cl^- and NO_3^- in Off-gas, moles x 10^3	Dissol'n Time, min	Solution Composition SS, g/l	H$^+$, M	Cl$^-$, M	Cl^- and NO_3^- in Off-gas, moles x 10^3
1.5 M HCl-3 M HNO_3					1 M HCl-3 M HNO_3				
0.5	6.14	3.76	1.54	Cl^- 1.73	0.5	1.17	2.85	0.98	
1.0	15.1	3.69	1.54		1.0	3.89	3.40	0.99	
1.5	27.8	2.63	1.48	NO_3^- 0.85	1.5	5.23	2.98	0.98	
2.0	36.4	2.14	1.52		2.0	8.13	2.25	0.98	NO_3^- 0.1
3.0	44.1	1.45	1.58	NO_3^-/Cl^- = 0.55	4.5	13.1	2.35	0.99	
4.0	51.4	1.24	1.62		7.0	8.18	2.95	0.99	
1.5 M HCl-4 M HNO_3					1 M HCl-4 M HNO_3				
0.5	17.0	4.25	1.39	Cl^- 2.23	0.5	1.51	4.89	0.99	
1.0	30.0	3.38	1.41		1.0	4.16	4.99	0.99	
1.5	39.2	2.85	1.42	NO_3^- 1.03	1.5	6.54	3.46	0.98	
2.0	42.5	2.65	1.47		2.5	8.18	3.54	0.96	NO_3^- 0.04
3.0	45.0	2.47	1.52	NO_3^-/Cl^- = 0.46	3.5	9.80	2.86	0.96	
3.5	45.8	2.50	1.54		4.5	15.5	2.99	0.96	
1.5 M HCl-5 M HNO_3					1 M HCl-5 M HNO_3				
0.5	16.4	5.00	1.31	Cl^- 1.73	0.5	0.74	5.95	0.94	
1.0	28.6	4.17	1.31		1.0	2.29	6.05	0.97	
1.5	33.9	3.88	1.32	NO_3^- 0.85	1.5	4.90	5.25	0.96	NO_3^- 0.05
2.0	36.0	3.86	1.32		2.0	6.94	5.25	0.95	
3.0	38.9	3.95	1.40	NO_3^-/Cl^- = 0.49	3.0	9.80	5.05	0.95	
4.0	39.2	3.93	1.42		3.5	9.80	6.17	0.90	

Table 3.3. "Saturation" of Dilute HNO_3-HCl Mixtures with Type 304L Stainless Steel and APPR Prototype

Temperature: boiling (100-109°C)

Original Conc., M		"Saturation Value," g/liter		Final Conc., M			Solution NO_3^-/Cl^- Ratio	
HCl	HNO_3	Stainless Steel	APPR Fuel[a]	H^+	Cl^-	NO_3^-	Initial	Final
1	3	38.6	-	1.1	0.98	2.1	3.0	2.14
1	4	30.6	-	2.9	0.98	3.3	4.0	3.4
1	5	30.9	-	3.3	0.86	3.1	5.0	3.6
1.5	3	55.8	-	0.8	1.45	1.79	2.0	1.23
1.5	4	58.4	-	1.12	1.34	2.84	2.67	2.12
1.5	5	36.7	-	3.50	1.33	3.72	3.3	2.80
2	3	51.8	-	0.73			1.5	
2	4	56.1	-	0.73			2.0	
2	5	66.3	-	1.13			2.5	
2	6	61.4	-	2.43			3.0	
1	3	-	49.5	1.00	1.02	2.06	3.0	2.02
1	4	-	39.3	2.40	1.01	3.08	4.0	3.05
1	5	-	49.6	2.55	0.94	3.66	5.0	3.91
1.5	3	-	64.2	0.50	1.47	1.87	2.0	1.27
1.5	4	-	70.2	0.90	1.38	2.51	2.67	1.82
1.5	5	-	56.7	2.40	1.29	2.22	3.3	1.72
2	5	-	94.8	1.6	1.85	-	2.5	-
2	3	-	71.7[b]	0.35			1.5	
2	4	-	84.6[b]	0.47			2.0	
2	5	-	83.3	0.82			2.5	
2	6	-	87.2	1.40			3.0	

[a] Based on APPR fuel element iron content of 61.8%.

[b] Brown precipitate due to hydrolysis.

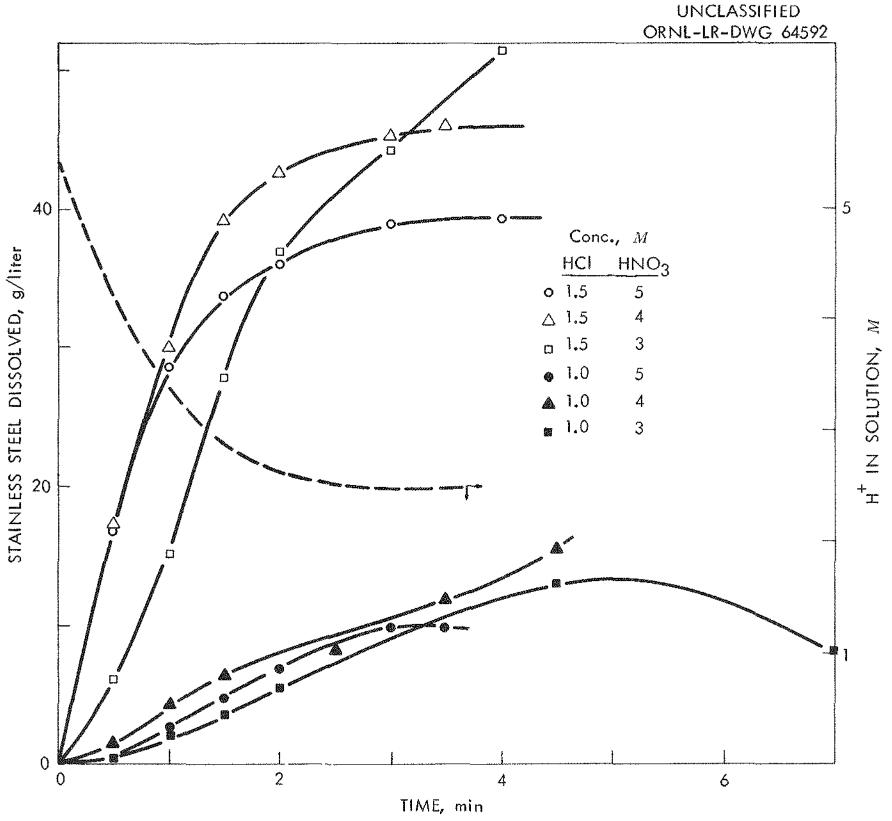

Fig. 3.2. Dissolution of type 304L stainless steel in dilute aqua regia as a function of time. Hydrogen ion concentration in the dissolver solution is shown for 4 *M* HNO_3-1.5 *M* HCl.

acid concentration was increased (at constant HCl concentration), less metal dissolved because passivation occurred. However, this effect was less with APPR fuel because the sinter was not passivated as readily as the stainless steel portion of the prototype fuel element. This was also observed by Kleinberg and Bowen in continuous dissolver operation. Since dissolution of UO_2 depends on oxidation of U(IV) to U(VI), the amount of UO_2 dissolved increased with an increase in the dissolvent nitric acid concentration or with an increase in the total acid concentration at constant nitric acid concentration. At the lower acid concentrations an appreciable amount of the dissolved iron was removed from solution by hydrolysis, showing that the total attack was considerably greater than that indicated by the iron determined in the solution. In 5 M HNO_3-2 M HCl, the stainless steel and UO_2 components of the APPR fuel appeared to dissolve at rates approximately proportional to the ratio in which they were present in the plate.

In the above experiments type 304L stainless steel and prototype APPR fuel element material were treated with boiling nitric acid until all visible reaction had ceased, and the amounts of material dissolved were determined from iron determinations on the solution (Fe = 69% of

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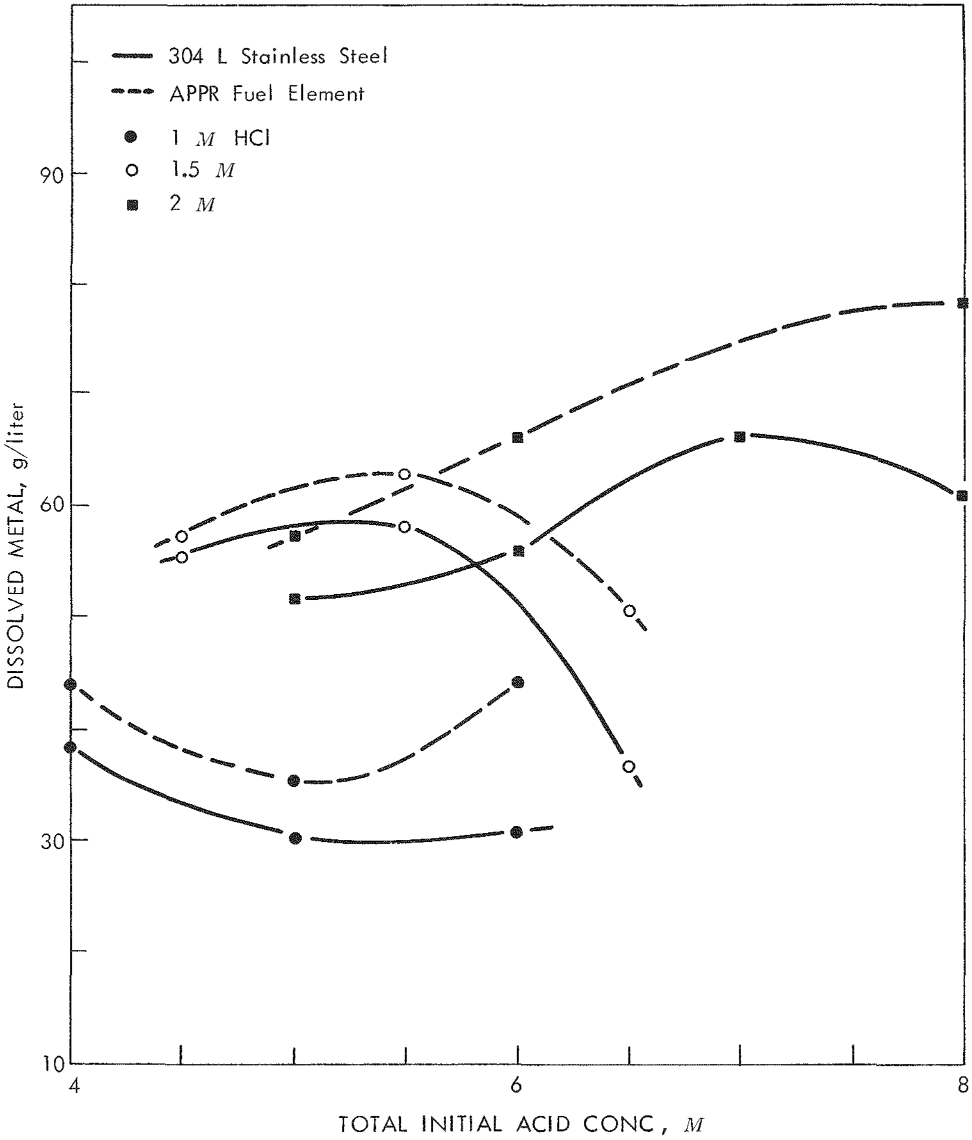

Fig. 3.3. Saturation of dilute HNO_3-HCl mixtures with type 304L stainless steel and APPR fuel element components.

type 304L stainless steel, 61.9% of APPR fuel element). When small coupons were added to the hot acid one by one and subsequent specimens were added only after the previous coupon had entirely disappeared, the amount dissolved was maximum when the initial total acid concentration was between 6 and 8 M (Fig. 3.4); this corresponds rather closely to the acid compositions at which dissolution rates are maximum.

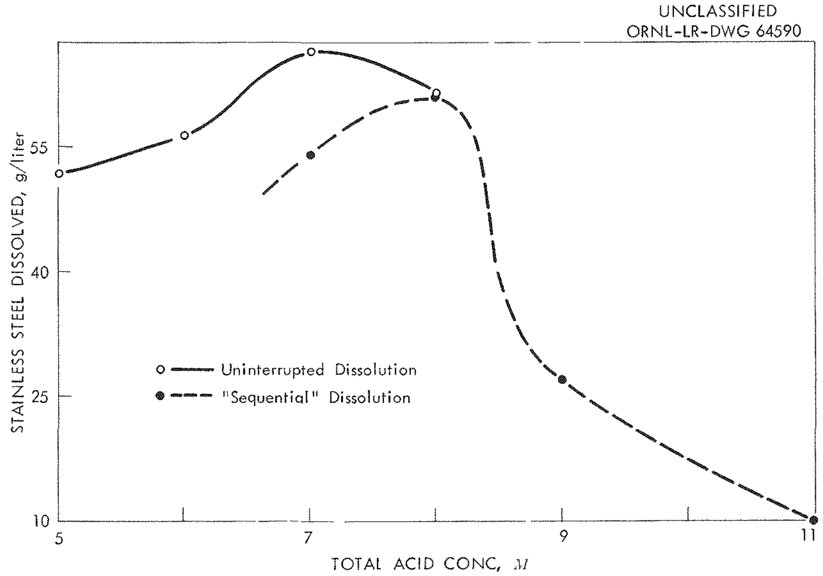

Fig. 3.4. "Saturation" of HNO_3-2 *M* HCl with type 304L stainless steel.

3.1.5 Dissolution of Irradiated Fuel

In laboratory experiments irradiated Yankee Atomic and APPR fuel specimens dissolved in aqua regia without difficulty except in two experiments when chloride in the dissolvent was too low. Silica and other insolubles that collected on the glass dissolver contained no uranium. Fission product distribution data during dissolution and chloride removal by simple distillation with nitric acid showed 75% of the iodine in the condensate, which could cause problems in acid recycle in processing of short-decayed fuel. Ruthenium volatilization was negligible, and 71% of the zirconium-niobium remained in the extraction feed.

3.1.6 Off-gas

When either type 304L stainless steel or prototype APPR-1 fuel plate was dissolved in 5 M HNO_3-2 M HCl in the absence of air or oxygen, only small amounts of NO_2 were present in the off-gas. Traces of air increased the NO_2 content to about 6 vol %. Only 0.5% of the chloride was found in the off-gas samples; analysis of the displacement fluid (saturated magnesium sulfate solution) accounted for about 40% of the chloride "lost" during dissolution. The total volume of off-gas from the dissolutions, collected by displacement, was about 275 liters per kilogram of either type 304L stainless steel or prototype APPR-1 fuel plate. The average values for consumption of hydrogen ion, chloride, and nitrate were calculated to be 0.0659, 0.0039, and 0.0162 mole per gram of alloy, respectively. In one experiment the off-gas was passed through two NaOH scrubbing towers to remove any Cl_2, NO_2, and boric acid. Analyses for nitrate and chloride showed:

	NO_3^-		Cl^-	
	% of total	moles	% of total	moles
Remaining in dissolver	76.06	1.23	87.75	0.53
NaOH scrubber	0.99	0.015	9.39	0.055
	77.05		97.14	

The large discrepancy in the nitrate material balance indicates that most of the nitrogen in the off-gas was present as unreactive N_2 or lower oxides of nitrogen. Increasing the chloride concentration in the dissolvent from 1 to 1.5 M increased the amounts of nitrogen oxides in the off-gas by a factor of 10-20 and the chloride from values below the level of detection to values twice as great as those of the nitrogen oxides (Table 3.2). This indicates that at 1 M chloride the attack in 4-6 M total acid is due primarily to displacement of hydrogen (probably accompanied by reduction to N_2O, N_2, and possibly NH_4^+, none of which would have been detected), with the chloride acting primarily to prevent passivation of the stainless steel surface.

Savolainen, who collected the off-gas by displacement of CO_2, found equal amounts of NO_2 and Cl_2 in the off-gas from the dissolution of stainless steel in 4 M HNO_3-3 M HCl:

Stainless Steel Dissolved		Off-gas Composition, mole %			
g/liter	moles/liter	NO	NO_2	Cl_2	N_2
10.9	0.20	30.0	24.5	32.4	11.3
21.7	0.40	32.6	25.7	31.6	10.0
32.4	0.59	50.3	21.5	16.4	11.7
53.4	0.98	64.0	15.6	6.0	14.2

The off-gas composition changed rather suddenly at about the half-way point in the dissolution, as indicated by an increase in the percentage of NO and a corresponding decrease in the evolution of Cl_2 and, to a lesser extent, of NO_2 (Fig. 3.5). This presumably indicates a change of mechanism, corresponding to the lower acid concentration resulting from the dissolution of the metal or to a lower effective chloride concentration due to the formation of complexes with dissolution products. No hydrogen was found in any of the gas samples.

3.1.7 Insolubles

A solution of prototype APPR fuel in 5 M HNO_3-2 M HCl contained solids amounting to 1.13% of the total element weight, but analysis of the solids indicated a negligible amount of uranium in them. The uranium loss was also negligible to the insolubles from a solution of 59.26 g of APPR fuel plate free of brazing alloy in 1 liter of 5 M HNO_3-2 M HCl, which amounted to 0.19% of the fuel weight.

Approximately 18% of a sample of APPR brazing alloy remained as insoluble SiO_2 after dissolution in 5 M HNO_3-2 M HCl, digestion, filtering,

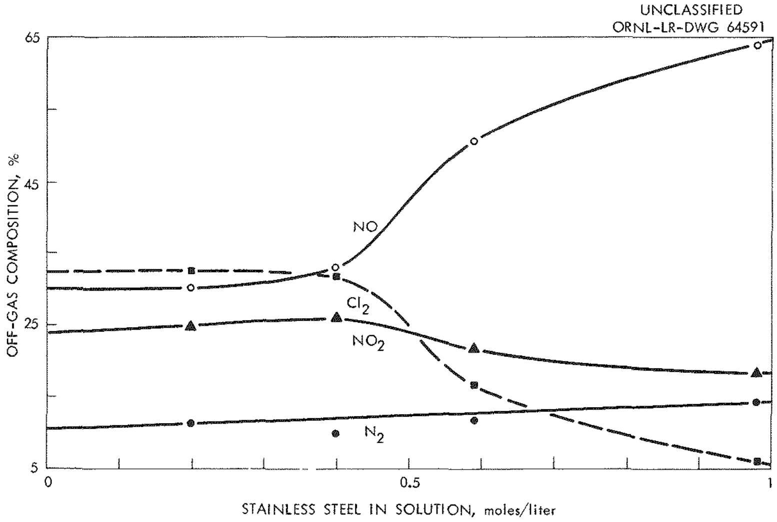

Fig. 3.5. Composition of off-gas from dissolution of stainless steel in 5 *M* HNO_3-3 *M* HCl.

and washing. Particle sizes ranged from 0.06 to 26 μ. The distribution of silicon in a typical APPR fuel assembly is 6 g in the type 304L stainless steel side plates, 5 g in the brazing alloy, 45 g in the matrix, and 18 g in the cladding.

3.1.8 Path of Boron

Based on a nominal boron content of 0.057% for the APPR fuel element, the distribution of boron after dissolution in 5 M HNO_3-2 M HCl was found to be 23.7% in the off-gas, 9.5% in the dissolver solution, and 35.1% in the solids centrifuged from the dissolver solution, a total of 68% recovered. The reason for the poor material balance is not clear, though it could be caused by inhomogeneities in the fuel. Since the amounts of boron involved are very small, analytical inaccuracy and/or errors in dissolution techniques could account for much of the discrepancy. Although results were not conclusive, they indicate that boron will be present in appreciable amounts in all process streams.

3.2 Semicontinuous* Dissolution

3.2.1 Low-UO_2 Fuel (APPR)

Fuel prototypes were dissolved in small-scale glass equipment (3 in. dia) to determine dissolution rates, loadings, reagent consumption, and off-gas compositions.

Dissolution Rate. Reaction rates of APPR prototype (5 to 11% UO_2-stainless steel) were about the same in 5 M HNO_3-2 or 1.5 M HCl and

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* In semicontinuous operation aqua regia is fed and dissolution product is removed continuously but solid fuel is charged in batches.

3 M HNO_3-2 or 1.5 M HCl for F/S ratios* < 0.5 cm/min (Fig. 3.6). However, at higher F/S ratios the rates leveled off at lower values for less concentrated acids. The effect of UO_2 on the reaction rate was negligible except in 3 M HNO_3-1.5 M HCl, in which the rate was about 50% higher when UO_2 was present than when stainless steel alone was dissolved.

The studies were made with 1-in.-dia stainless steel tubing and sections of unirradiated APPR plate. Aqua regia at 105°C entered the dissolver at the bottom and dissolver product left through the open upper end of a vertical standpipe which regulated the liquid level. The metal stood on end and continuously sank into the liquid as the immersed end dissolved, providing an essentially constant area of metal exposed to dissolvent. Initial aqua regia compositions are reported, but steady-state operation produced a well-mixed liquid phase, and dissolution actually occurred in aqua regia of a composition represented by the chloride and nitric acid content of the dissolution product.

If the stainless steel is assumed to enter solution as 0.7 M Fe^{3+}, 0.2 M Cr^{3+}, and 0.1 M Ni^{++}, 2.9 moles of H^+ would be consumed in the actual dissolution. The balance must be consumed in the formation of noncondensable oxides of nitrogen and chlorine-containing species, e.g. NO, NO_2, N_2O, and NOCl. Since hydrogen was not detected in the off-gas, essentially all the H^+ consumed formed water. The plot of stainless steel dissolution rate as a function of nitrate consumption rate (Fig. 3.7a) was best represented by two lines: one for 5 M HNO_3-2 M HCl and 3 M HNO_3-1.5 M HCl, from which a nitrate consumption of 1.41 moles per mole of stainless steel dissolved was calculated; and the other for 5 M HNO_3-1.5 M HCl and 3 M HNO_3-2 M HCl, from which a ratio of 0.35 mole per mole was calculated.

Off-gas Compositions. Noncondensable off-gas compositions were not appreciably affected by the presence of 5.5 to 11% UO_2 in the stainless steel except with 5 M HNO_3-2 M HCl, where it suppressed chloride loss to some extent (Table 3.4). Chloride losses ranged from 0.2 to 4.6% and nitrogen losses from 8.6 to 28.3%. The part of the off-gas reported as N_2 contains all the KOH-insoluble components, such as N_2O.

Metal Loading. The metal loading in the fuel solution decreased as the F/S ratio increased for the four aqua regia compositions studied (Fig. 3.8) and for a given F/S value, decreased as the feed acidity decreased. There was evidence that loadings > 50 g/liter contained some material in suspension rather than in true solution. Similar curves could be calculated from

$$L = R/(F/S)$$

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* Acid feed rate in cm^3 per min/surface area in cm^2. The F/S ratio is analogous to the space velocity term commonly used as a characteristic of heterogeneous reactions in continuous reactors containing packed beds of solid phase and is independent of the liquid volume held up in the dissolver and of the fuel element and dissolver geometry as long as the liquid phase is well mixed.

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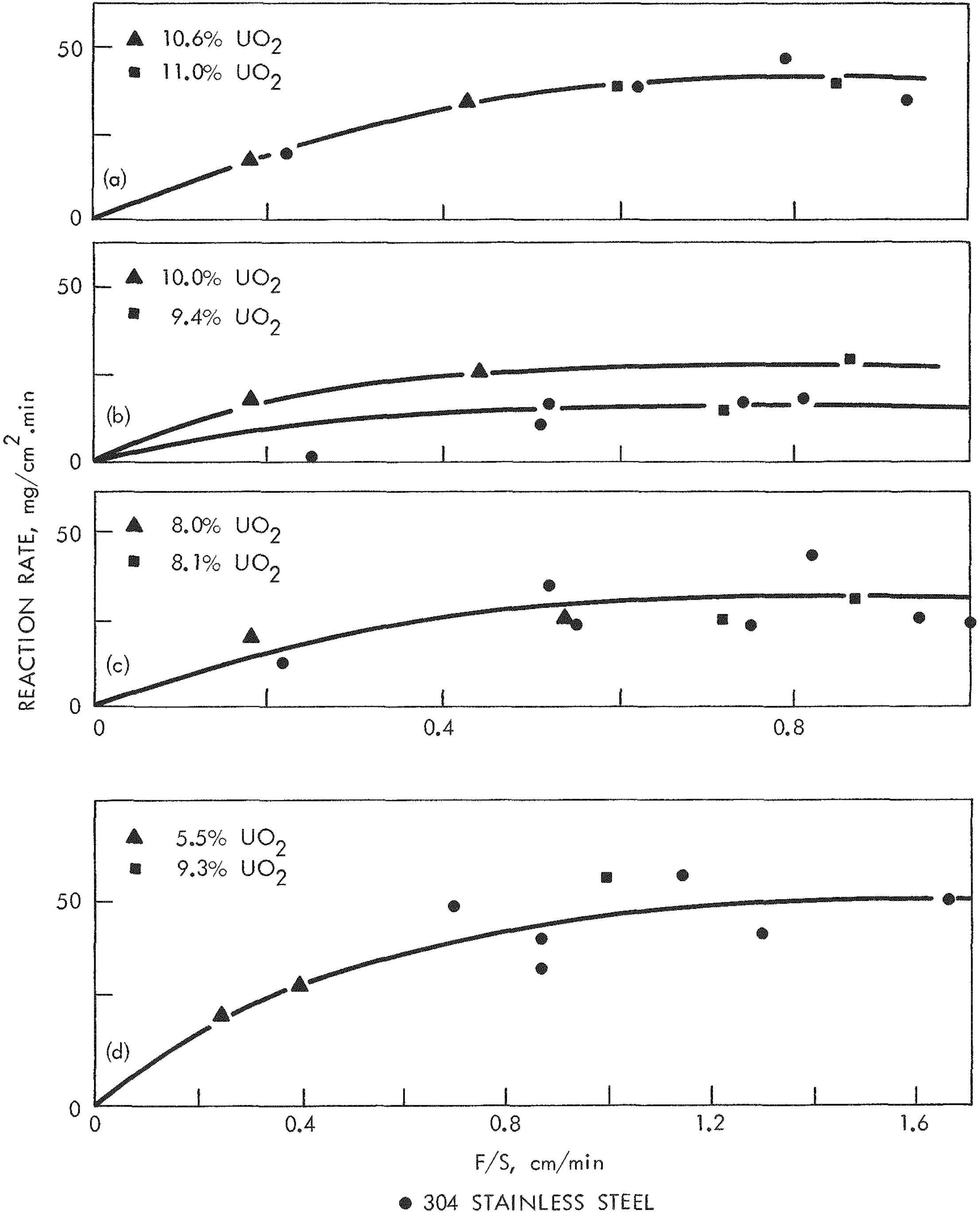

Fig. 3.6. Dissolution rate of sintered UO_2-stainless steel and of stainless steel cladding as a function of acid feed rate to surface area ratio in acids of the compositions: (a) 5 *M* HNO_3-1.5 *M* HCl, (b) 3 *M* HNO_3 1.5 *M* HCl, (c) 3 *M* HNO_3-2 *M* HCl, and (d) 5 *M* HNO_3-2 *M* HCl.

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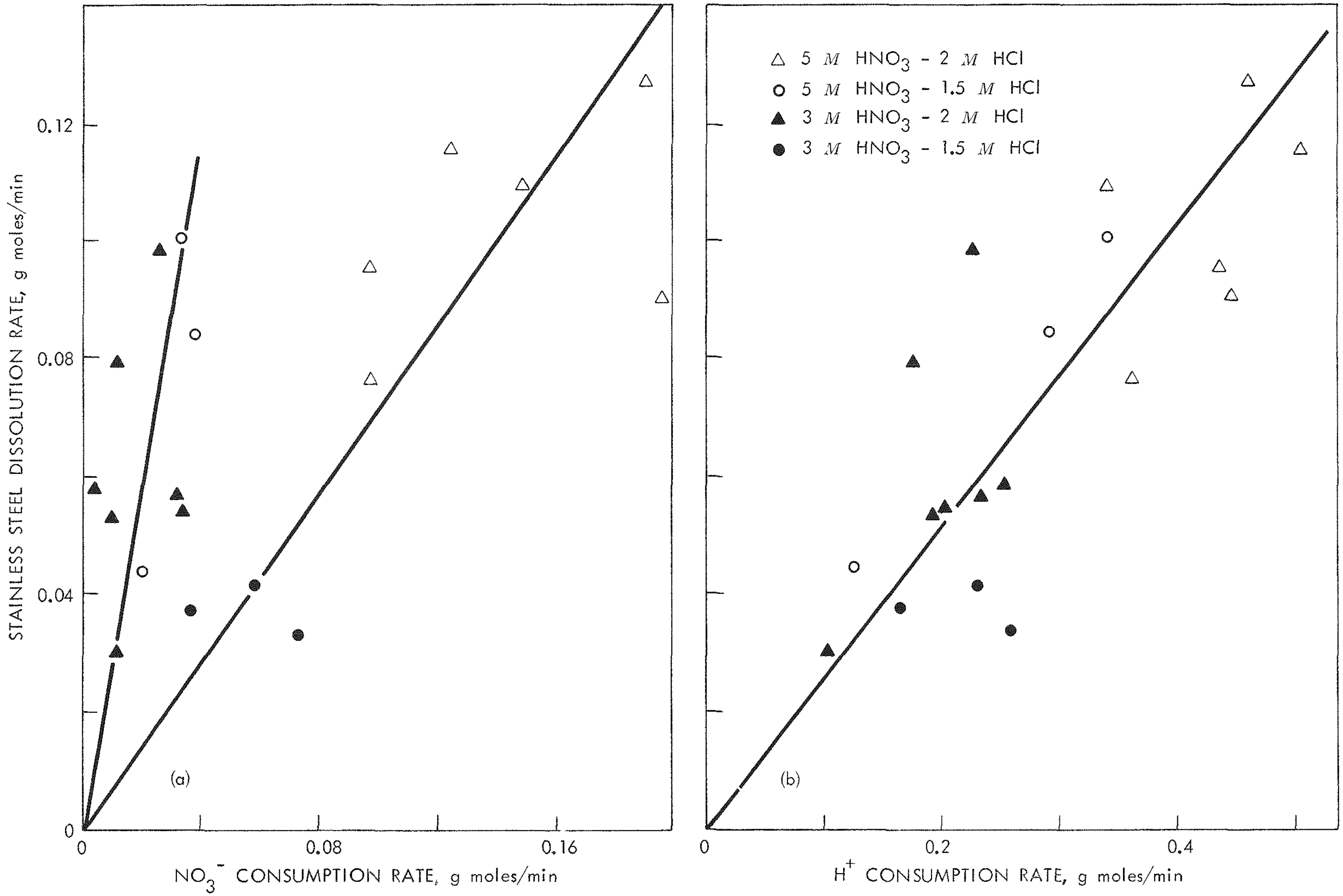

Fig. 3.7. Stainless steel dissolution rate as a function of (a) nitrate ion and (b) hydrogen consumption rate.

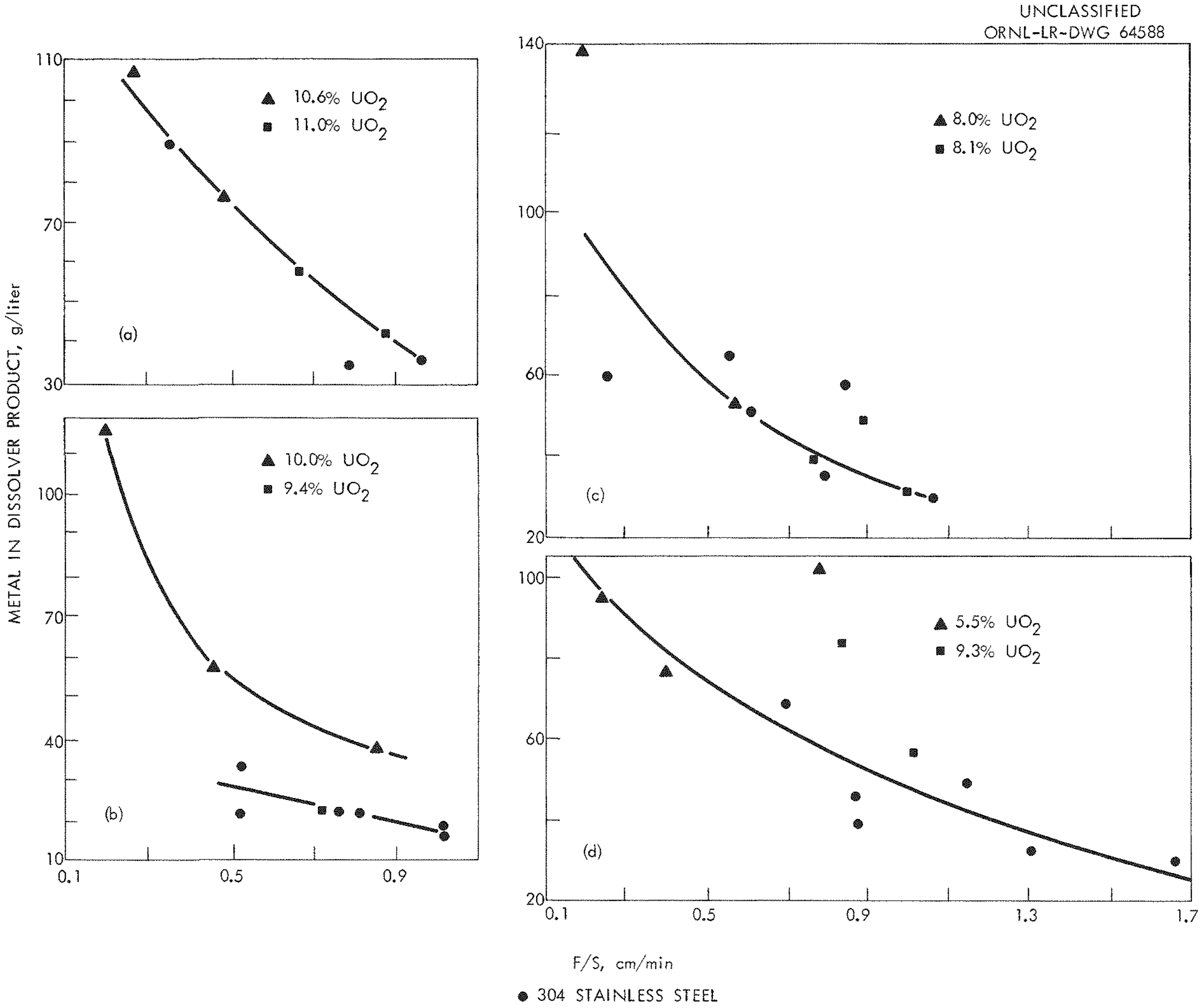

Fig. 3.8. Metal loading of dissolver product as a function of acid feed rate to surface area ratio for dissolvent of compositions: (a) 5 *M* HNO_3-1.5 *M* HCl, (b) 3 *M* HNO_3-1.5 *M* HCl, (c) 3 *M* HNO_3-2 *M* HCl, and (d) 5 *M* HNO_3-2 *M* HCl.

Table 3.4. Dissolver Off-gas Compositions and Rates

Acid Feed Composition, M		UO$_2$ in Stainless Steel, wt %	Off-gas Composition, %				Loss, %	
HNO$_3$	HCl		Chloride[a]	NO$_2$	NO	N$_2$	Cl	N
5	2	0	4.4	57.0	10.0	28.7	4.6	24.6
5	2	9.3	1.1	75.1	7.1	16.6	1.0	20.2
3	2	0	1.0	49.2	28.7	21.0	0.2	8.6
3	2	8.0	< 1	57.1	23.9	18.9	< 0.3	20.3
3	1.5	0	< 1	50.6	23.3	25.8	< 0.7	19.0
3	1.5	10.0	1.0	41.0	41.0	17.0	1.0	28.3

[a] Not analyzed by molecular species but as total chloride.

where L = loading, g/liter; R = reaction rate, mg/cm^2·min; F = feed rate, cm^3/min; and S = surface area, cm^2.

Reagent Consumption. From the dissolution rate of stainless steel plotted as a function of the hydrogen ion consumption rate, it was calculated that 3.9 moles of hydrogen ion was consumed per mole of stainless steel dissolved (Fig. 3.7b).

3.2.2 High-UO$_2$ Fuel (Yankee Atomic)

Owing to the heterogeneous nature of the fuel and the separation of the pellets from each other upon dissolution of part of the stainless steel cladding, detailed study of the dissolution characteristics of the system was not feasible.

Dissolution Rate. In preliminary studies the initial reaction rates of UO$_2$ pellets in aqua regia solutions of 3 to 6 M HNO$_3$-2 M HCl were approximately the same as those for stainless steel, but for 1 M HCl they were much higher (Fig. 3.9).

Metal Loading. In an exploratory dissolution in 5 M HNO$_3$-2 M HCl with an initial F/S ratio (based on the surface area of the stainless steel cladding) of 1 cm/min, the uranium concentration in the dissolver product stream increased steadily to 123 g/liter after 78 min (Fig. 3.10).

Off-gas Consumption. After 50 min dissolution time all the stainless steel had been consumed and NO in the off-gas had decreased from 15 to 0.1% and the Cl$_2$ had increased from 2 to 15% (total chloride reported as Cl$_2$).

Optimization. At initial F/S ratios from 0.1 to 0.5 cm/min, with 5 M HNO$_3$-1 M HCl dissolvent, dissolver capacity was maximum with an initial F/S of 0.22 (Table 3.5).

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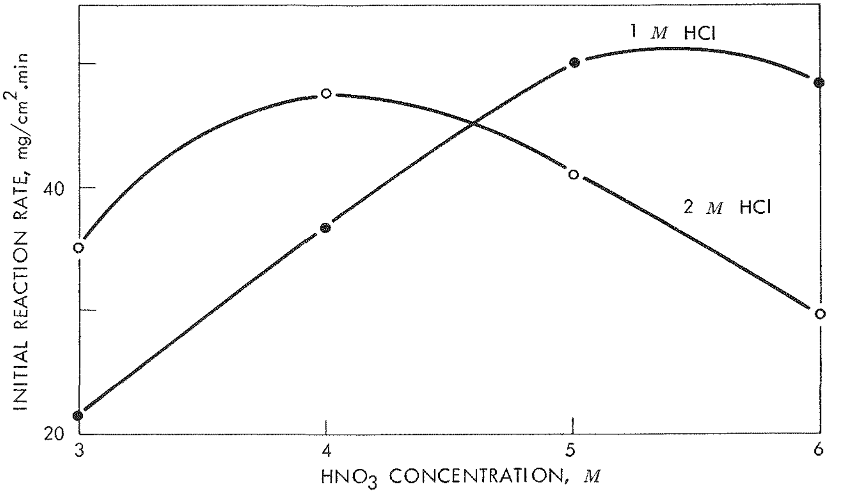

Fig. 3.9. Initial reaction rate of UO_2 with dilute aqua regia.

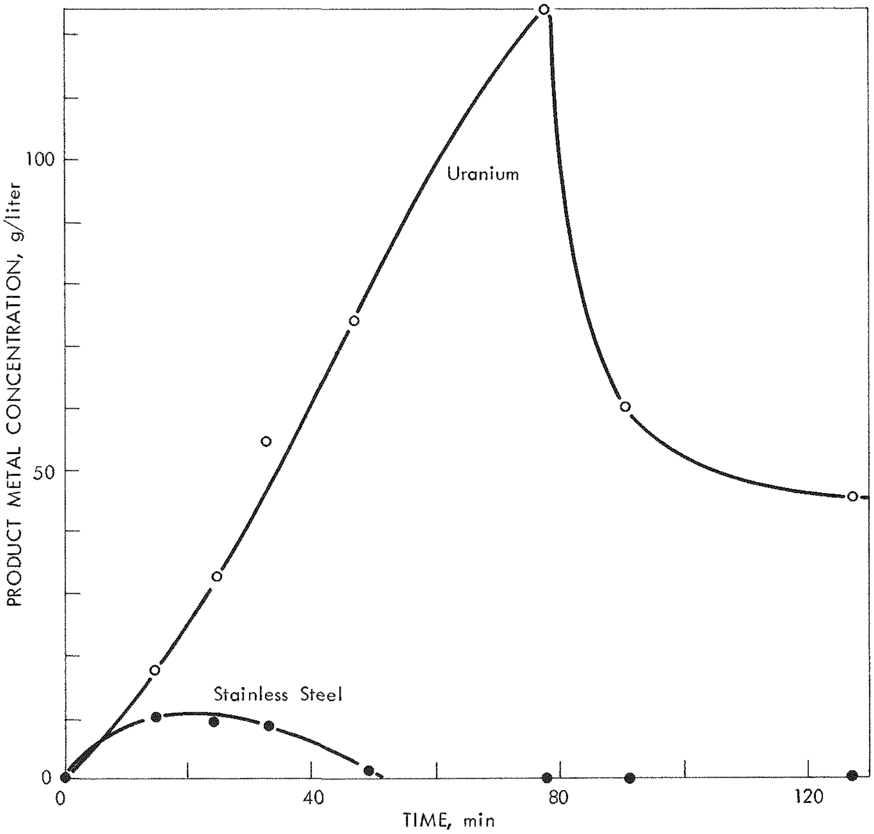

Fig. 3.10. Metal concentration of dissolver product stream as a function of time in the dissolution of simulated Yankee Atomic fuel. Acid feed: 5 M HNO_3-2 M HCl; initial F/S = 1 ml/cm^2 min.

Table 3.5. Continuous Dissolution of UO_2-Stainless Steel in 5 M HNO_3-1 M HCl

Initial F/S, cm/min	No. of Fuel Rods Dissolved	Time, hr	Avg.[a] U Conc. in Effluent, g/liter	No. Dissolved per 24 hr
0.09	20	16	112	30
0.22	8	5	144	38.5
0.47	4	3	120	32

[a] Instantaneous uranium concentration varied as much as 20% from value reported.

3.2.3 Runs for Scale-up Data

The optimum dissolvent having been established in batch studies as 5 M HNO_3-2 M HCl, continuous dissolution runs were made in 1- and 6-in.-dia dissolvers to obtain data for design of larger scale units.

1-in.-Dissolver. "Fuel elements" fabricated of type 304 stainless steel strips, 24 by 0.6 by 0.016 in., with 0.016-in. spacers between the plates were continuously dissolved in a 1-in.-dia glass dissolver, 8 ft high. The average weight of an element was 575 g. The last, most significant, run was made with three elements, which dissolved completely in 65 min in 21 liters of 5 M HNO_3-2 M HCl. The dissolution rate was 26.6 g/min and the stainless steel in the product was 82 g/liter.

The results of the runs indicated that the dissolvent should be fed into the dissolver at the bottom and flow upward past the element and that the product should be removed through a side-arm takeoff (the optimum location of the side arm with respect to the bottom of the dissolver was not determined). The dissolution reaction was too violent for the liquid level in the dissolver to be regulated by an air lift, although the level in a side arm probably could be regulated by this means. Dissolution took place primarily on the lower 12 in. of the fuel element (the area of attack is probably dependent on the dissolvent flow rate). Recycling a portion of the product back through the dissolver was not advantageous, nor was returning the condensate to the dissolver. This dilute mixed acid stream could be sent directly to an acid catch tank, thus decreasing the load on a feed adjustment tank.

The 6-in.-dia Dissolver. A 6-in.-i.d. glass dissolver (Fig. 3.11) similar to the 1-in. model was operated in dissolution studies on both stainless steel and full-size APPR prototype (depleted uranium fuel elements) All runs were made with 5 M HNO_3-2 M HCl. The consumption rate of fuel elements and their limited availability prevented detailed study of the various dissolution rate parameters, but the results of eight runs (Table 3.6) indicated that a tall cylindrical dissolver of practical diameter is operable. The APPR braze metal dissolved more slowly than the clad

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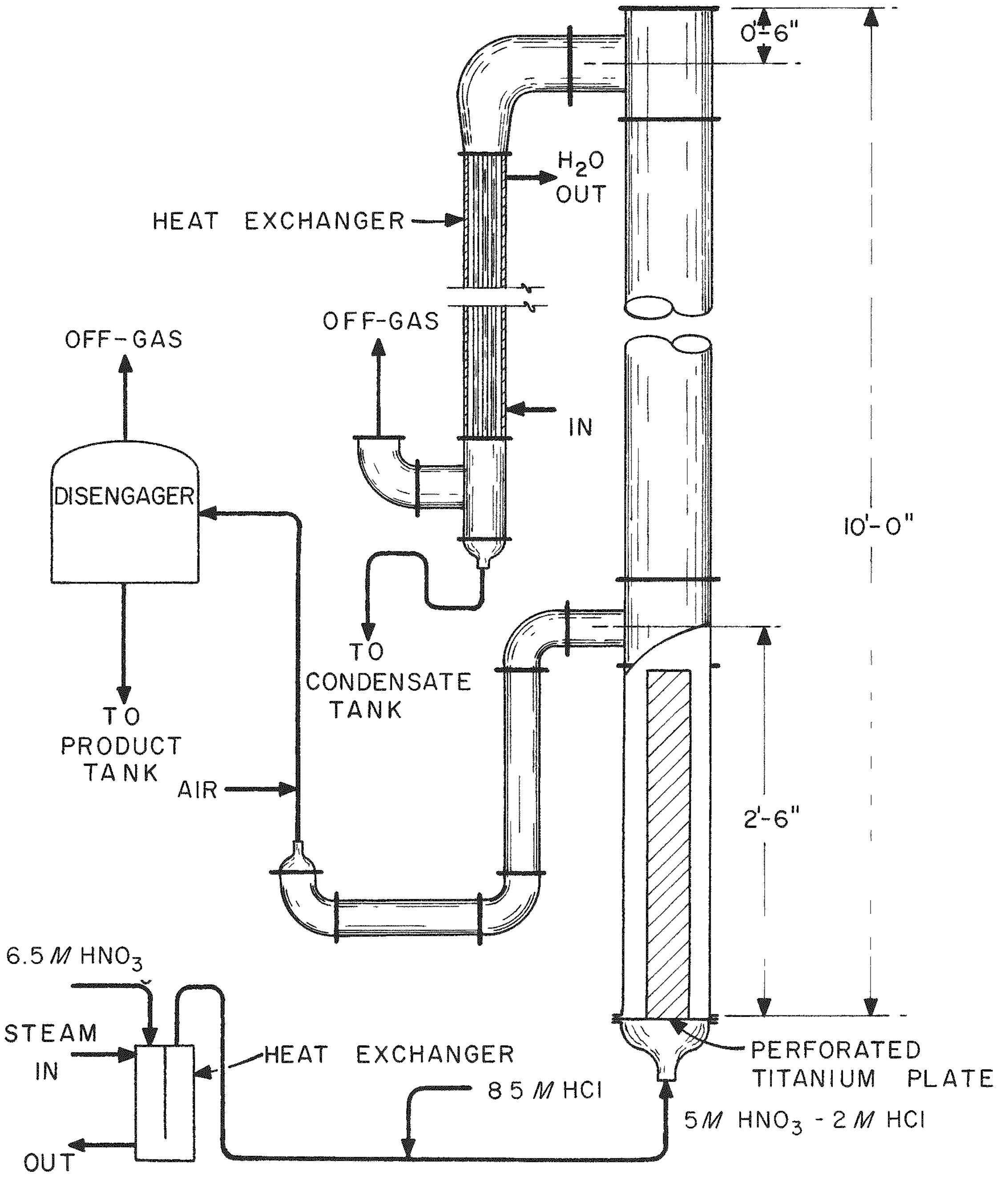

Fig. 3.11. Continuous dissolver, 6 in. i.d.

Table 3.6. Dissolution of Simulated and Unirradiated Prototype APPR Fuel Elements in Aqua Regia

Dissolver: 6 in. i.d. x 10 ft high, Pyrex
Dissolvent: 2 $\underline{M}$ HCl-5 $\underline{M}$ HNO_3, 80-90°C at inlet

Run No.	No. of Fuel Elements	Fuel Element Composition	Total Wt, g	Wt of U, g	Aqua Regia Flow Rate, liters/min	Dissolution Time, min	Avg Dissolution Rate, g/min	Foam Height, ft
2	1[a]	SS	4,640	-	4.5	15	310	~ 6
3	3[b]	SS	16,344	-	4.1	52[c]	260	~ 9
4	~0.5[d]	SS				[e]		
5	1	SS + U	5,240	550	4.3	19*	276	~ 6
6	1	SS + U	5,450	447	4.2	19	283	~ 6
7	1	SS + U	5,448	384	4.3	20	203[f]	~ 6
8	1	SS + U[g]	5,440	296	4.2	20	272	
9	1	SS + U[h]	5,900	1,000	4.5	21	275	7

* Complete dissolution except braze metal; 82.7 liters of aqua regia.

[a] Simulated APPR fuel element: stainless steel plates spaced 0.125 in. apart with stainless steel tubing and tack-welded to side plates.

[b] Two similar to those in run 2; plates of third brazed to side plates.

[c] Shut down before complete dissolution because of inadequate off-gas facilities; dissolution about 50% complete. Condensate not returned to dissolver but collected separately.

[d] Portion of fuel element remaining from run 3.

[e] Braze metal (Coast Metals NP, 50% Ni, 11.8% Si, 29.3% Fe, 3.5% P, 5.4% Mo) did not dissolve.

[f] 1362 g of the fuel element was undissolved at shutdown, accounting for the low dissolution rate.

[g] Oxidized by 16 hr heating at 1200°F.

[h] Oxidized by 69 hr heating at 1675°F.

material, but a dissolution time of 1 hr for three APPR elements appears feasible. Air-lifting of the dissolver product at boiling temperatures appeared feasible, and 16 ft was sufficient height to prevent "bumping" of dissolver solution into the condenser. Some provision must be made to keep small pieces of undissolved metal from leaving the dissolver with the effluent.

In the series of runs little difference was observed between dissolver operation with three elements and with one element. In run 4, made with the undissolved portion of the element from run 3, dissolution started immediately when the hot aqua regia contacted the element, indicating that there was no passivation as the result of shutdown. The braze metal dissolved very slowly even though it was being contacted with hot, fresh aqua regia. Braze metal is very brittle, and since the pieces are thin, it may be possible to break them up and jet them from the dissolver. The dissolver product from run 5 showed 3.05 M total H^+, 2.05 M Cl^-, and 9.23 g of uranium and 66.5 g of stainless steel per liter. A total of 65 liters of dissolver product and 4.5 liters of condensate (2.4 M total H^+, 0.81 M Cl^-) were collected. In run 7 the side plates and cladding dissolved completely but some of the "meat" portion of the fuel plates remained.

The results of the two runs with air-oxidized fuel elements indicated that neither the initiation nor rate of reaction was affected by surface scale. The element in run 8 was attacked instantaneously, and the run was very similar to runs with unoxidized elements. The thin oxide coating flaked off the surface but did not dissolve completely, nor did the braze metal (Coast Metals NP). The product was 2.95 M H^+, 1.92 M Cl^-, and had an average stainless steel loading of ~70 g/liter. In run 9, at shutdown the uranium-bearing portion of the fuel element had completely dissolved, but the rails, spacers, and braze metal remained. The total weight of residual material (later dissolved in batches) was 459 g. The dissolver product was 4.21 M H^+, 1.65 M Cl^-, and had a metal loading of ~60 g/liter.

4.0 CHLORIDE STRIPPING

The most attractive method for removing chloride from the fuel solution, so that stainless steel processing equipment can be used, is countercurrent stripping with nitric acid. The mixture of nitric and hydrochloric acids produced is adjusted and recycled as dissolvent.

4.1 Preliminary Calculations

The relative volatilities of HNO_3 and HCl in a dilute HNO_3-HCl-H_2O system were correlated (Fig. 4.1) from data of Morgan and Bond. Although deviations from theoretical equilibrium are large in the Darex system because of decomposition at the high concentrations, calculations based on the extrapolated data indicated that increasing the V/L and the HNO_3 concentration would decrease the number of stages required in a countercurrent contactor to remove chloride to a specified level (Fig. 4.2). The composition of the dissolution product was assumed to be 4.3 mole % HCl (~2 M) and 7.3 mole % NO_3^- (~5 M), with the assumed species Fe^{3+}, Cr^{3+}, and Ni^{2+} acting as H^+ ions with no adverse effect on the HCl volatility. A low V/L was desired to give a high HCl concentration in the recycle stream, and the highest acid concentration considered was the azeotrope (38.3 mole %, 15.2 M). The curve for V/L ≈ 1, y_{HNO_3} = 0.383, the desired conditions, should lie between the curves for y_{HNO_3} - 0.40 and 0.20.

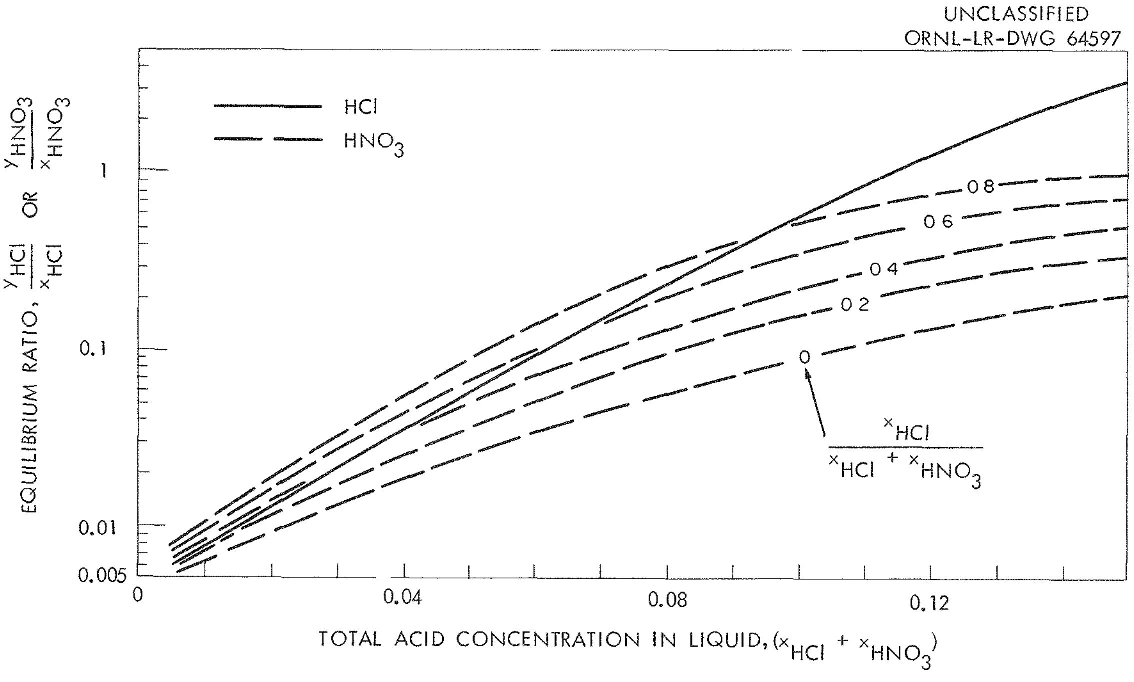

Fig. 4.1. Vapor-liquid equilibrium in HCl-HNO_3 system, based on experimental data from MIT-SPR-X-258. The symbols x_{HCL} and y_{HCL} represent mole fractions of HCl in liquid and vapor respectively; x_{HNO_3} and y_{HNO_3} are corresponding designations for HNO_3.

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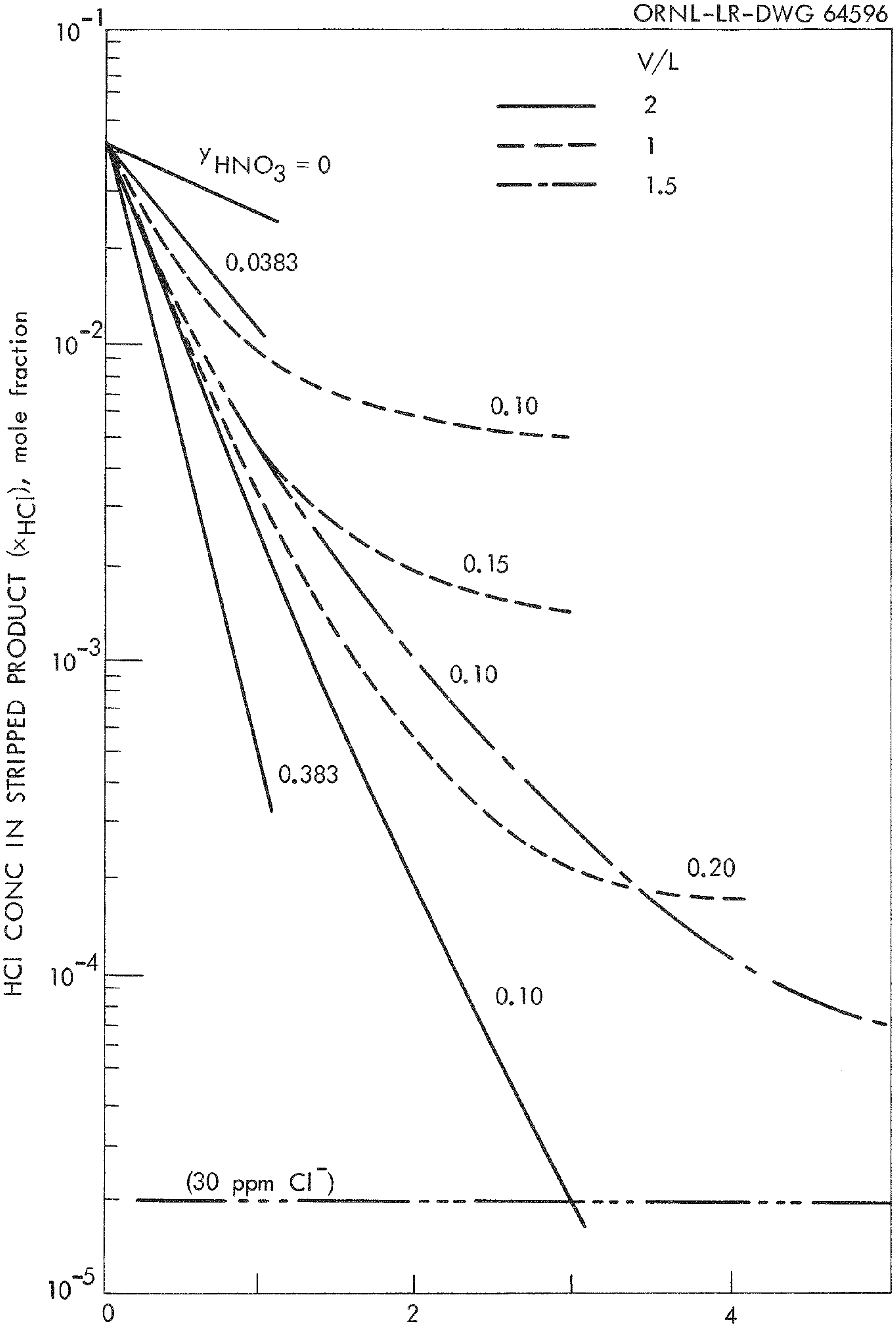

Fig. 4.2. Effect of *N*, V/L, and y_{HNO_3} on x_{HCl} in continuous stripping of HCl from $HCl\text{-}HNO_3\text{-}H_2O$ solution. V/L is the mole ratio of vapor to liquid flow at steady state; y_{HNO_3} is the mole fraction of HNO_3 in the stripping vapor.

4.2 Preliminary Experimental Data

The considerably greater effectiveness of 15.2 M HNO_3 than of 12 M in removing chloride was shown (Fig. 4.3) by successive laboratory-scale distillations of nitric-hydrochloric acid solutions containing dissolved stainless steel components in a Gillespie still. In this apparatus the pot and distillate compositions are those for equilibrium conditions between vapor and liquid phases. The volume of the distillate was replaced each time by nitric acid for the subsequent distillation. In the presence of iron, stripping was more difficult (Table 4.1) than in the ternary HNO_3-HCl-H_2O system because of chloride complexing in the solution.

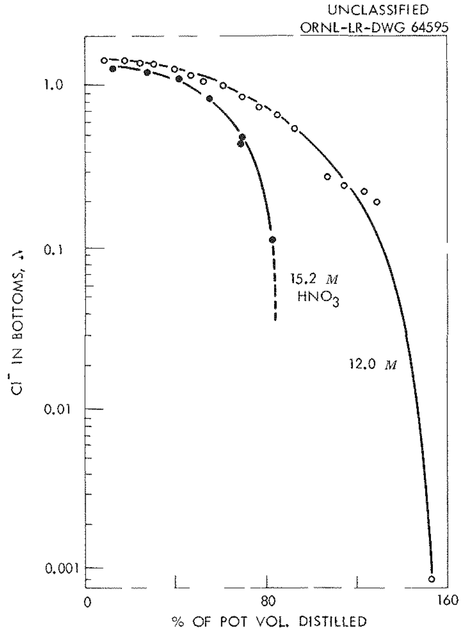

Fig. 4.3. Batch chloride stripping from simulated fuel solution by nitric acid reflux.

Table 4.1. Liquid-Vapor Equilibrium Compositions for the HNO_3-HCl System in the Presence of Dissolved Metal Ions

	Equilibrium Solution Composition, M					
Solution	Fe^{3+}	Cr^{3+}	Ni^{+2}	H^+	Cl^-	NO_3^-
Pot	1.06	0.37	0.27	3.60	0.11	8.31
Distillate	-	-	-	2.20	0.003	2.20
Pot	1.03	0.32	0.25	1.55	2.35	3.80
Distillate	-	-	-	0.28	0.06	0.22
Pot	0	0.3	0.22	7.90	0.05	9.02
Distillate	-	-	-	3.28	0.41	2.87
Pot	0.51	0	0	7.96	0.66	8.91
Distillate	-	-	-	3.38	0.45	2.93

The feasibility of stripping the chloride from fuel solutions with HNO_3 vapor was confirmed by the results of eight continuous stripping runs in a 4-in.-i.d. Pyrex column consisting of 12 Vycor single-bubble-cap plates (Fig. 4.4) with 6-in. plate spacing, which showed that the chloride concentration in the stripped product could be decreased to 30 ppm or lower. With 15.8 M HNO_3-H_2O stripping vapor, a V/L as low as 0.9 was effective, but with 9.5 M HNO_3 vapor, a V/L of > 1.6 was required.

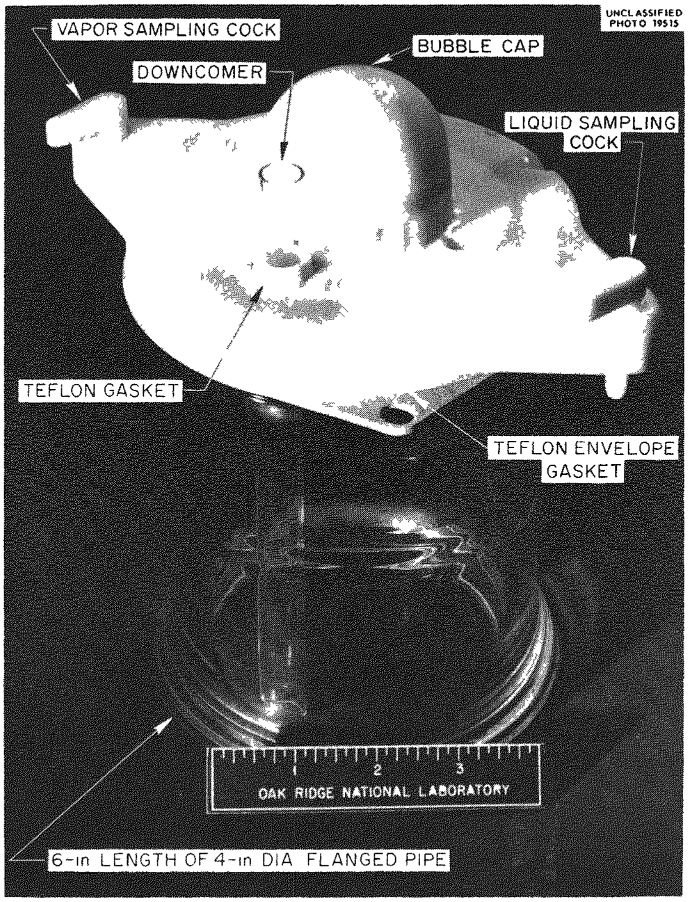

Fig. 4.4. Bubble-cap assembly.

As V/L increased, the nitrate in the overhead increased but in the bottoms product the change was slight (Table 4.2). With 15.8 M HNO_3 vapor, the chloride loss to the noncondensable gas was 60-90%, but in later work with a downdraft condenser, chloride losses were only about 10% at a V/L of ~1.

The stripping column was equipped with a nitric acid boiler, condenser, and feed-metering and product takeoff systems. Feed for all the runs was prepared by dissolving type 304 stainless steel to 50-60 g/liter in 5 M HNO_3-2 M HCl. In two runs the feed also contained about 12 g of uranium per liter, which apparently had no effect on the chloride stripping. Direct calculation of plate efficiency was not possible because of the

Table 4.2. Effect of V/L and Stripping Vapor Concentration on Chloride Removal

HNO_3 in Stripping Vapor, mole %	V/L	Cl^- Loss, %	NO_3^-, N Overhead	NO_3^-, N Product	Cl^- in Product, ppm
20 (9.5 M)	1.3	38	1.75	12.3	1300
	1.6	35	3.36	12.2	375
	5.2	5	7.6	12.6	17
	6.1	5	7.2	11.8	27[a]
40 (15.8 M)	0.9	65	4.56	15.0	27
	1.1	75	7.16	14.7	12
	2.1	90	12.9	15.9	16
	2.1	90	12.9	16.2	10[a]

[a] Uranium in feed.

lack of vapor-liquid equilibrium data for aqua regia solutions of stainless steel salts, but plate efficiency for the rectification of 65 wt % HNO_3 in the stripping column was about 30%. Hence three to four theoretical stages were used to carry out the separations reported.

Attempts to concentrate the stripper overheads by removing water in a rectifying column similar to the stripping column were unsuccessful. A dilute acid solution containing approximately equimolar amounts of HNO_3 and HCl was found at the top of the rectifier even when the feed was dilute acid containing no metal salts (Fig. 4.5) and with oxygen introduced to oxidize any NO present. The presence of absorbable gases (produced by decomposition reactions between HNO_3 and HCl) was believed responsible for this behavior since a mixture of NO and Cl_2 was completely absorbed when the gas mixture and acid vapor were passed through a packed rectifier-absorber and reflux condenser (Table 4.3).

In three runs with a downdraft condenser instead of the rectifying column, recycle of the stripper overheads to the dissolver appeared feasible when a portion of the total HNO_3 required was added along with concentrated HCl to adjust to dissolvent composition. This limited the V/L in the stripper to 1 or less and made the use of at least 15.2 M HNO_3 imperative for removal of chloride to the desired level in three or four stages.

4.3 Reflux Flowsheets (laboratory scale)

Both batch and semicontinuous* flowsheets for chloride stripping

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* In semicontinuous operation chloride removal begins before dissolution is complete; continuous flow of dissolution product is assumed.

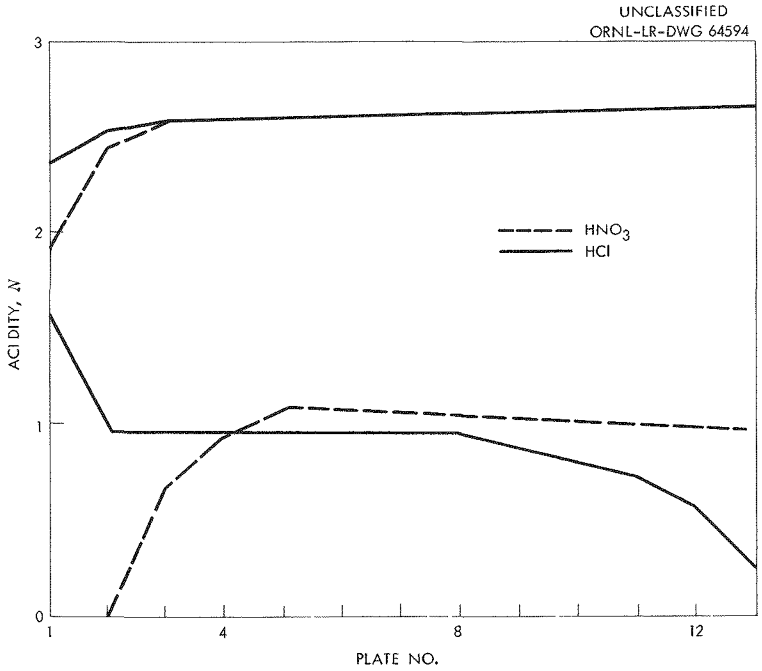

Fig. 4.5. Concentration profiles in rectifying column.

Table 4.3. Absorption of Darex Off-gas Under Varying Rectification Conditions

NO and Cl_2 introduced into still pot containing boiling 5.25 M HNO_3-0.7 M HCl

NO/Cl_2 Mole Ratio	Oxygen Added	Relative Length of Absorber to Rectifier Section	Gas Absorbed, %		
			Cl_2	NO	Total
2/1	None	Short	93.6	29.2	50.7
2/1	None	Short	97.0	34.0	55.0
1/2	None	Short	27.0	100	51.5
5/1	None	Short	98.5	22.4	35.0
2/1	130% excess	Short	92.0	84.7	87.1
2/1	30% excess	Short	95.2	94.2	94.6
2/1	None	Long	98.7	33.6	55.3
2/1	30% excess	Long	99.4	99.4	99.4

with refluxing nitric acid were developed. To avoid generation of a radioactive head-end waste stream by water removal, the most concentrated nitric acid available, 95 wt % (22.5 M), was originally investigated. However, 60 wt % (~13 M) was finally selected since 95 wt % HNO_3 requires special handling and there is a possibility of pyrophoric reaction between titanium, the metal of construction proposed for the Darex equipment, and

97-100% HNO_3. The advantages of semicontinuous operation over batch are the smaller process vessel and the decreased cycle time required since chloride removal can start when fuel dissolution is only partially complete. However, the batch process is simpler and easier to operate. In all reflux flowsheets, radioactive chloride-containing nitric acid is recycled only to the dissolution step, where it is completely used in the next batch; the nitric acid added in the chloride removal procedure is only the amount necessary to provide the HNO_3 required in the solvent extraction feed (~3 M) and to regenerate dissolvent for the subsequent batch.

95 wt % HNO_3. In 13 laboratory-scale batch chloride stripping tests (Fig. 4.6) a batch of dissolver product was charged to a 2-liter flask and 95 wt % HNO_3 was added. Mixed HCl-HNO_3 was boiled off, and the distillate, containing about half the chloride present in the feed, was recycled to the dissolution step after addition of concentrated HCl and HNO_3. To the residue, which had the highest metal concentration and lowest volume (~21% of the original) of any step in the process, another 95 wt % HNO_3 addition was made and the solution was refluxed to remove the remaining chloride. Only water dilution of the product was necessary to produce solvent extraction feed.

Even in the first, highly exploratory, runs it was evident that chloride could be removed to the desired level by volatilization followed by oxidation in refluxing nitric acid (Table A.1, Appendix). It also was shown that an acid waste cut for water removal was unnecessary, and that the mixed acid volatilized could be adjusted to dissolvent composition in the volume allowed. The reproducibility of the process was shown in runs 8, 9, and 10. There was no difficulty in doubling the size of the batch of fuel solution (run 14) although chloride removal and recovery were somewhat poorer with a lower boilup rate (run 11, Fig. A.1, Appendix). Slightly weaker nitric acid (92.5 and 90 wt %) was used satisfactorily in two runs (39 and 41), but the lower concentration limit was not established.

In semicontinuous chloride stripping (Fig. 4.7) nitric acid is added to the dissolver effluent as it accumulates in the collection vessel. When the desired amount has accumulated, mixed acid is boiled off at the same rate as the fuel solution is entering, giving a constant volume in the vessel until all the fuel solution has been added. More nitric acid is then added, and the remainder of the mixed acid is removed. At this point the volume of the solution is low and its metal concentration is high. Nitric acid is again added, and the solution is refluxed exactly as in the batch flowsheet.

The laboratory runs (Table A.2) were made with 3700 ml of dissolution product metered to the chloride removal flask to simulate the discharge of a continuous dissolver. First, 1250 ml of fuel solution and 250 ml of 95 wt % HNO_3 were charged. Then 2450 ml of mixed acid was taken off while the remaining 2450 ml of fuel solution was added and boiling was continued until a total of 2700 ml of mixed acid had been removed. A 350-ml batch of 95 wt % HNO_3 was added, another 600 ml of mixed acid was boiled off, and a 600-ml batch of 95 wt % HNO_3 was added. The solution was then refluxed 2 hr and diluted with water to yield 3700 ml of solvent extraction

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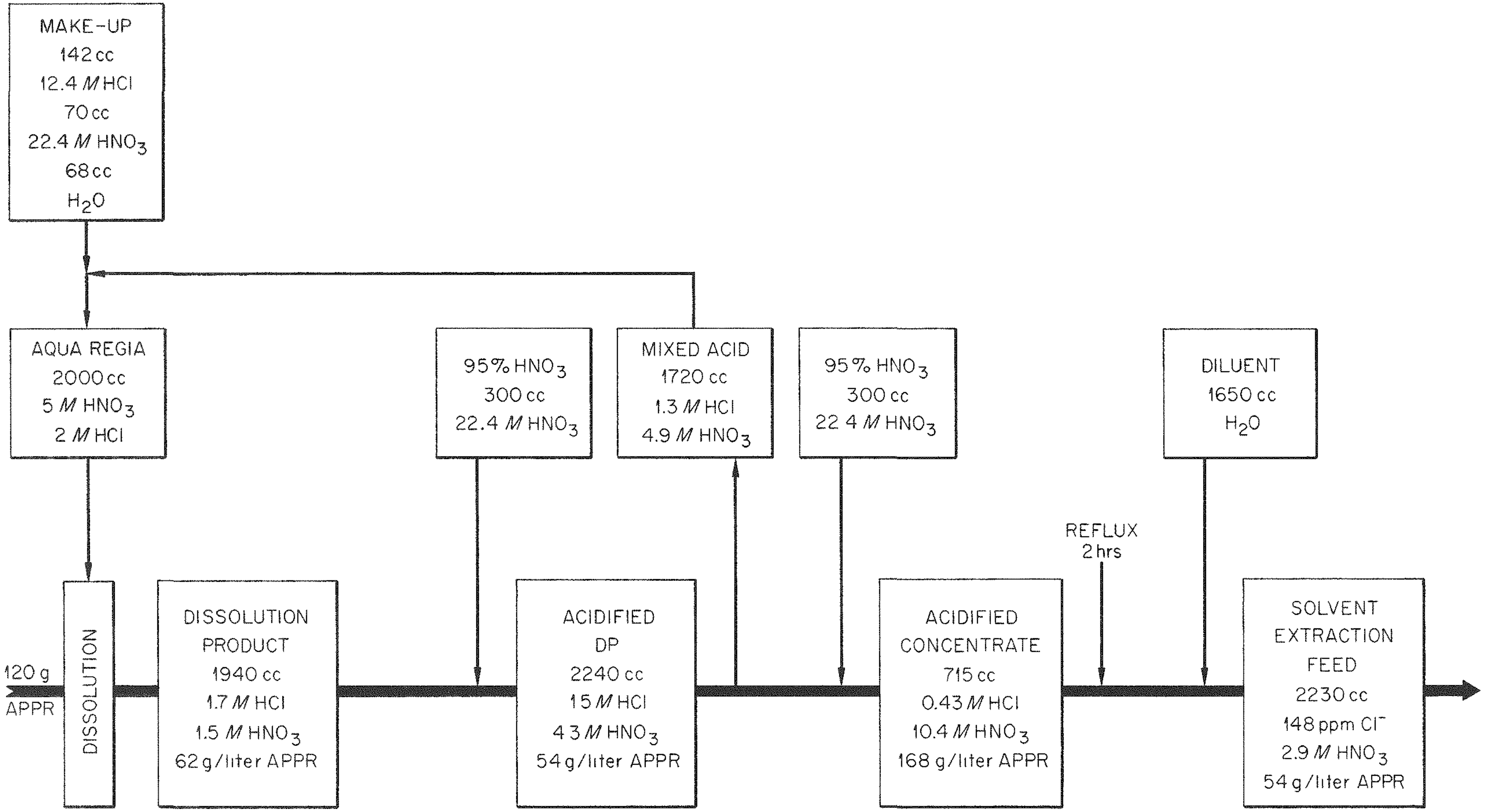

Fig. 4.6. Darex process feed preparation (APPR fuel) with batch chloride removal by refluxing 95 wt % HNO_3 (run APPR-14).

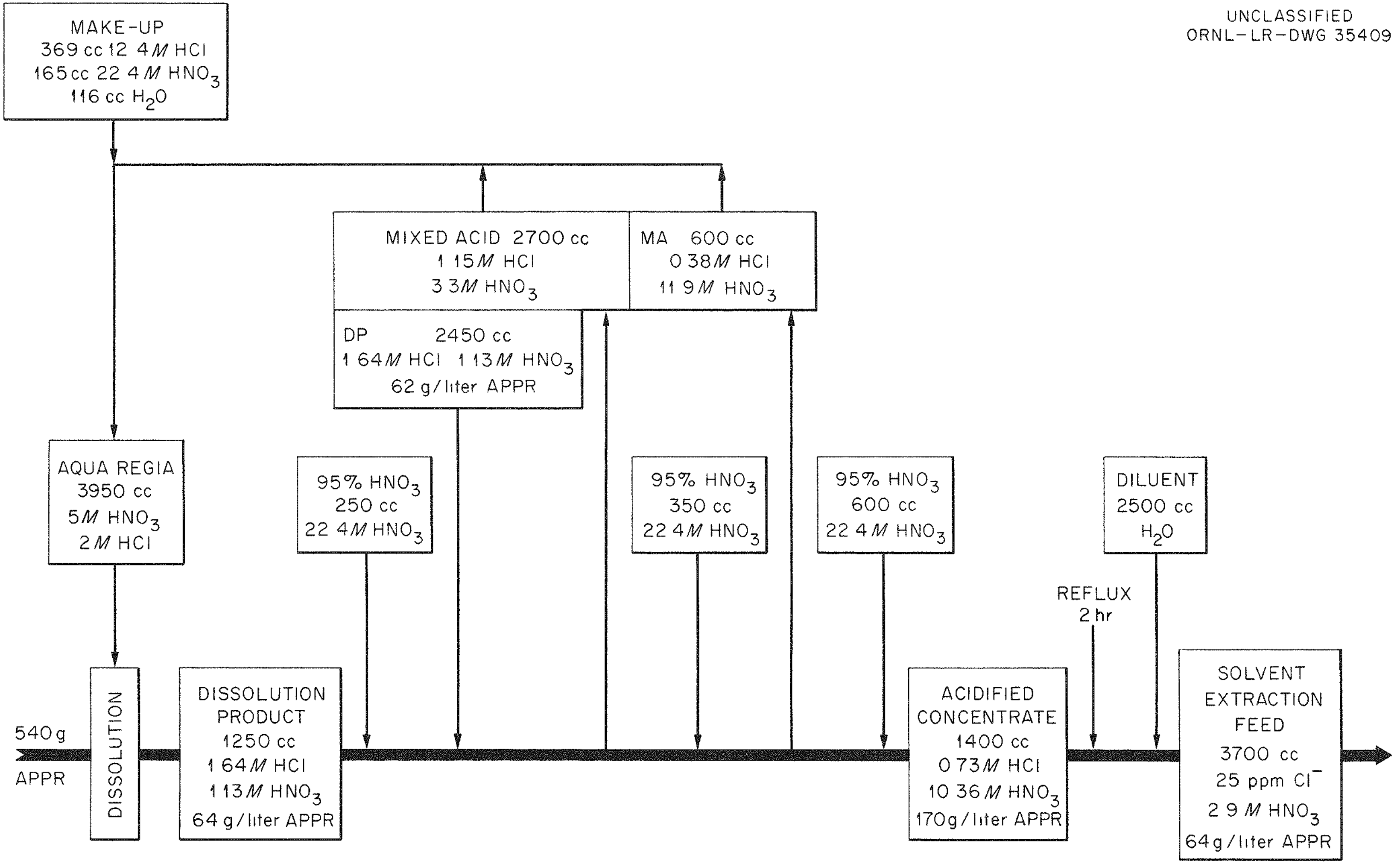

Fig. 4.7. Darex process feed preparation (APPR fuel) with semicontinuous chloride removal by refluxing 95 wt % HNO_3 (run APPR-13).

feed. The compositions of the solution after various steps in the process are given in Table 4.4.

Table 4.4. Dissolver Product Composition after Various Steps in Process (Run APPR-13)

Solution	H^+, M	Cl^-, M	Vol, ml	Density, g/ml	Metal Conc, g/l
Dissolution product	2.77	1.64	3700	1.233	64
Initial charge to tank (1250 ml of dissolution product + 250 ml of 22.5 M HNO_3)	6.12	1.38	1480	-	54
After addition of remainder of dissolution product and removal of 2700 ml of mixed acid	3.24	2.06	1175	1.584	202
After addition of 350 ml of 22.5 M HNO_3	8.26	1.71	1410	-	168
After removal of 600 ml mixed acid	2.52	1.23	830	1.755	285
After addition of 600 ml 22.5 M HNO_3	11.10	0.73	1400	-	170
After 2 hr refluxing	8.46	86 ppm	1270	1.660	186
After dilution with water to solvent extraction feed concentrations	2.90	25 ppm	3700	1.257	64

61 wt % HNO_3. Since a flowsheet for semicontinuous operation with 95 wt % HNO_3 was being developed when 61 wt % HNO_3 was adopted as the preferred stripping medium, semicontinuous operation with the less concentrated acid was also investigated (Fig. 4.8). The chief difference between the two flowsheets is the need for initial waste and post-reflux mixed acid cuts when the less concentrated acid is used. Work on a semicontinuous process was stopped when a 48-in.-dia cylindrical feed adjustment tank with batch criticality control was selected since the smaller tank volume in the semicontinuous process was no longer an advantage.

In the final semicontinuous runs with 61 wt % HNO_3, 700 ml of dissolver product was charged to a 2-liter boiling flask and 300 ml of dissolution product was continuously added while 300 ml of dilute acid was removed to waste. Then a 300-ml batch of 61 wt % HNO_3 was added and an air sparge started. The remaining 400 ml of dissolver product was added continuously, with mixed acid being removed until the concentrate volume was 300 ml. Then a 600-ml batch of 61 wt % HNO_3 was added. the solution was refluxed 2 hr with sparging, and an additional 250 ml of mixed acid

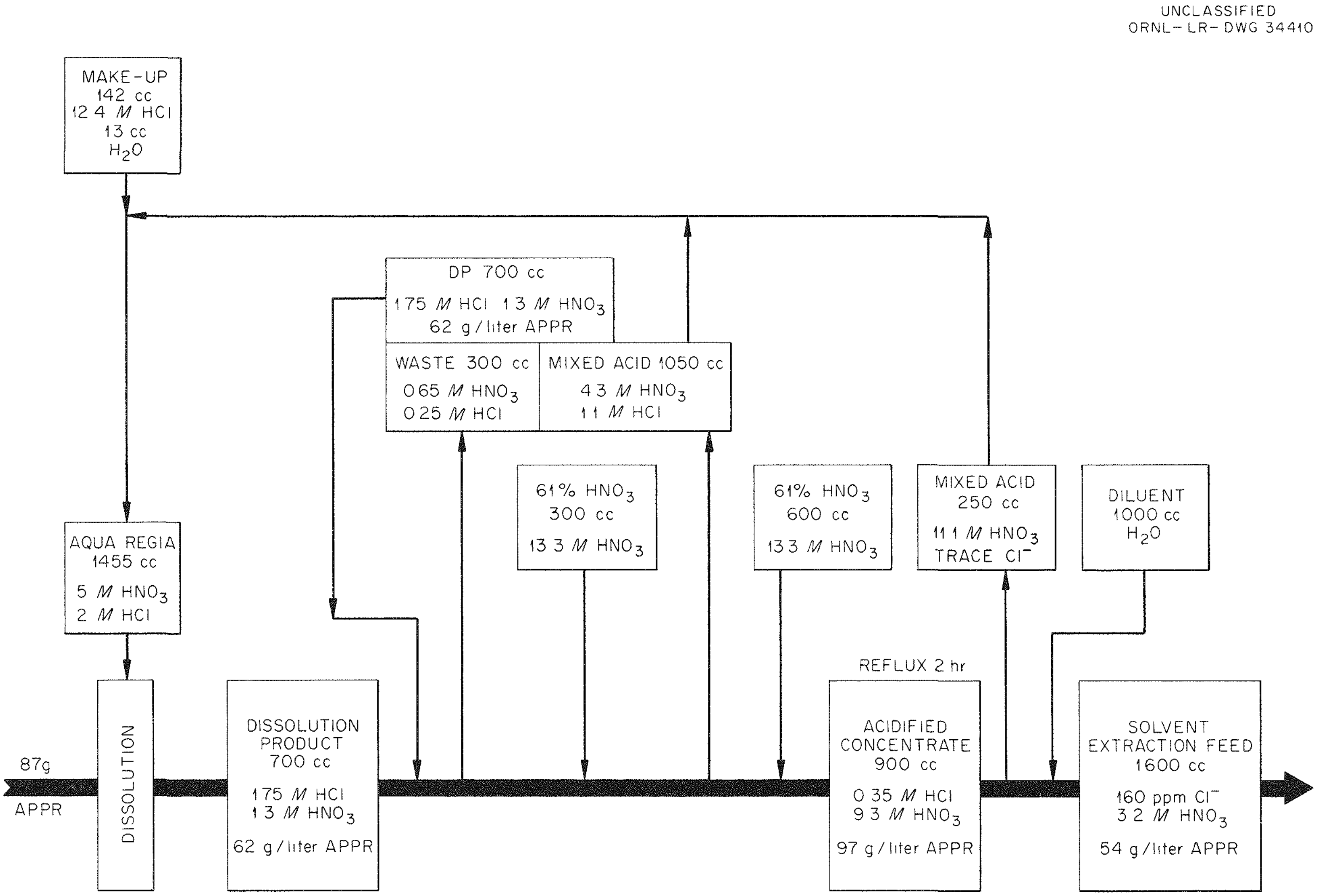

Fig. 4.8. Darex process feed preparation (APPR fuel) with semicontinuous chloride removal by refluxing 61 wt % HNO_3 (composite data from several runs).

was boiled off (HNO_3 with a trace of chloride). The residue was diluted with water to 1600 ml of solvent extraction feed.

Five runs were made in establishing the feasibility of the flowsheet (Table A.3). The need of a gas sparge to meet the 350 ppm chloride specification was shown in the first two runs. The third run showed the need for a waste cut; although more mixed acid was taken than could be recycled and more 13.3 M HNO_3 than necessary to make 3 M solvent extraction feed was added before refluxing, the final chloride concentration was higher than in the runs with the waste cut. The last two runs showed the value of sparging, with oxygen and air being equally effective.

A batch flowsheet with 61 wt % HNO_3, using principles developed for the flowsheet described above, was operated successfully in the first run (Fig. 4.9). Eight additional runs were made to optimize variables (Table A.4). In run 28, on which Fig. 4.9 is based, it was coincidental that no makeup nitric acid had to be added to the mixed acid to regenerate aqua regia. The operation of larger scale equipment in this way would not be attempted.

The laboratory work on which the flowsheet is based was done in a 2-liter flask with 1400-ml batches of dissolution product produced by dissolving prototype APPR elements (~10% depleted uranium) to 62 g of metal per liter in 5 M HNO_3-2 M HCl. The solution was boiled to evaporate 250 ml of dilute acid waste and then 250 ml of 61 wt % HNO_3 was added and an air sparge started at 0.25 scfh. Mixed acid (~1060 ml) was boiled off until the volume of the concentrated product was 300 ml. Then 600 ml of 61 wt % HNO_3 was added, the mixture was refluxed 2 hr, and another 250 ml of mixed acid (HNO_3 with trace chloride) was boiled off. The remaining product was diluted to 1600 ml of solvent extraction feed containing less than 350 ppm of chloride.

In plant operation an entire batch of dissolver product would be charged to the chloride removal vessel and a waste cut ($\leq$ 1.0 M total acid) removed. Nitric acid would be added to increase chloride volatility, and mixed acid, containing about half the chloride in the initial solution, removed. The metal concentration is the highest and the volume lowest (about 21.4% of the original) at this point. Nitric acid would again be added, the solution refluxed to decompose the remaining chloride, and the chloride-free (< 350 ppm) product boiled to remove excess nitric acid. Only water dilution of the metal-containing solution would be required to produce solvent extraction feed. The HNO_3 distilled off would be combined with the first mixed acid and adjusted to 5 M HNO_3-2 M HCl in a volume equal to or less than the original dissolvent volume. The dilute acid waste could be treated with excess caustic and used in off-gas scrubbing to minimize the volume of the radioactive chloride-containing waste.

4.4 Large-scale Evaluation of Three 61% HNO_3 Batch Flowsheets

Since batch treatment of the dissolver product with 61% HNO_3 was considered the preferable method for removing chloride, large-scale tests were made on three flowsheets for this step. The reference flowsheet,

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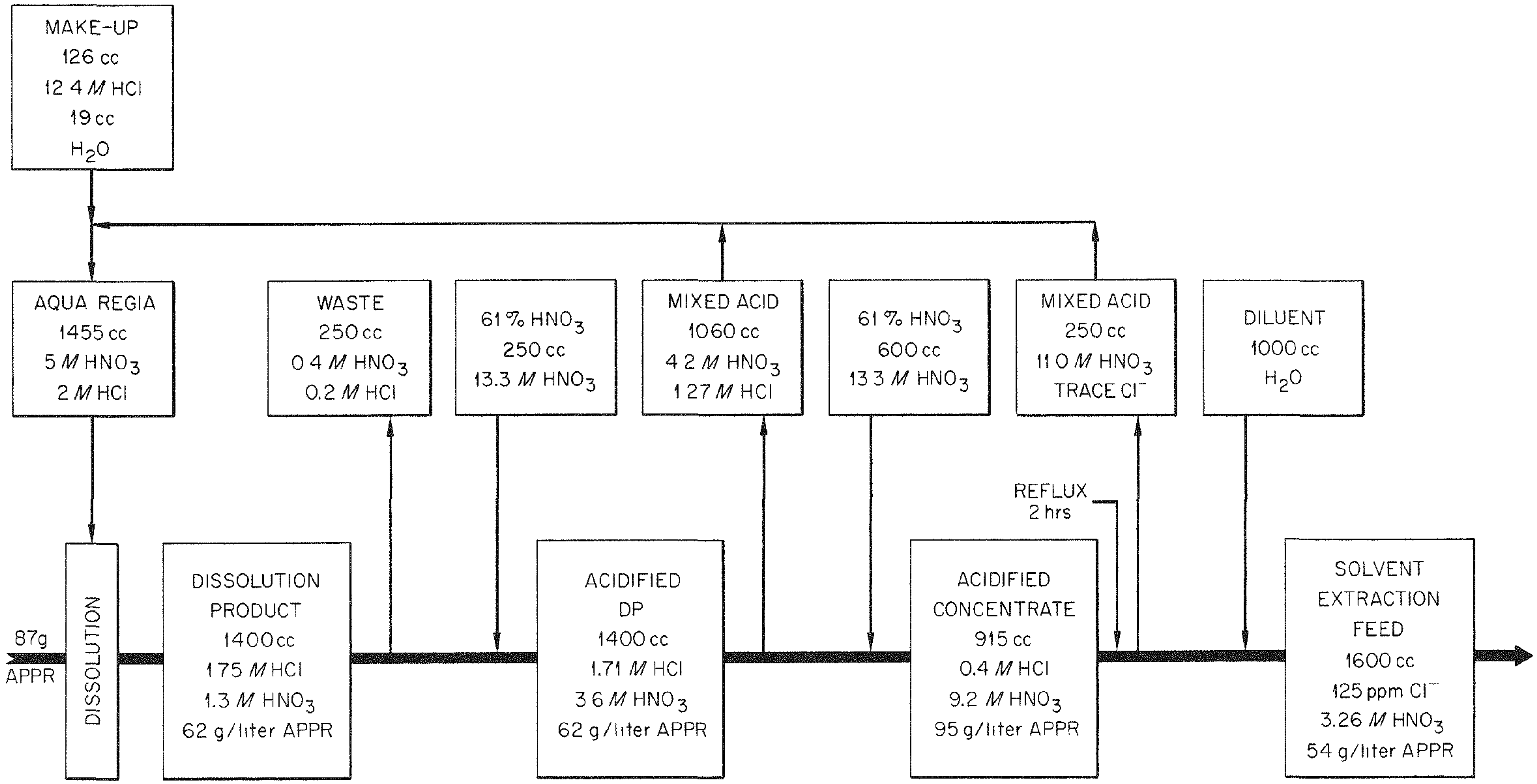

Fig. 4.9. Darex process feed preparation (APPR fuel) with batch chloride removal by refluxing 61 wt % HNO_3 (run APPR-28).

the best procedure of the three, is characterized by a continuous addition of recycle HNO_3 (~12 M HNO_3 with trace chloride) and batch addition of fresh 13.3 M HNO_3. Refluxing and gas sparging may be used if necessary and the two batches of recycle acid (aqua regia and ~12 M HNO_3 with trace chloride) are completely consumed in the next batch prior to the addition of fresh 13.3 M HNO_3. The reflux flowsheet uses two batch additions of fresh 13.3 M HNO_3 with ~450% concentration of the solution just prior to the second addition. Refluxing and sparging are necessary but only one recycle stream (aqua regia) is involved. The recycle flowsheet uses only continuous addition of recycle HNO_3 with trace chloride mixed with makeup 13.3 M HNO_3. There is no refluxing and sparging provided, and more HNO_3 than can be consumed in the next batch is returned as two recycle streams.

The reference flowsheet incorporates more desirable features than any other 61 wt % HNO_3 flowsheet (Table 4.5). The waste volume, 27% of the aqua regia feed, is not the lowest (19% in the reflux flowsheet) but it is less than the recycle waste (32%). Continuous addition of HNO_3 allows the HNO_3 concentration in the solution to increase while the chloride concentration decreases, thus avoiding the decomposition resulting from boiling a high-HNO_3 high-chloride solution (as in the reflux flowsheet). The possibility of eliminating the reflux step and gas sparging (depending on the performance of larger equipment) adds to the attractiveness of the reference flowsheet.

The processing vessel for experimental runs was a 4-in.-i.d. by 6-ft high Pyrex pipe with a titanium steam coil 1 ft long (1.25 ft^2) as the heat source (Fig. 4.10) and a titanium bottom flange; no titanium was exposed in the vapor phase. The condenser was a 2.7-ft^2 single-pass Pyrex heat exchanger, operated either up- or downdraft. The equipment was operated at either zero or total reflux, and nitric acid was fed both batch and continuously. In plant operation the entire chloride removal procedure, including water dilution to produce solvent extraction feed, could be accomplished in a single processing vessel.

Reference Flowsheet. In 11 runs following this flowsheet (Table A.5, Fig. 4.11), operation was generally satisfactory. A dissolver product containing 1.65 or 1.75 M chloride was the starting material, and in most runs a diluted product (solvent extraction feed) containing < 50 ppm chloride was obtained. Eight of the runs were with APPR fuel and three with a special stainless steel.

The procedure followed was: 5.4 liters of dissolver product (5.5 g of uranium, 60 g of total metals per liter) was charged to the processing vessel and 1.5 liters of dilute acid waste was distilled off. Then 4.7 liters of recycle acid (12 M HNO_3, trace chloride) was added continuously while 4.7 liters of mixed acid was boiled off. Virgin 61 wt % HNO_3 (13.3 M) was added and the mixture was refluxed (zero time in this equipment, 2% plant scale, although refluxing was required in other equipment; see Sect. 4.5). Then 4.7 liters of 12 M HNO_3 containing a trace of chloride was distilled off and held for use in the next run. The product was diluted in the same equipment to 6.2 liters (2-3 M HNO_3, < 350 ppm chloride, < 5 g of uranium per liter) of solvent extraction feed. This method of

Table 4.5. Comparison of Three Batch Flowsheets for Chloride Stripping with 61 wt % HNO_3

	Reference	Reflux	Recycle
Waste vol, % of aqua regia vol	27	19	32
1st HNO_3 addition	Continuous 12 M	Batch 13.3 M	Continuous 13 M
2nd HNO_3 addition (13.3 M)	Batch	Batch	Continuous
Composition of acidified concentrate			
HNO_3, M	11.1	9.0	9.2
Cl^-, M	0.1-0.2	0.5-0.9	0.12
Reflux	If needed	Necessary	No provision
Vol of acid returned, % of aqua regia vol	167	90	225
Max metals loading, g/liter	170	290	200
Cl^- in solvent extraction feed, ppm	28-51	135-330	220

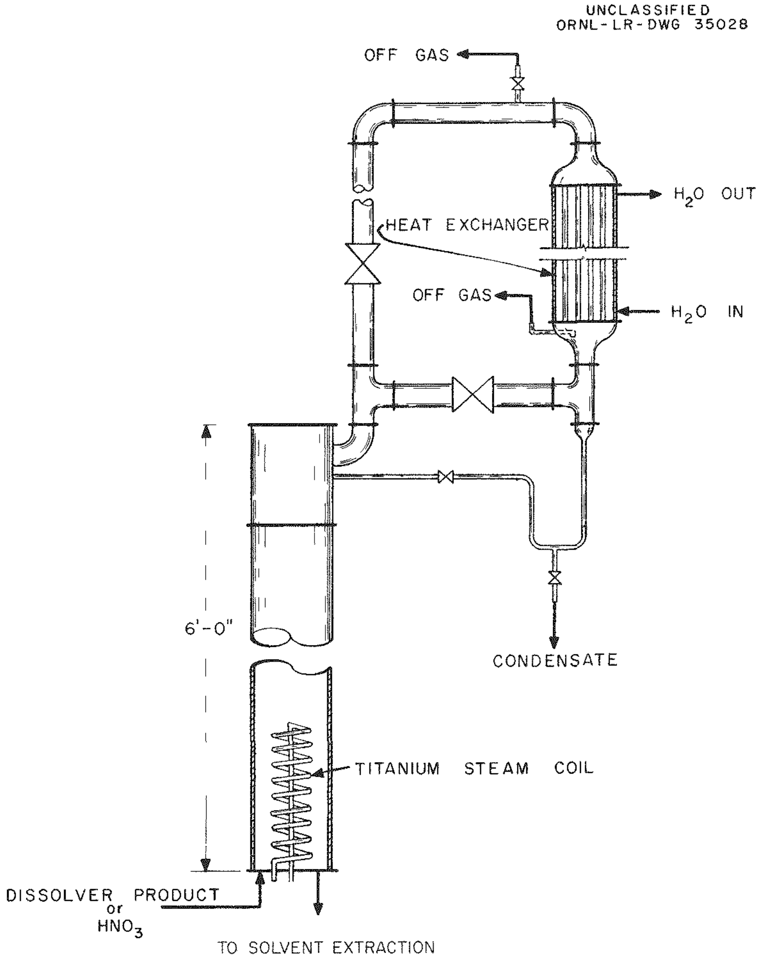

Fig. 4.10. 4-in.-id Pyrex chloride stripping and feed adjustment equipment.

operation, complete utilization of chloride-containing HNO_3 prior to the reflux step, eliminates the possibility of chloride buildup in the recycle acid, which is inherent if a larger excess of HNO_3 is used (the recycle flowsheet).

Aging the dissolution product did not adversely affect chloride removal. In run 65, made with a portion of the same batch of dissolver product used 60 days earlier in run 56, the chloride concentration of the solvent extraction feed was only 154 ppm. The presence of titanium in the vapor phase also did not affect the results; in run 67 ~1 ft^2 of titanium screen, 20 mesh, made of 0.010-in.^{2} wire and 122 in.^{2} of 0.010-in.-thick titanium sheet were exposed in the unheated vapor space above the boiling liquid. Chloride in the solvent extraction feed was 70 ppm.

Chloride was much more easily removed from a special stainless steel solution (~60 g/liter total metals) than from APPR fuel solution. Neither reflux nor HNO_3 recycle was required. In the first two runs (Table A.5, runs V-5 and 6) only one 13.3 $\underline{M}$ HNO_3 addition and mixed acid recovery were necessary to give chloride concentrations of < 100 ppm in the solvent

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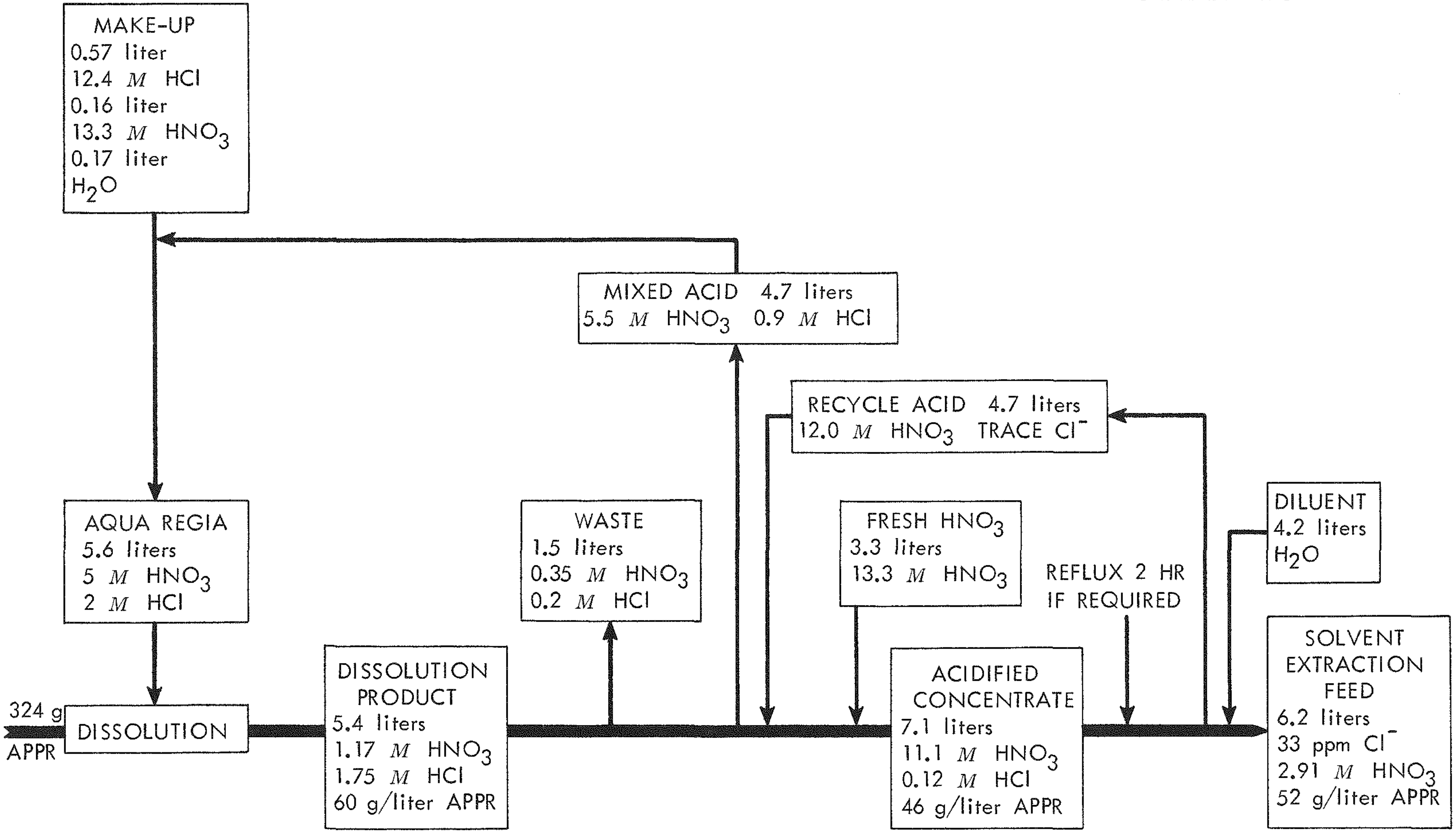

Fig. 4.11. Darex process: reference flowsheet for batch chloride removal using 61 wt % HNO_3.

extraction feed; however, the mixed acids could not be adjusted to 5 M HNO_3-2 M HCl without exceeding slightly the original dissolvent volume. In the third run a small waste cut was taken initially to allow more flexibility in the process and increase its reliability. Chloride in the product was ~40 ppm and the mixed acid could be recycled. The volume of the waste cut should be kept to a minimum since HNO_3 and HCl molarities here were considerably higher (columns 8 and 9) with this material even though the waste cut was a smaller percentage of the dissolver product volume.

Reflux Flowsheet. Thirteen runs by the reflux flowsheet with 61 wt % HNO_3 (Table A.6, Fig. 4.12) showed that chloride could be decreased from 1.75 M in APPR dissolution product to < 350 ppm in the solvent extraction feed.

For these runs, 10 liters of APPR dissolution product (5.5 g U/liter, ~55 g SS/liter) was charged to the processing vessel and 2 liters of dilute acid waste was distilled off. Then a 1.8-liter batch of 13.3 M HNO_3 was added and 7.5 liters of mixed acid was boiled off. Another addition of 4 liters of 13.3 M HNO_3 produced an acidified concentrate which was refluxed 2 hr with air sparging. Another 1.9 liters of mixed acid (HNO_3 + trace chloride) was removed and the solution was diluted to 11.5 liters of solvent extraction feed containing < 350 ppm chloride, 2.7-3.1 M HNO_3, and < 5 g U/liter.

The method of operating the condenser, i.e. updraft vs. downdraft, appeared to be of little importance in recovery of mixed acid (runs 30 and 33 vs 32), but updraft operation was more effective in chloride removal during reflux (runs 33, 32, and 37 vs 43, 42, and 44). Air sparging during refluxing improved chloride removal (runs 33, 32, and 37 vs 43, 42, and 44); during mixed acid recovery it decreased chloride recovery (runs 30, 31 vs 32 and 33) without affecting the chloride in the acidified concentrate (run 32 vs 33). The HNO_3 concentration of the acidified concentrate should be ~9 M or higher for satisfactory chloride removal (run 35 vs other runs).

The data for runs 43, 48, 49, and 50 made with no sparging and an updraft condenser indicate that chloride removal to < 350 ppm cannot be ensured without an air sparge. The reproducibility of results was very good except for the chloride content of the acidified concentrate and the solvent extraction feed. Chloride removal was to 351, 510, 590, and 320 ppm, respectively, but chloride in the acidified concentrate was 0.8 M for runs 43, 48, and 49, 0.6 M for run 50. This might account for the acceptable value of 320 ppm in run 50, but it does not account for the 351 ppm in run 43 (same conditions as 48 and 49). The high HNO_3 in the acidified concentrate of run 48 should have produced a chloride concentration lower than 510 ppm in the solvent extraction feed. The optimum sparging rate for maximum chloride removal in the 4-in.-dia equipment was not determined since a different rate probably would be required in equipment of a different geometry.

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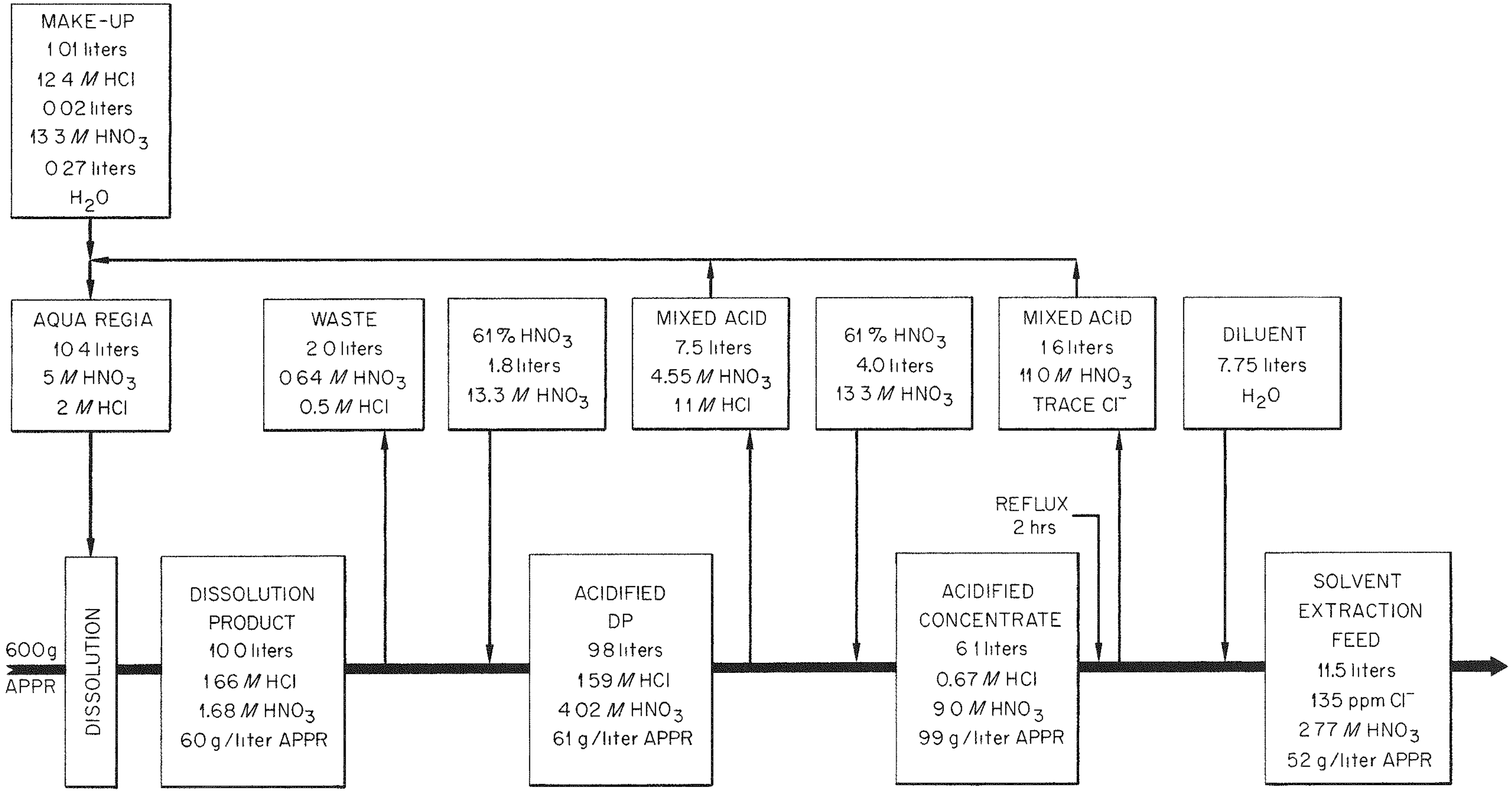

Fig. 4.12. Darex process: reflux flowsheet for batch chloride stripping 61 wt % HNO_3 (run APPR-31).

Material balances for the 13 runs account for about 90% of the nitric acid added both as aqua regia and nitric acid in the liquid streams, with about 10% in the composite off-gas as nitrogen oxides and NOCl. From 40 to 60% of the chloride is recovered in the mixed acid. About 1% of the total nitric acid is lost in the waste acid stream and 2-3% of the chloride.

Recycle Flowsheet. In the recycle flowsheet (Fig. 4.13) an amount of HNO_3 considerably larger than that consumed per batch is added and chloride-contaminated HNO_3 is recycled. Chloride is removed wholly by volatilization with no provision for refluxing.

The procedure was as follows: a waste cut of 3 liters was distilled from the 9-liter volume of fuel solution. Then 7.7 liters of recycle acid was added continuously while the mixed acid cut, 7.7 liters, was being removed. The composition of the recycle acid was chosen to approximate the steady-state concentration after a series of runs. The 10.3-liter mixed recycle acid addition, a mixture of recycle acid and virgin 13.3 M HNO_3, was made simultaneously with the removal of the first 10.3 liters of recycle acid; this removal was continued until 13.3 liters of recycle acid had been withdrawn, leaving somewhat less than 3 liters of concentrated product. This was diluted to 9 liters, producing solvent extraction feed containing 220 ppm chloride and 1.65 M HNO_3.

In the material balance for the one recycle run (run 40), aqueous streams accounted for about 90% of the HNO_3 charged, but the 10% loss to the off-gas represents a greater number of moles than in the reference and reflux runs since the total number of moles involved is larger. Chloride recovery in the mixed acid was 78%. The HNO_3 and HCl losses to the aqueous waste were 0.4 and 5.6%, respectively.

4.5 Evaluation of Reference Flowsheet in a 10-in.-dia Vessel

A chloride removal tank of titanium with 2 ft^2 heat transfer area (Fig. 4.14) and capacity ~4% of a proposed pilot plant was tested to establish the feasibility of processing in a vessel equipped with external convective boiling loops. Feed solutions used were made by dissolving prototype Yankee Atomic and Nuclear Ship Savannah fuel to ~60 g stainless steel, and APPR and special stainless steel (SSS) fuel materials to 60 g total metals per liter in 5 M HNO_3-2 M HCl. The flowsheet used was the ORNL Reference flowsheet (Figs. 4.11 and 2.2) with only an abbreviated version required for the special stainless steel. The procedure was: an acid waste cut (principally H_2O) was distilled from the dissolution product. Then ~12 M HNO_3 was fed at the same rate at which aqua regia was removed (for recycle). Then a batch of 13.3 M HNO_3 was added, followed by refluxing and HNO_3 recovery. The remaining concentrated product was diluted with water to produce solvent extraction feed.

APPR Fuel. Seven runs were made with prototype APPR-fuel solution. In runs 57, 58, and 59 (Table A.7), chloride removal was satisfactory but since the vessel was not equipped with splash plates or liquid separator the solution intermittently bumped up into the vapor line. Run 60 was similar to 59 except that a smaller batch size (8.7 instead

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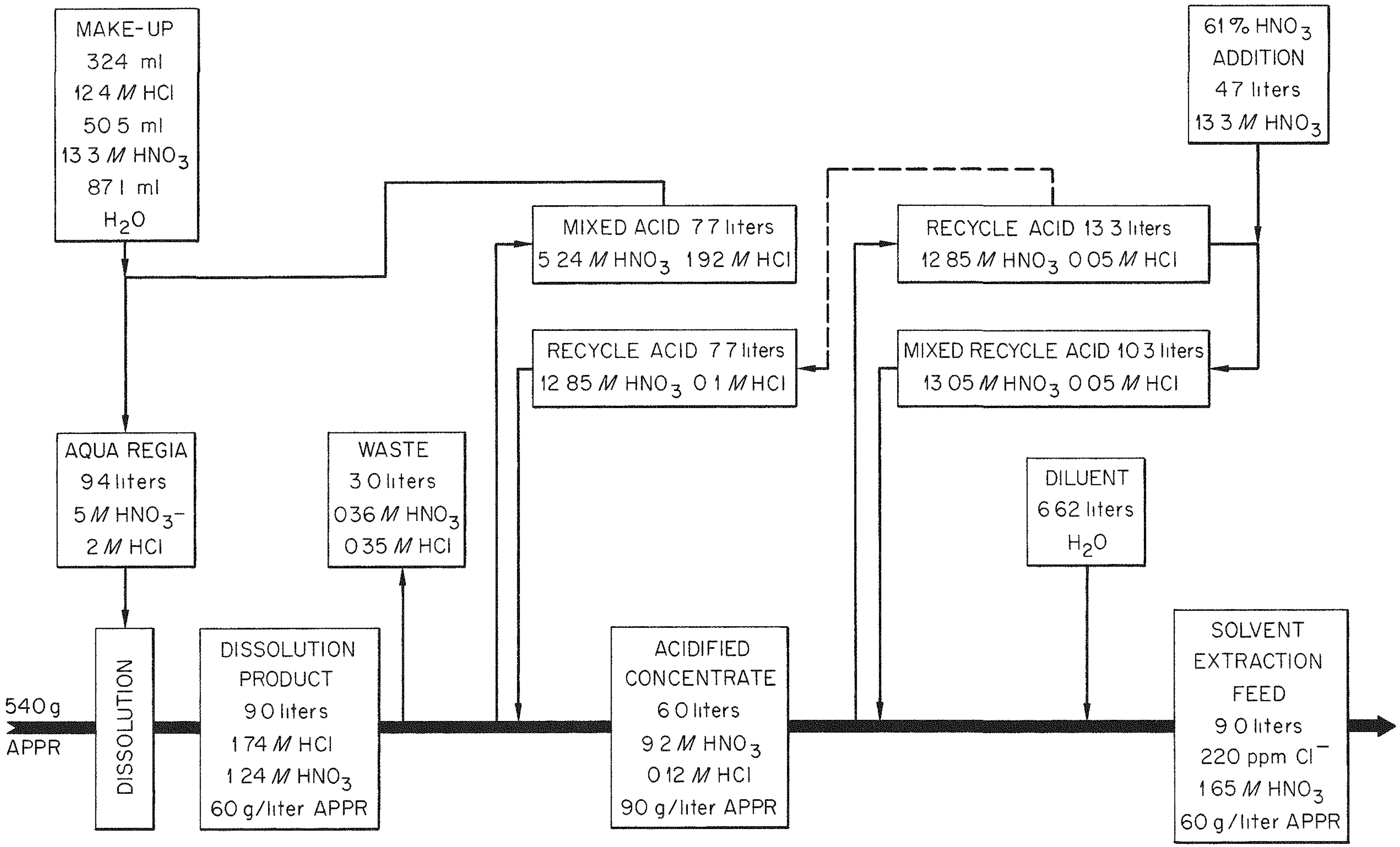

Fig. 4.13. Darex process: recycle flowsheet for batch chloride stripping 61 wt % HNO_3 (run APPR-40).

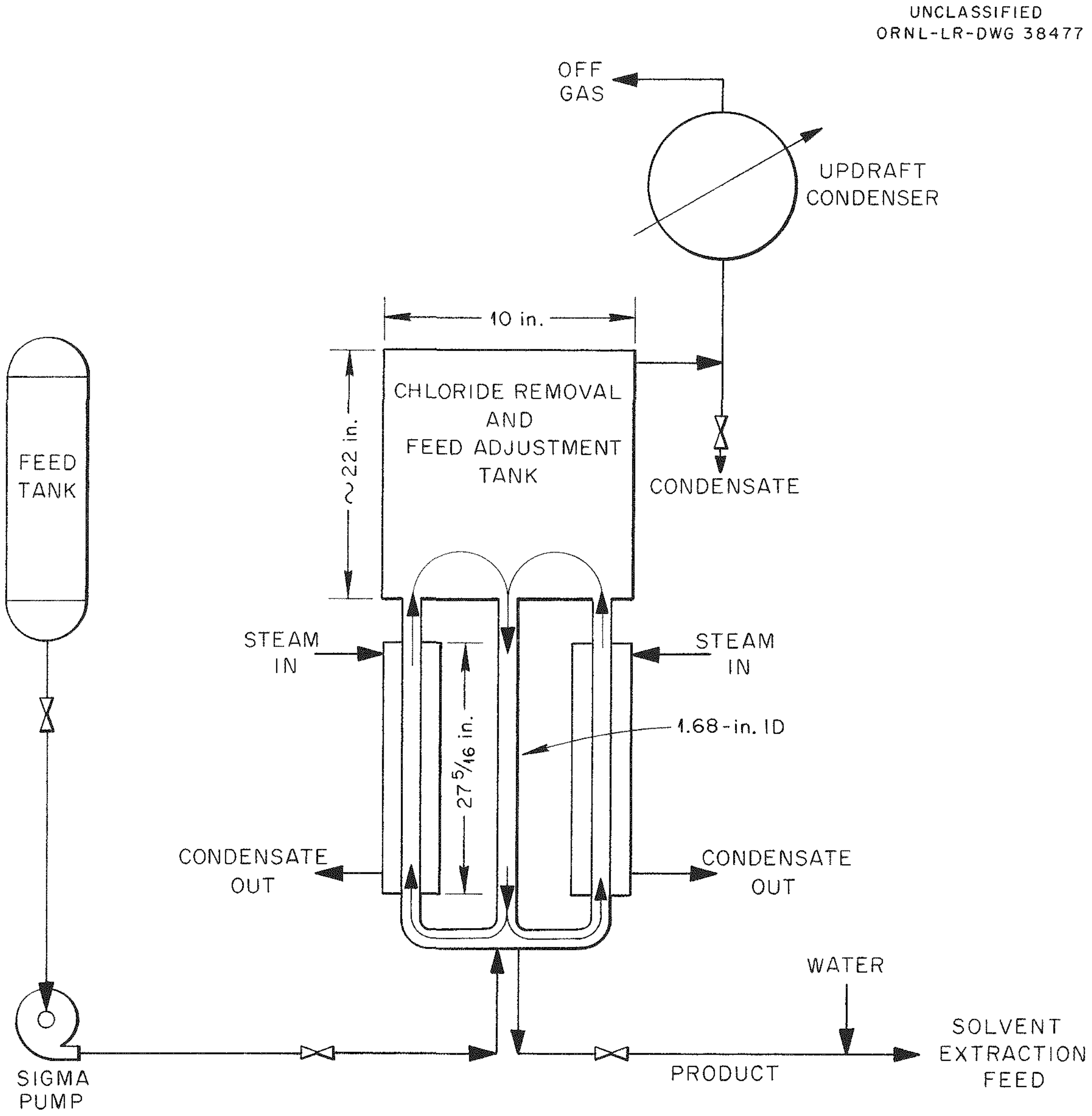

Fig. 4.14. Schematic diagram of chloride removal system with titanium tank.

of 10.8 liters) was used and "bumping" was decreased. No explanation can be offered for the high chloride value in the product except the slightly shorter cycle time. If such values should be obtained repeatedly in future tests, reflux and/or air sparging should be incorporated into the flowsheet.

Run 63 also was made with 8.7 liters of fuel solution. Boilup rates were high and chloride was removed to only 730 ppm even though 2 hr reflux was used. Very little chloride was removed during the second hour of refluxing. Run 64 was a duplication of run 59 except an attempt was made to hold the temperature difference (steam to solution) constant at 15°C; chloride was removed to 306 ppm. In run 66, in which 2 hr reflux and an air sparge of 1.6 liters/min was used, solvent extraction feed containing 70 ppm chloride was produced. After 1 hr reflux the chloride concentration in the acidified concentrate had been reduced to 464 ppm and after 2 hr to 275 ppm.

Yankee Atomic Fuel. In run 61 chloride was removed to 440 ppm in the solvent extraction feed, slightly above the specification of 350 ppm. In run 68, with 2 hr reflux and air sparging at 1.6 liters/min during reflux and recycle acid recovery, chloride in the solvent extraction feed was 64 ppm. After 1 and 2 hr refluxing the acidified concentrate contained 325 and 184 ppm chloride, respectively.

Nuclear Ship Savannah Fuel. Run 69 (Fig. 2.2) produced solvent extraction feed containing 68 ppm of chloride, 1.05 $\underline{M}$ HNO_3, and the same metals loading as the dissolver product. The flowsheet developed for Yankee Atomic fuel was applicable directly to NSS prototype without modification even though the U/SS ratio changed from 3.64 to 2.23.

Special Stainless Steel. Seven runs indicated that processing of special stainless steel fuels by a reference flowsheet without an acid waste cut or HNO_3 recycle but with 2 hr reflux and a minimum air sparge of 0.18 liter air/liter solution·min is feasible. The first HNO_3 addition might be either batch or continuous if it is followed by a batch addition prior to refluxing. In runs V-8 and 9 (Table A.8), one with and one without a waste cut, chloride was not removed below 1000 ppm in the solvent extraction feed, and the mixed acid volume collected was too large to allow readjustment to 5 $\underline{M}$ HNO_3-2 $\underline{M}$ HCl without exceeding the volume of dissolvent required. In run 8 the continuous addition of HNO_3 and the low steam pressure resulted in a low HNO_3 loss, while in run 9, the higher initial HNO_3 concentration and higher steam pressures resulted in appreciable HNO_3 loss. Although chloride was removed to < 350 ppm in the solvent extraction feed in run 10, the batch addition of a larger volume of HNO_3 resulted in higher HNO_3 loss even though the steam pressure was lower.

Run 11 was a duplicate of run V-7, made in 4-in. glass equipment with chloride removal to < 10 ppm. It differed from run 9 only in that the HNO_3 addition was batchwise. Chloride removal was unsatisfactory and losses were higher even though steam pressure was lower. In run 12, with 2 hr reflux, acceptable chloride removal was not achieved because the acidified concentrate contained only 6.5 $\underline{M}$ HNO_3. In runs 13 and 14 the amount of HNO_3 added was increased and split into two portions; the second addition boosted the HNO_3 molarity to 8.15 at the beginning of reflux. An air sparge was used during reflux but the rate was not measured; chloride removal was to < 25 ppm. In run 14 an air sparge of 0.18 liter air/liter solution·min was used during reflux and chloride was removed to 100 ppm. In the last two runs the decrease of HNO_3 molarity during reflux was negligible.

Discussion. From this series of runs in a plant prototype titanium vessel processing four different fuels, it was concluded that the increased difficulty of chloride removal (over the 4-in. cylindrical tank) was attributable to the change in system geometry as it affected internal vapor-liquid contacting and to shorter residence times resulting from higher boilup rates, and not to the larger exposed titanium surface area. Chloride can be reduced to the specified < 350 ppm in solutions with both high and low SS/U ratios by using appropriate periods of refluxing and air sparging. The feed adjustment tank should be provided with ~100% freeboard (based on maximum liquid volume), and as an added precaution the vapor line from the tank should be equipped with a de-entrainer with return to the tank.

Summaries of successful reference flowsheets for four different fuels representing two distinct fuel types are shown in Table 4.6. Although the stainless steel loadings of all four dissolution products are similar (50-60 g SS/liter), the U/SS weight ratios range from 0.1 to 3.6. The Yankee Atomic and Nuclear Ship Savannah flowsheets are quite similar but the APPR and SSS are unique in some respects. Only the SSS did not require acid waste removal while only APPR met the chloride specification of < 350 ppm without reflux or air sparging. SSS used no HNO_3 recycle but required about the same percentage of 13.3 $\underline{M}$ HNO_3 as the SS-UO_2 pellet fuels; the APPR fuel solution required more HNO_3 since it was necessary to produce a higher acidity in a larger volume of solvent extraction feed. The SSS fuel had the highest acid consumption since more HNO_3 makeup was required and a greater amount was lost in a still larger volume of 3 $\underline{M}$ solvent extraction feed. The SSS feed could be processed with a lower acidity in the acidified concentrate since the chloride decomposition reaction was more efficient in this system.

5.0 SOLVENT EXTRACTION FEED ADJUSTMENT

Both laboratory and engineering-scale runs showed the feasibility of continuously adjusting the ~14 $\underline{M}$ HNO_3 effluent from the chloride stripper by evaporation to remove nitric acid and dilution to the 2-3 $\underline{M}$ HNO_3 needed for solvent extraction feed. The advantages, over dilution alone, are recovery of nitric acid for recycle, decrease in solvent extraction waste volumes, and silica dehydration.

5.1 Laboratory-scale Studies

In exploratory batch work, chloride-free product from azeotropic stripping runs (~14 $\underline{M}$ HNO_3) was concentrated from ~30 to 260 g of stainless steel per liter by boiling off HNO_3-H_2O. The nitric acid concentration of the distillate dropped from 15.2 to 14.1 while that of the solution decreased to 2 $\underline{M}$ (Fig. 5.1). Such a stripper product concentrated to 120 g of metal per liter could be diluted with 2 vol of H_2O, yielding a feed solution 3 $\underline{M}$ in HNO_3 containing 40 g of stainless steel per liter. The final volume would be 75% of that of the initial solution. When the above experiments were repeated with solution containing ~5 g of uranium per liter, the data points fell on the same curves.

Table 4.6. ORNL Darex Reference Flowsheet as Applied to Four Reactor Fuels

	Run APPR-64	Run YA-68	Run NSS-69	Run SSS-14
Dissolver product				
Stainless steel, g/liter	55	58	60	50
Uranium, g/liter	5.4	211	134	8.7
Waste vol, % of dissolver product vol	28	28	28	None
HNO_3 recycle vol, % of dissolver product vol	87	87	87	None
Fresh 13.3 M HNO_3 added, % of dissolver product vol	61	51	51	50
Composition at start of reflux				
HNO_3 conc, M	11.3	10.1	9.6	8.3
Chloride conc, M	0.16	0.19	0.20	0.02
Reflux time, hr	None	2	2	2
Air sparge, liter/min.liter solution	None	0.12	0.10	0.18
Solvent extraction feed				
Vol, % of dissolver product vol	115	100	100	183
HNO_3 conc, M	3.18	1.15	1.05	3.50
Chloride conc, ppm	306	64	68	100
Overall heat transfer coefficient, $Btu/hr.ft^2.°F$	182-323	193-282	181-272	310-428

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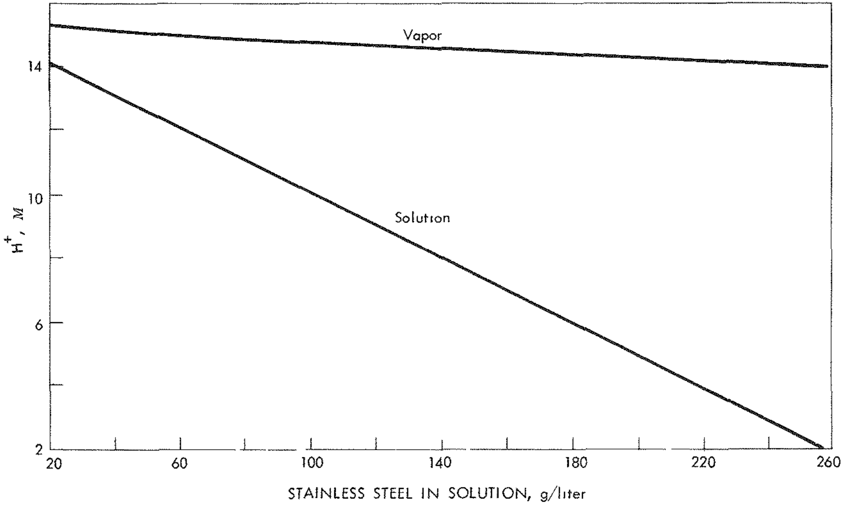

Fig. 5.1. Effect of solution metal loading on HNO_3-H_2O vapor produced and solution free acidity.

In three continuous feed adjustment runs of 7, 6, and 7 hr duration in laboratory glassware, constant temperature, the value of which is dependent on the metal loading, was shown to be the most convenient method of operation. A typical material balance (Fig. 5.2) accounted for 98, 91.7, and 100% of the HNO_3, H_2O, and $SS(NO_3)_{2.85}$, respectively. The feed, which had a high chloride content to allow tracing of the chloride, was concentrated by a factor of 3.8. Calculations were based on analytical results with the assumption that densities and volumes are additive.

5.2 Engineering-scale Runs

A series of 8 feed adjustment runs in engineering-scale equipment (Table A.9) showed that both APPR and Yankee Atomic fuel solutions containing ~13.5 M HNO_3 can be concentrated by factors of 4-8 in a continuous boiler (feed adjustment tank), ~15 M HNO_3 being recovered in the overhead. The concentrated product required only dilution with H_2O to produce solvent extraction feed of desired acidity and metals loadings. The desired acidity/metals ratio is obtained by maintaining the appropriate boiling temperature in the adjustment vessel. Operation over the temperature range 125-135°C was demonstrated. The overhead requires only slight upgrading of the HNO_3 concentration for recycle to the HNO_3 boiler feeding the stripper. The small amount of chloride in the stripped product was split between the overhead and product streams, with some escaping as noncondensables.

The evaporator in the equipment system (Fig. 5.3) used in these tests was a stainless steel tank 30 in. high x 6-3/8 in. i.d., in whose bottom a 13-in.-high x 2-3/8-in.-o.d. void cylinder was centered to decrease the volume. The static volume was ~6 liters but holdup during operation was only ~3 liters; the level was controlled by a jackleg in the product line. The tank was electrically heated, with the heat input regulated to maintain a pre-set temperature through a recorder-controller and air-driven powerstat. Control of the system was very good and operation

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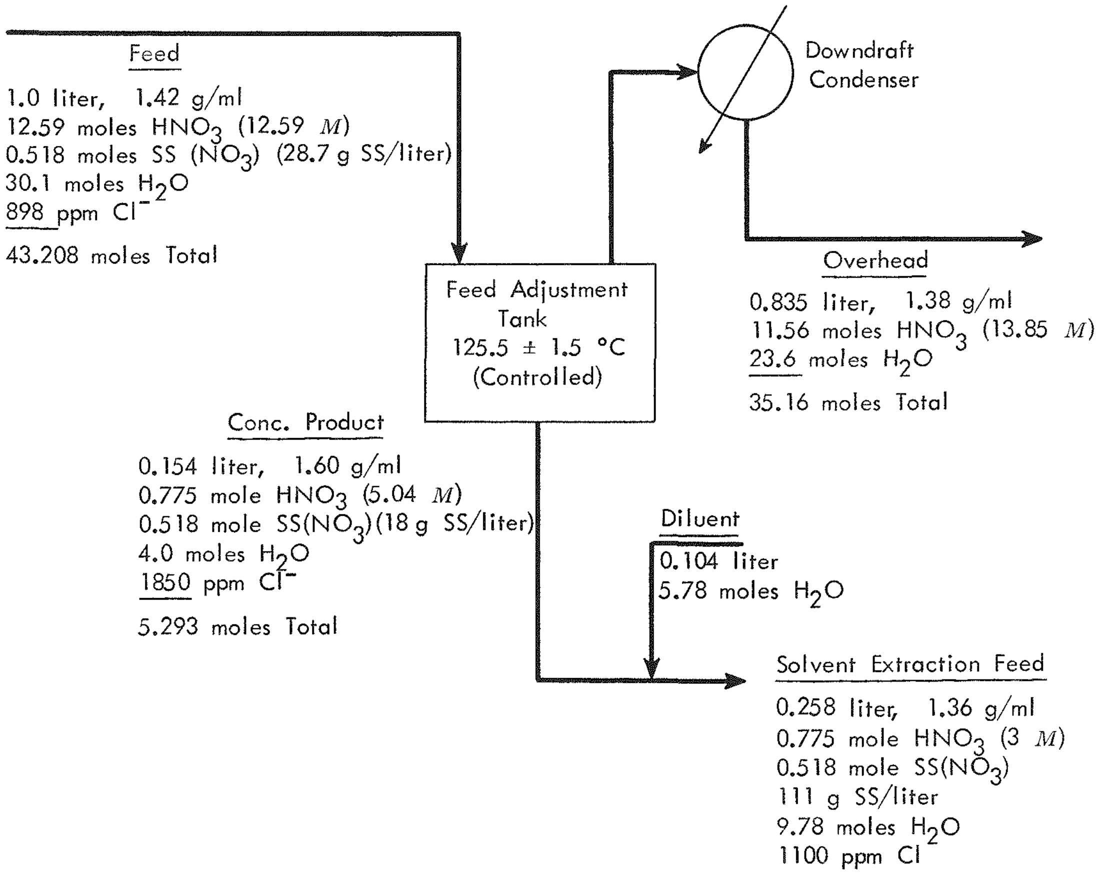

Fig. 5.2. Material balance for feed adjustment Run 3. Basis: 1 liter of chloride-stripped solution.

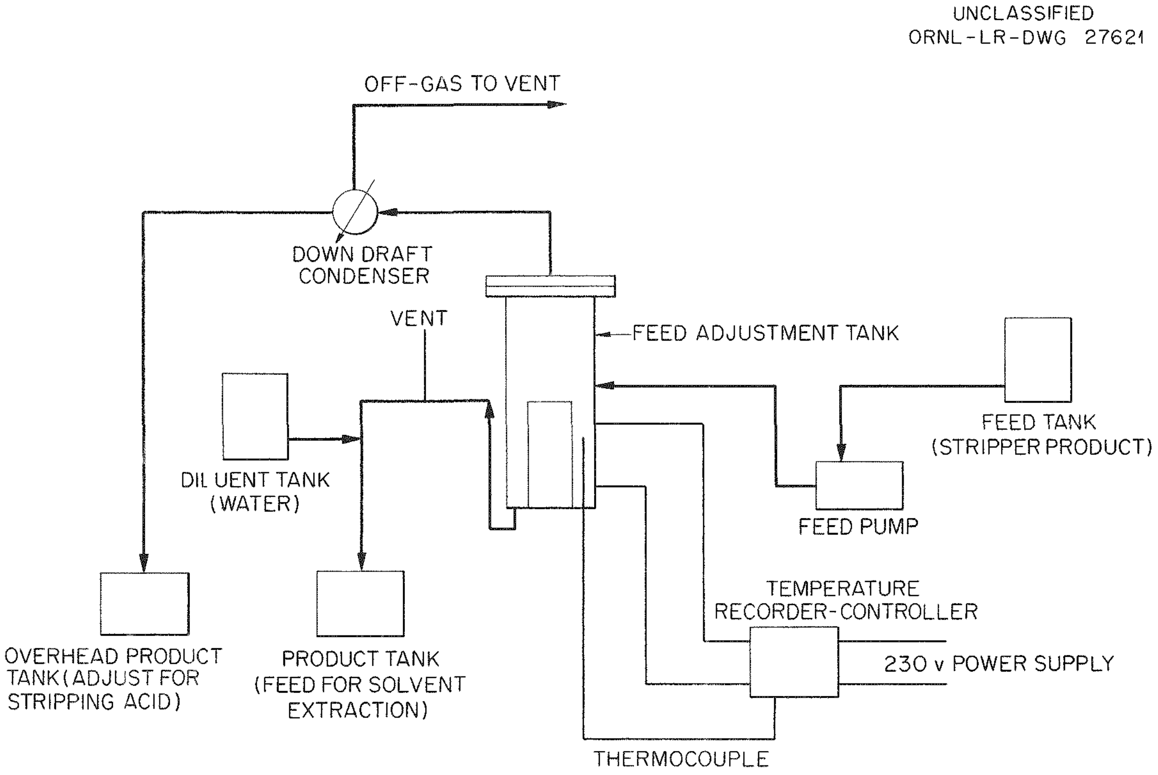

Fig. 5.3. Feed adjustment tank installation.

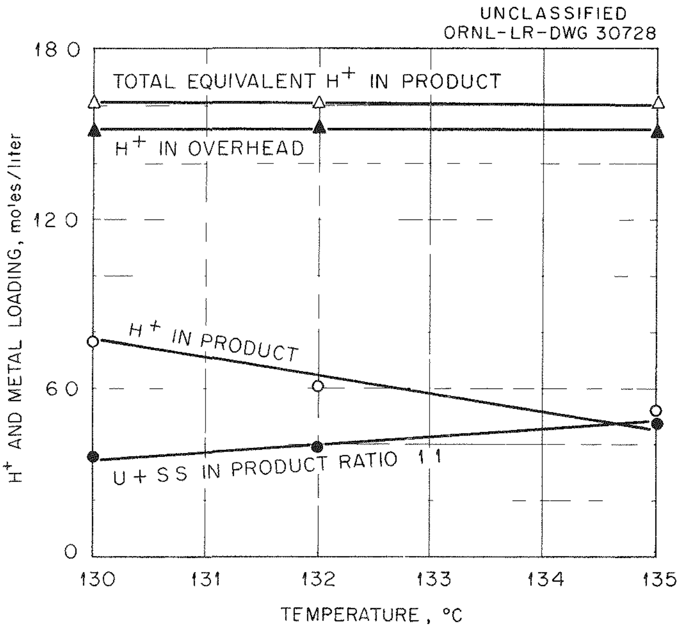

Fig. 5.4. Continuous concentration of stripped Darex dissolver product in acidity and metal loading as a function of temperature.

was quite satisfactory except for occasional plugging of the external jackleg that controlled the liquid level. This could have been eliminated by more careful temperature control in the line since the concentrated salt solution solidified on cooling or with excessive concentration by boiling in the line. Higher temperatures in the boiler corresponded to more concentrated product solutions; less concentrated products contributed to greater ease of operation.

In early runs cold feed was introduced to the vessel without incident; however, to operate with hot stripper product as feed it was necessary to add to the vessel 6 in. of Yorkmesh and above it a 3-ft vertical section of 3-in.-i.d. pipe containing 5/8-in. stainless steel Raschig rings to prevent foaming or bumping of the concentrate into the overhead condenser. After this modification all runs were made with hot feed without difficulty.

5.3 Temperature-Composition Correlation

Continuous feed adjustment runs at three different temperatures with a simulated Yankee Atomic Darex dissolver product which had been stripped with azeotropic HNO_3 showed an increase in the metals loading and a decrease in the HNO_3 content of the product with an increase in the operating temperature (Fig. 5.4). The mole ratio of uranium to stainless steel was approximately 1/1. The curves are represented by the equations

$$Y = 0.25X - 29.05 \qquad (1)$$

where Y = moles of uranium + stainless steel per liter and X = temperature in °C, and

$$Y^* = 90.92 - 0.64X \qquad (2)$$

where Y^* = moles of HNO_3 per liter and X - temperature in °C. These particular equations hold true only for feeds prepared under the conditions stated, but similar equations could be developed for other stripping media and uranium-to-stainless steel ratios. Laboratory-scale batch and continuous feed adjustment studies had shown that the sum of the nitrate ion in the concentrated product remains essentially constant even though the acidity and metals loading of the product may vary. This relation also held true in continuous concentration of the Darex stripped product. It can be expressed by

$$\text{moles}_{HNO_3} + k(\text{moles})_{U + SS} = K \qquad (3)$$

where k = 2.43, the average of the nitrate ion combined with the stainless steel and the uranium; k will have a different value for each SS/U ratio. When eqs. 1 and 2 are substituted in eq. 3, K varies from 16.16 to 16.0 over the temperature range 130-135°C. The relative constancy of K implies that the nitric acid content of the overhead stream would also be relatively constant, which was found experimentally.

6.0 INTEGRATED DISSOLUTION-STRIPPING-FEED ADJUSTMENT SYSTEM

6.1 Continuous 4-in.-dia Stripping Column -Dissolver Loop

Stainless Steel Processing. Six significant runs were made with stainless steel in a loop system containing a titanium dissolver (Fig. 6.1,, glass bubble-cap stripping column, nitric acid reboiler, and downdraft condenser. Operation was generally satisfactory after minor adjustments were made during five short shakedown runs. Average stainless steel dissolution rates were 20-50 mg/cm^2-min and chloride in the dissolver product was stripped to < 250 ppm in all runs except run 50 (Table 6.1). Material balances showed HNO_3 and HCl recoveries of 80 to 110% (Figs. A.2-A.11). The runs were made with type 304 stainless steel, which was added to the continuous dissolver as 11-in. lengths of 3/4-in.-dia thick-wall tubing, each piece weighing ~200 g. The mixed acid from the stripper was recycled to the dissolver; concentrated HNO_3 and HCl were added at rates calculated to maintain 5 $\underline{M}$ HNO_3-2 $\underline{M}$ HCl dissolvent.

Table 6.1. Data for Continuous Dissolver-Stripper Runs with Stainless Steel

Run No.	Duration, hr	Avg V/L	Product Cl$^-$, ppm	HNO_3 in Stripping Vapor, $\underline{M}$	Loss, moles/mole SS Dissolved HNO_3	HCl	Avg Dissolution Rate, g/min
45	13	0.88	225	15	0.96	0.21	6.12
47	50	0.85	50-250	15	~1	0.32	4.26
50	47	Very Variable	1500	15	0.67	0.276	4.73
53	32	0.98	100	15.8	1.5	0.25	4.26
54	47	0.956	50	15.8	0.6	0.154	4.99
70	5	0.954	20	15.8	0.25	0.136	6.16

For the material balances the volumes of the various streams were calculated from measured flow rates (rotameter readings, tank level changes, etc.). Compositions and densities were determined by averaging analytical values and by direct weighing of 10-ml samples at room temperature. When analytical results appeared questionable, metal loadings were calculated from flow rates and stainless steel dissolution rates. In run 45 the stripped product metal loading obtained by averaging analytical results agreed with the calculated values within 5% (2 g/liter). Since the compositions and flow rates of the off-gas streams are highly questionable, the percentages listed on each material balance include only the contents of the aqueous streams. Also because of this uncertainty, chloride loss was estimated as the amount of makeup HCl required to maintain a constant chloride level in the system. The N^{x+} (present at N_2O, NO, NOCl, and NO_2) loss is based on either the overall NO_3^- balance or the balance around the dissolver.

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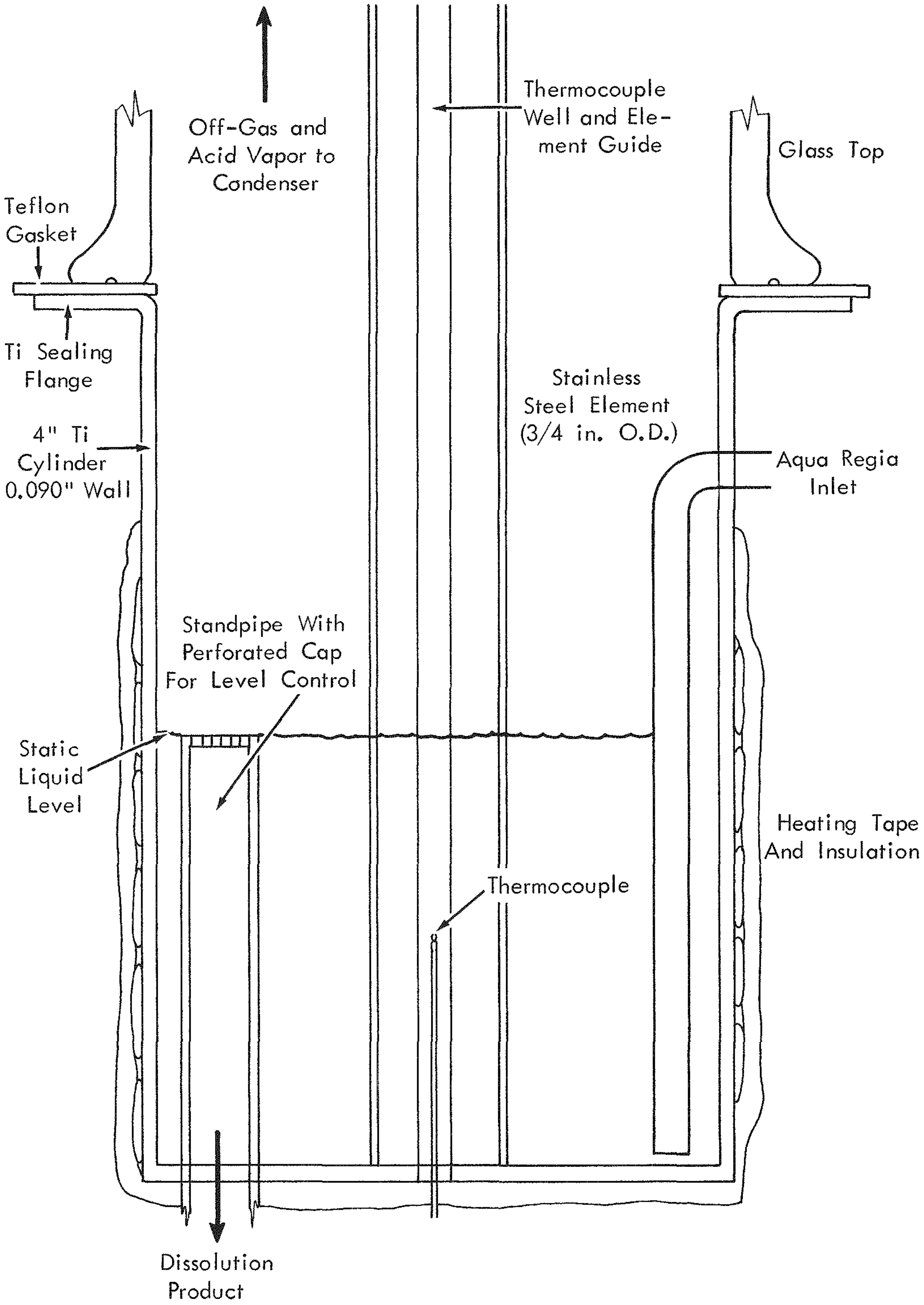

Fig. 6.1. Continuous Darex dissolver.

The off-gas was not considered, and HNO_3 and HCl balances are low on the dissolver but high on the stripper since material from the dissolver off-gas was absorbed in the downdraft condenser. The dissolver and overall H_2O balances should be ~105% since 2 moles of H_2O is formed in the dissolution.

The relative sizes of the number of moles in various streams may cause percentage figures to be misleading. For instance, the calculation of the H_2O balance around the stripper involves numbers greater than 100 moles, where a relatively large absolute error yields a low percentage error, while the HNO_3 balance around the dissolver involves numbers of the order of 10 where a small absolute error results in a large percentage error. The largest error in the composition of any one stream should be in the calculation of the number of moles of water present, since this is determined by difference. It contains cumulative errors from the determination of HNO_3 and HCl molarities, loading, volume, and density. In the HNO_3 balance around the dissolver the moles of $SS(NO_3)_{2.85}$ in solution are taken to be equivalent to 2.85 moles of HNO_3. A 100% balance on the metals is assumed since it seems reasonable that there should be no loss of metallic salts in passing through the system.

Operation in run 45 was satisfactory except for the last hour prior to shutdown when liquid levels fluctuated in both dissolver and stripper. In run 47, operation was smooth for 24 hr with only two, momentary, cessations of dissolution, about 8 hr apart. However, the dissolver discharge then became erratic and remained so for the remainder of the run. The trouble was apparently caused by intermittent partial plugging of the standpipe dissolver outlet by small stainless steel flakes, which float just before their dissolution is complete.

In run 50 the liquid level in the dissolver was controlled by a 1-11/16-in.-dia horizontal product overflow line, rather than by a standpipe, which limited the static liquid depth to 6.5 in. Dissolver operation was still characterized by cyclic discharge, causing the stripper to run alternately near flooding and then "dry" for short periods. The difficulty was apparently caused by foaming, resulting in a varying liquid holdup in the dissolver, changing compositions, and unsteady-state operation. Two plates (making a total of 13) and a 6-in.-high titanium section had been added to the stripper prior to this run to facilitate entry of the titanium discharge line carrying both the liquid product and off-gas from the dissolver.

In run 53 the large overflow line from the dissolver was replaced by separate off-gas and liquid (with jackleg for liquid level control) lines. Dissolver operation was improved, but the stripper still required constant attention to prevent flooding. Stripper throughput was lower than in previous runs because of almost complete plugging of the ports in some of the bubble caps with a tightly adherent siliceous deposit. For run 54 the stripping column was reassembled with clean plates and operation was satisfactory. Oxygen was bled into the stripper to convert NO to NO_2. The high HNO_3 balance around the stripper indicates that more material was absorbed from the off-gas as a result of the O_2 addition.

Prototype Fuel Processing. Two runs (60 and 61) of 5 and 20 hr duration were made with prototype Yankee Atomic fuel, in a slab dissolver-stripper system. In run 61 a feed adjustment tank was added. The fuel was 0.4-in.-o.d. stainless steel tubing, 0.010-in. wall, filled with UO_2 pellets, 22 ft being used in the first run and 75 ft in the second. Fuel was charged to the dissolver, 4.5 by 1 by 6 in. deep, in 3.75-in. lengths and dissolved in 6 M HNO_3-1.5 M HCl. A static level of 4 in. in the dissolver was controlled by an external jackleg. Fuel was charged in a horizontal position by dropping from a charger consisting of two concentric glass tubes with slits which aligned when the inner tube was rotated.

In both runs chloride was stripped to < 7 ppm, with HNO_3 and HCl losses of 0.9 and 0.12 mole, respectively, per mole of stainless steel dissolved in run 60 and of 1.0 and 0.2 in run 61. The lower iron concentration probably contributed to the improved chloride removal (< 10 ppm). The stripper contained 13 plates and the stripping vapor was 15.8 M HNO_3 in both runs. The mixed acid overhead stream was adjusted externally so that only a constant composition 6 M HNO_3-1.5 M HCl was fed to the dissolver.

In run 61 all three major loop components (dissolver, stripper, and feed adjustment tank) were operated continuously. Errors were about 8% in the stripper chloride and H_2O material balances. Overall balances would have little meaning since the V/L was slightly higher than it should have been for loop operation. The HNO_3 recovery stream value represents experimental data, but it was not upgraded and recycled. All the makeup added to the HNO_3 boiler was virgin 15.8 M HNO_3.

After these runs two surge tanks were added to the system, which decreased fluctuations in both flow rates and compositions of the nitric acid and aqua regia recycle streams. Instrumentation was added to regulate automatically the flow of makeup HNO_3 to the boiler by sensing the liquid level to the boiler rather than by manual constant rate control. The stripper overhead was surged and adjusted to dissolvent composition by manually regulated addition of concentrated HNO_3 and HCl.

6.2 Instrumented Loop Operation

Three runs in the instrumented loop with APPR fuel element prototype showed that automatic operation (Fig. 6.2) is feasible. In the products of all three runs chloride was < 350 ppm. The composition of the aqua regia stream was not automatically controlled, but two physical properties such as density and boiling point change might have been used. Upgrading of the HNO_3 acid recovered in the feed adjustment tank was the only previously unproved automatic operation, and under operating conditions, with 15.0 M HNO_3 (simulating recovered acid) fed to the surge tank whose contents were maintained at 15.8 M, the automatic addition of 22.5 M HNO_3 by density control was satisfactory. The difference between the volume of this adjusted stream and that required for stripping vapor was supplied by an external makeup stream of the same composition; this addition was controlled by the liquid level in the HNO_3 boiler.

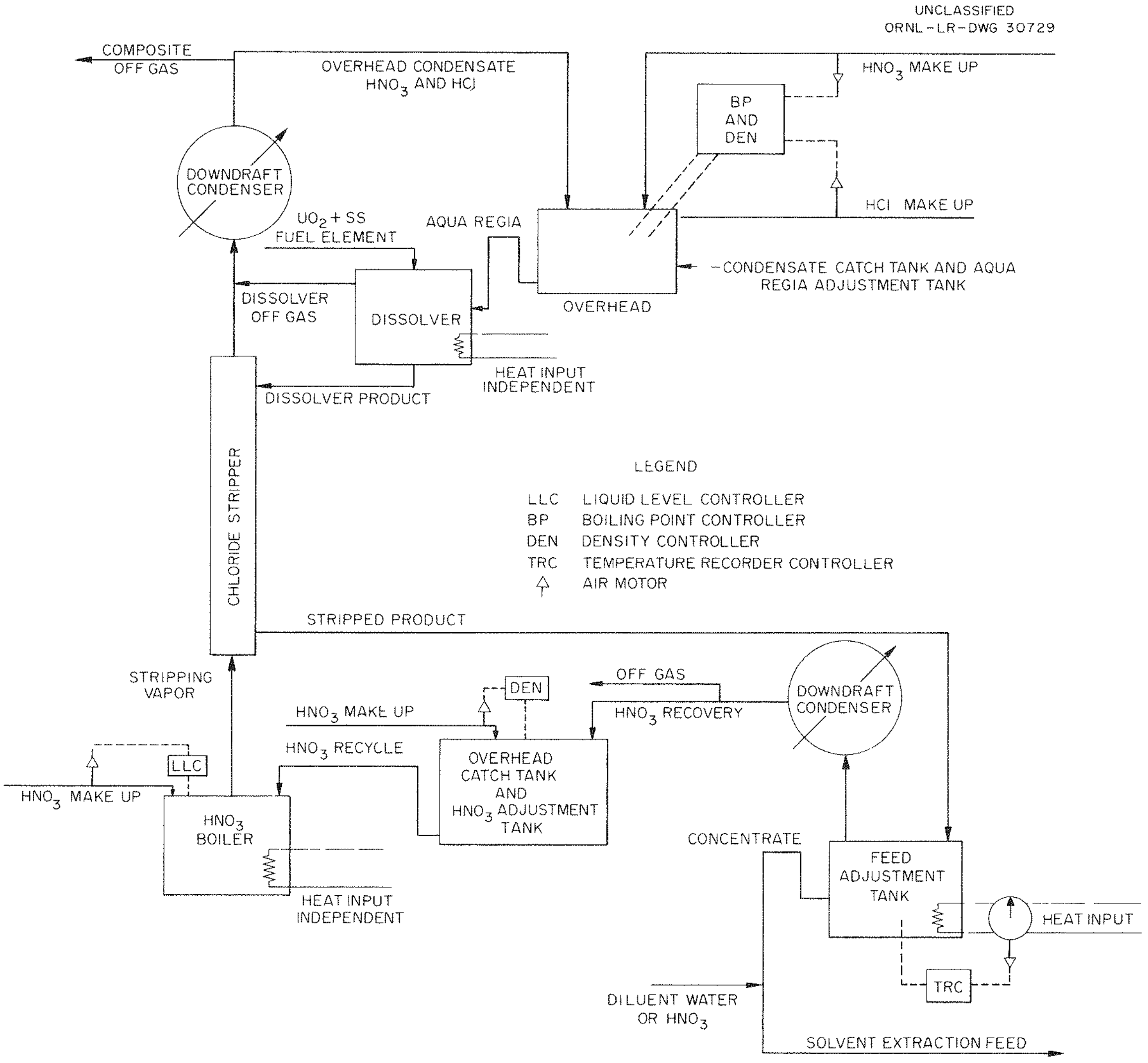

Fig. 6.2. Schematic diagram of Darex equipment including instrumentation.

A long period of steady-state operation was not achieved in any run, chiefly because siliceous (type 302 stainless steel used in APPR fuel elements contains 2-3% silicon) deposits on the interior of the bubble cap stripping column caused erratic operation and eventual flooding (see Sect. 6.3). A bubble cap column of this type therefore could not be recommended for use in processing this fuel.

In the first run of 13 hr duration (run 72, Fig. A.12), the titanium slab dissolver described earlier (Sect. 6.1, runs 60 and 61) was used for the 5/16- by 5/16- by 3.74-in.-long APPR laminated "fuel." The automatic valve in the makeup HNO_3 line to the HNO_3 recycle surge tank would not close fully and the acidity in the tank rose to 16.4 M rather than being controlled at the desired 15.8 M; this also resulted in excessive HNO_3 in the aqua regia recycle to the dissolver.

In runs 73 and 76 (Fig. A.13) a cylindrical titanium dissolver 4.5 in. i.d. by 7 in. deep, was used and full-sized prototype APPR fuel (2-7/8-in. sq by 22 in. long) was dissolved. A jackleg in the product outlet maintained a static liquid depth in the dissolver of 3.5 in. The dissolution rate in nominal 5 M HNO_3-2 M HCl dissolvent was 6.5 g/min at a flow rate of 100 ml/min. Run 73 was a short shakedown run with stainless steel fuel, but run 76 was continued 11.5 hr with a fuel element containing 91% stainless steel, 7% uranium, and 2% silicon. Operation of all components was satisfactory until flooding began after about 3 hr as a result of silica deposits, even though the column had been thoroughly cleaned with 2 M NaOH immediately before this run.

6.3 Solids Deposition on Interior Surfaces

In runs 73 and 76 with APPR prototype fuel, in which the stainless steel contains 2-3% Si, deposits of silica on the chloride stripping (bubble cap) column prevented proper column operation. These deposits were found on all interior surfaces of the column. Figure 6.3a shows deposits on a glass rack and corrosion specimens (the majority were titanium) On long operation of a continuous dissolver on 304L stainless steel, a hard adherent deposit with a dendritic structure formed on the walls of the glass container. X-ray analysis showed the material was largely amorphous. This deposit was removable by boiling with 2.77 M (10%) NaOH solution with no apparent deleterious effect on the corrosion resistance of the titanium. The thickest deposits were on the wetted horizontal top surfaces of the plates (Fig. 6.3b) with very little on the unwetted bottom surfaces. Figure 6.3c shows a clean plate and two degrees of deposition.

Analysis of samples of the solids in the dissolver product stream, stripped product stream, and NaOH wash water showed:

	Amount, wt %		
Material	In Dissolver Product	In Stripped Product	In NaOH Wash Water
Si	17.13	9.19	13.83
Fe	9.32	0.87	14.69
Ni	0.52	0.09	1.85
Cr	12.91	0.48	4.66
U	< 0.5	0.30	2.24
Acid insoluble	23.0	10.16	11.22
	63.38	21.09	48.49

An appreciable amount of each sample consisted of acid insolubles. A qualitative spectrographic analysis did not give additional information. Niobium was found when materials containing it were processed.

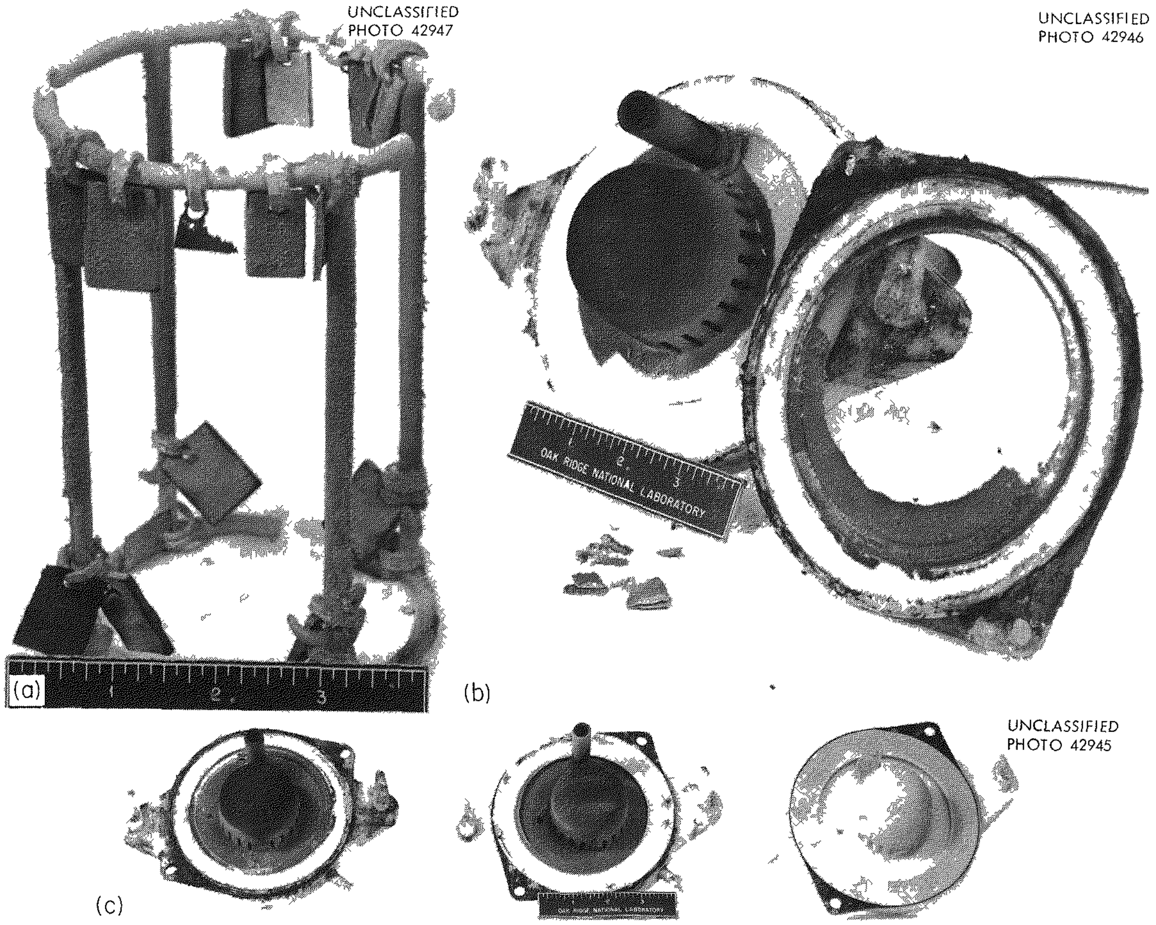

Fig. 6.3. Siliceous deposits on (a) corrosion specimens and rack; (b) Vycor bubble caps; and (c) bubble cap at various stages.

7.0 MATERIALS OF CONSTRUCTION

7.1 Corrosion Rates

Head-end Equipment. Titanium, titanium-6 wt % aluminum-4 wt % vanadium, tantalum, the high-cobalt alloys S-816 and Haynes 21, Zircaloy, and crystal-bar zirconium were tested for corrosion under Darex conditions following promising preliminary corrosion results in the $HCl-HNO_3-UO_2^{++}$ system. The result, confirmed at Idaho (IDO-14479) indicated that titanium will withstand all normal Darex dissolver, condenser, stripper, and feed adjustment conditions. It showed corrosion rates << 1 mil/mo under all process conditions tested (Table 7.1), showed no hydrogen embrittlement when in contact with dissolving uranium metal (Fig. 7.1a), and failed only when the solution was depleted of nitrate and the metal was then attacked by the residual azeotropic HCl. Such a condition would never occur under process conditions. The titanium-aluminum-vanadium alloy showed no advantage over titanium. Tantalum showed negligible corrosion rates under all conditions tested but became slowly embrittled due to hydrogen pickup when held for long times at the potentials of tantalum specimens in contact with dissolving uranium metal (Fig. 7.1b). In the operating Darex dissolver, S-816 and Haynes 21 corrosion rates were < 0.9 and 0.5 mil/mo, respectively, but in simulated dissolver solutions were 6 and 1.5 mils/mo. Crystal-bar zirconium was corroded at rates of 59-69 mils/mo under active dissolver conditions.

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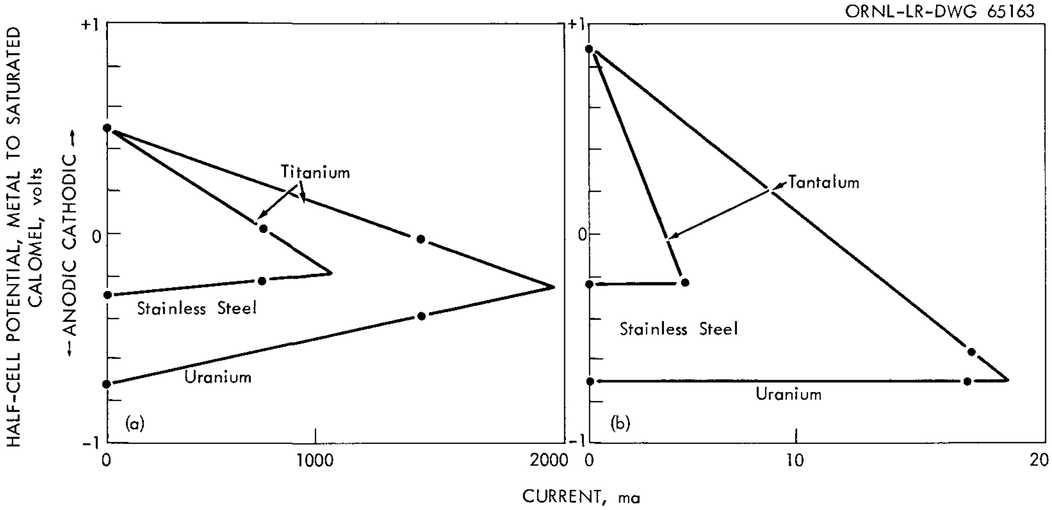

Fig. 7.1. Polarization curves for uranium, type 304 stainless steel, and (a) titanium and (b) tantalum in boiling 5 M HNO_3-2 M HCl.

Welded titanium specimens exposed in operating dissolvers slowly became coated with a hard, green siliceous scale, which was not removed by vigorous scrubbing but was removed readily by boiling with 10% NaOH. Plain, welded, and stressed specimens exposed in the continuous dissolver (Fig. 7.2) for 13 weeks (2008 hr) were removed weekly and treated for 3 hr with boiling 10% caustic, and then put back, after being weighed.

Table 7.1. Corrosion of Candidate Alloys in Various Darex Environments

All temperatures boiling, "gain" = very slight weight gain

	a. Simulated Darex Dissolver Solution (static)					b. Active Darex Systems			c. Simulated Darex Chloride Stripper (batch)		
	Beginning Solution		Midpoint Solution		Final Solution,	Batch		Continuous			
Material	No Ru	100 ppm Ru	No Ru	50 ppm Ru	No Ru	Dissolver		Dissolver	7 M	9 M	10.6 M
Titanium	1320 hr	661 hr	1320 hr	661 hr	661 hr	1839 hr	2483 hr	9 wks	16 wks	19 wks	16 wks
Vapor	0.21	0.33	0.05	0.05	0.01	0.01-0.07	0.02-0.03	0.0	Failed* rapidly	0.0	0.0
Interface	0.45	0.02	0.01	gain	0.0	gain	gain	0.0	Failed* rapidly	0.0	0.0
Liquid	0.77	0.02	0.01	gain	gain	0.03**		0.0	0.0	0.0	0.0
Ti-6 wt % Al-4 wt % V					661 hr			1000 hr			
Vapor					0.06			0.15-0.19			
Interface					0.0						
Liquid					0.0						
S-816	1323 hr	659 hr	1298 hr	639 hr	639 hr	1839 hr					
Vapor	238	2.15	0.40	0.68	0.07	0.52-0.69					
Interface	5.08	5.38	0.94	1.07	0.83	0.73					
Liquid	5.82	6.19	1.10	1.11	0.92	0.81					
Haynes 21	639 hr		639 hr		639 hr	1839 hr		2207 hr			
Vapor	0.32		0.14		0.03	0.24-0.43		0.09			
Interface	0.67		0.35		1.13			0.38			
Liquid	0.81		0.38		1.45	0.35					
Tantalum	1320 hr	661 hr	1320 hr	661 hr	661 hr	1839 hr		2483 hr	9 wks	9 wks	9 wks
Vapor	0.0	0.0	gain	gain	gain	0.01		0.02-0.03	0.0	0.0	gain
Interface	gain	gain	gain	gain	0.1			gain	0.0	gain	0.0
Liquid	gain	gain	gain	gain	0.15				gain	gain	gain
Zircaloy-2					661 hr						
Vapor					0.0						
Interface					0.0						
Liquid					0.0						
Crystal-bar zirconium	637 hr		637 hr	661 hr	637 hr			45 hr			
Vapor	1.43		0.01		gain			67-69			
Interface	1.06		gain	0	0			67-69			
Liquid	1.25		0		0			59-68			

a. Solution Composition, M

	H^+	Cl^-	NO_3^-	Fe^{3+}	Cr^{3+}	Ni^{2+}	U^{6+}
Beg.	7.0	2.0	5.1	0.011	0.003	0.0012	0.004
Mid.	4.0	1.9	4.7	0.55	0.15	0.06	0.20
Final	1.0	1.8	4.5	1.1	0.30	0.12	0.40

b. Solution Composition Changed from 5 M HNO_3-2 M HCl as dissolution proceeded

c. Solution Composition, M

	HNO_3	$UO_2(NO_3)_2$	$Fe(NO_3)_3$	$Cr(NO_3)_3$	$Ni(NO_3)_2$
7 M	7.0	0.40	1.10	0.30	0.12
9 M	9.0	0.40	1.10	0.30	0.12
10.6 M	10.6	0.35	0.97	0.27	0.11

* At 12 hr the corrosion rate was 0.0. Analysis of the solution indicated that all HNO_3 had been destroyed and remaining solution was essentially azeotropic HCl.

** In condenser.

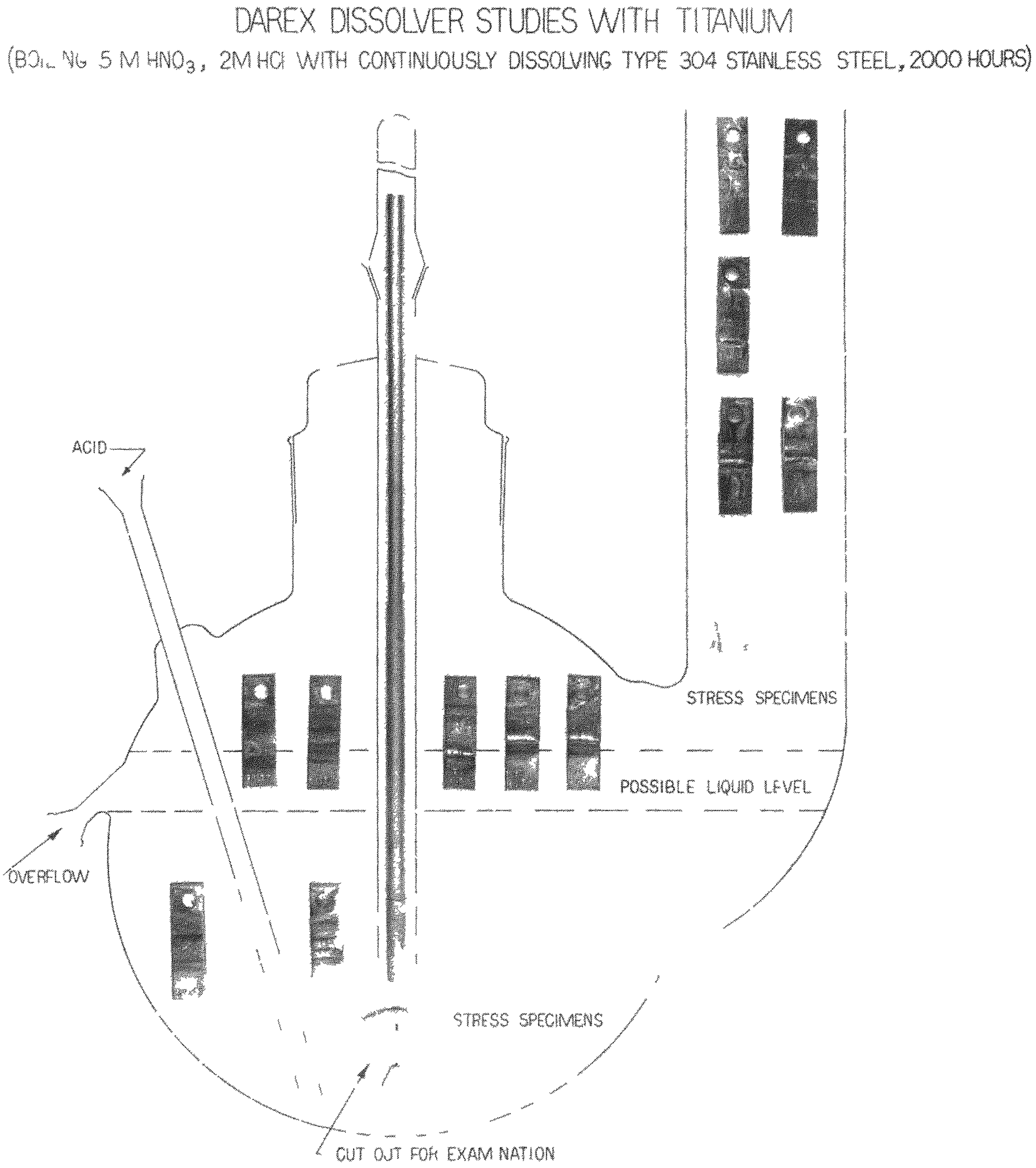

Fig. 7.2. Location of titanium corrosion specimens in 2000-hr continuous Darex dissolution test. Dissolvent: boiling 5 *M* HNO_3-2 *M* HCl.

Weight changes indicated very low corrosion rates in all cases. Metallographic examination showed no localization or crevice-weld attack in either stressed or unstressed specimens. Specimens that were scratched daily with a sharp stainless steel rod to simulate abrasion by fuel elements showed no accelerated attack as a result of such abrasion.

In order to evaluate corrosion under heat-transfer conditions, steam at about 135°C was passed through titanium tubes immersed in solutions under the following conditions:

	(moles/liter)							B.P., °C	Exposure, hr
	H^+	Cl^-	NO_3^-	Fe^{3+}	Cr^{3+}	Ni^{2+}	U(VI)		
Dissolvent	7.0	2.0	5.0	-	-	-	-	-	2049
Beginning	7.0	2.0	5.05	0.01	0.003	0.0012	0.004	-	2000
Middle	4.0	1.89	4.73	0.55	0.15	0.06	0.2	-	2000
Final[a]	4.0	1.0	5.9	0.45	0.13	0.048	0.51	109	3893
Feed adjustment	3.4	trace	12.7	1.62	0.48	0.17	1.35	124	3511, 3647, 3826

[a] These solutions correspond to feed expected from Yankee Atomic fuel; APPR fuel solutions are represented by the beginning and middle solutions.

The only tube that showed any sign of attack was that exposed in the dissolvent, where there was some general roughening of the surface. Average corrosion rates (estimated from measured decrease in thickness of the tube on metallographic sectioning) were 1.5-2 mils/mo for the first 2010 hr, somewhat less than the 4 mils/mo reported by Hanford. A few hairline cracks appeared in one section of tube near the interface after 1040 hr and in the weld metal after 2049 hr, probably because of original imperfections in the metal. Sectioning showed them to be shallow and apparently no cause for concern. This uncontaminated acid represents the most aggressive solution used, and no extended exposure to this solution would ever be encountered in actual processing. A thin white coating, easily removed by water, formed on the immersed portion of this tube. Stressed specimens showed indication of localized attack.

Solution Transfer Lines. The use of type 304L stainless steel pipe to transfer solution from the Darex dissolver is not recommended. Some welded and machined type 304L stainless steel specimens were severely attacked by this solution, while others were attacked very little or not at all. This attack occurred in solution stirred at 6 linear ft/sec and at a temperature as low as 105°F. It appears that temperature, stirring rate, and chloride concentration are important to this active-passive state. For the tests, stainless steel specimens were placed in a synthetic dissolver solution, i.e. 1.2 M HNO_3, 1.75 M HCl, 0.68 M Fe^{3+}, 0.21 M Cr^{3+}, 0.09 M Ni^{++}, and 100 g of U(VI)/liter (all salts added as nitrates) and stirred at 3 and 6 linear ft/sec, at 125°F.

Extraction System. The absence of any evidence of corrosion in specimens of type 347 stainless steel exposed 2 years to solutions containing chloride contamination such as might occur during Purex extraction of uranium from Darex solutions indicated that this steel will be suitable for extraction equipment. Two types of aqueous solutions were used, both 2 M in HNO_3, one high in stainless steel and low in uranium and the other high in uranium and low in stainless steel. Chloride varied from 2 ppm to 1.00 wt %. The aqueous solutions were mixed with an organic phase, 1 vol of TBP + 2 vol of Amsco 125, in a ratio of 2/3. Specimens in the form of disks, coupons stressed to 90% of their yield strength, and coupons bent past their elastic limit into the shape of horseshoes were submerged in the aqueous phase at room temperature.

For the first few weeks the solutions were shaken vigorously several times daily and the specimens were removed daily and examined. After the first few months, the specimens were inspected only at about 6-month intervals, and after 2 years the study was discontinued. No sign of attack was observed on any specimens except a slight brightening of the surfaces. Weight changes were insignificant. No cracking or other localized attack could be found even by metallographic study of the specimens from the solutions with the highest chloride contaminations.

Fission Product Recovery. Neither type 304L nor 347 stainless steel would be recommended for equipment used to extract fission products from the Darex-Purex raffinate. Specimens of these two steels were heavily surface-corroded in 1000 hr exposure (Fig. 7.3) to boiling solutions of the composition expected for such processing, i.e. 3 M HNO_3 containing the equivalent of 60 g of type 304 stainless steel per liter (as chromium, iron, and nickel nitrates) and 0, 400, and 800 ppm of chloride. The specimens had a lengthwise weldment, and half were bent into horseshoe shape and held in tension by keepers of the same material. The specimens were surface ground so that no weld bead remained, but the keepers were not ground and had a transverse weld bead at the apex.

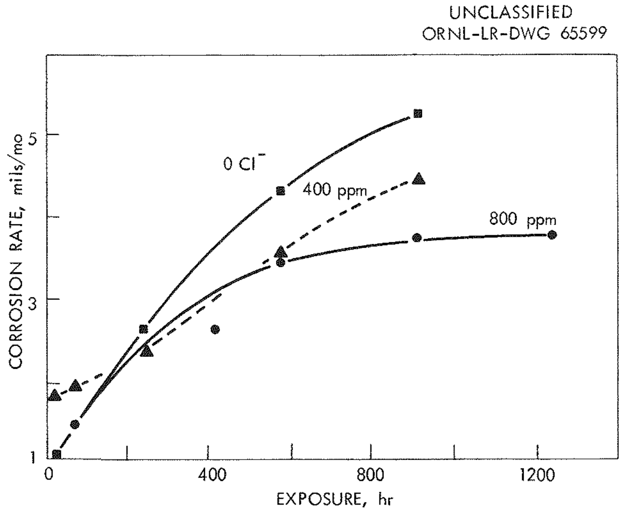

Fig. 7.3. Corrosion of submerged type 347 stainless steel coupons in boiling 3.0 *M* HNO_3 containing metal equivalent to 60 g of type 304L stainless steel per liter and chloride.

There was no stress corrosion cracking, but a knife-line attack in one of the stressed type 347 specimens was so pronounced that the weldment was completely separated from the parent metal. Although both these stainless steels are reasonably resistant to localized attack by such acid, intergranular attack was considerable on all specimens, localized in the heat-affected areas of type 347 specimens and uniformly distributed on the 304L specimens. [redacted] That the Cr(VI) was not responsible for the attack was shown by the presence of less than 5 mg of Cr(VI) per liter in the spent solutions. The high Fe(III) was probably the causative agent.

Waste Disposal. The appreciable intergraular attack on specimens of type 304L stainless steel welded with type 308L rod in simulated Darex-Purex raffinate waste indicated that stainless steel waste tanks will be subject to this type of attack if stainless steel nitrate wastes are stored in them at temperatures as high as 50°C. Welded, unwelded, and stressed specimens were exposed to 5 M HNO_3 containing 1.82 M dissolved stainless steel as nitrates and 0 to 100 ppm of chloride at temperatures of 50, 65, and 80°C for 2000 hr. The stressed specimens showed no indication of localized attack, but all specimens showed grain boundary attack after 500-1500 hr of exposure. The increasing slope of the weight loss-vs-time curve at 80°C (Fig. 7.4) indicates that the attack will continue. This attack was independent of the level of chloride contaminant. Cumulative corrosion rates were:

Temp, °C	Time, hr	Corrosion Rate, mils/mo			
		Welded			Stressed,
		Vapor	Interface	Solution	Solution
80	2132	0.02	0.23	0.40	0.41
		0.02	0.22	0.38	0.41
65	1945	0.01	0.05	0.09	0.10
		0.01	0.05	0.09	0.10
50	2371	0.01	0.03	0.03	0.03
		0.01	0.03	0.04	0.03

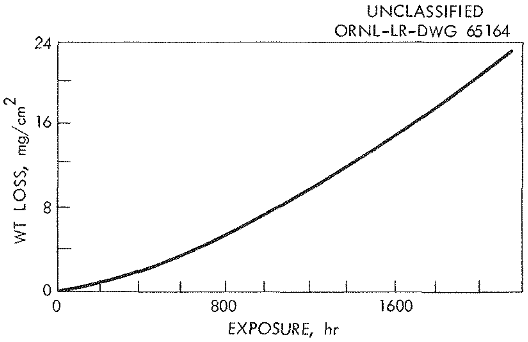

Fig. 7.4. Average weight loss of two welded type 304L stainless steel specimens in simulated Darex-Purex waste solution at 80°C. Solution: 5.0 *M* HNO_3, 1.82 *M* stainless steel, 100 ppm of chloride.

7.2 Overall Heat Transfer Coefficients

For larger scale equipment design the overall heat transfer coefficients for boiling water and the various process solutions were determined in the 10-in.-dia chloride removal vessel. The overall steady-state heat transfer coefficients for boiling H_2O, based on the overhead condensate, for the range of temperature difference $\Delta T = 20 - 55\,^\circ F$ were 300-450 Btu/hr·ft^2·°F. The overall heat transfer coefficient increased with temperature difference as a result of an increase in the convection velocity of the water through the heated tubes. Heat transfer rates for APPR, Yankee Atomic, and Nuclear Ship Savannah fuel solutions were little more than half this, with special stainless steel solutions showing higher values than the other three and approaching the rates for H_2O.

The overall coefficients for the 0.109 in. Ti wall, based on vaporizing acid (mixed and recycle) from APPR and Yankee Atomic type dissolver products, varied from 170-320 Btu/hr·ft^2·°F over a temperature difference (condensing steam to boiling liquid) range of 25-64°F, whereas the coefficients for vaporizing water increased from 340-460 Btu/hr·ft^2·°F over a similar range (Fig. 7.5). There is considerable scatter in the acid data, which may be attributed to the fact that each coefficient was based on the collection of only 1 liter of acid. There was no significant difference between vaporizing mixed acid (HNO_3 + HCl) and recycle acid (HNO_3 + trace chloride) from either the APPR or Yankee Atomic dissolver products, although the APPR dissolver product had a greater tendency to foam. The coefficients for the recycle acid (9.2-14 $\underline{M}$ HNO_3) recovery step for run APPR-66 were significantly higher than for run 64 (Table 7.2); the air sparging used in this portion of run APPR-66 apparently increased the coefficient by increasing the turbulence. In run NSS-69 overall heat transfer coefficients were 193 to 272 Btu/hr·ft^2·°F for temperature differences of 22.2-42.4°F (Table 7.3).

Special Stainless Steel. Overall heat transfer coefficients were 310-428 Btu/hr·ft^2·°F during runs 8-12 and 15 over the temperature difference range 30-68°F (Table 7.4, Fig. 7.6). The heating medium was condensing steam, and the titanium wall thickness was 0.109 in. Apparently there was a dependency of U on ΔT which may not apply above $\Delta T = 60\,^\circ F$. The total H^+ of the acid condensate is noted for each point in Fig. 7.6. All these points were derived from data for the vaporization of 1 liter of mixed acid (HNO_3-HCl), but in the absence of heat-of-vaporization data for the ternary system, calculations were made from the heat of vaporization for nitric acid at the same total acidity.

Table 7.3. Overall Heat Transfer Coefficients for 10-in.-dia Titanium Feed Adjustment Tank for Darex Run NSS-69

H^+, M	Density, g/ml	Time, min/liter	Mass Rate, lb/hr	L_v, Btu/lb	ΔT, °F	U, Btu/hr·ft²·°F
0.37	1.011	7.92	16.8	950	33.3	240
0.45	1.013	8.25	16.2	945	31.1	246
0.85	1.027	9.25	14.7	920	31.8	213
2.70	1.089	9.42	15.3	850	32.1	203
4.80	1.154	7.83	19.5	775	36.4	208
5.97	1.191	6.42	24.5	727	41.9	213
6.62	1.210	6.05	26.4	715	42.3	223
7.27	1.229	6.33	25.6	685	42.4	207
7.90	1.246	6.75	24.4	665	41.2	197
8.60	1.265	6.92	24.1	645	40.3	193
9.10	1.278	6.92	24.4	625	39.6	194
10.15	1.305	8.47	20.4	590	23.8	252
11.00	1.325	7.55	23.2	565	27.0	243
11.50	1.335	7.47	23.6	555	27.4	239
12.15	1.349	6.83	26.1	535	29.2	239
12.60	1.359	6.00	29.9	520	34.2	228
13.05	1.368	6.00	30.1	510	33.3	231
13.50	1.377	7.50	24.2	500	22.2	272

Table 7.4. Heat Transfer Data for Runs V-8 - V-13

H^+, M	Density, g/ml	Time, min/liter	M, lb/hr	T_s, °F	T_{bl}, °F	ΔT, °F	L_v, Btu/lb	U, $\frac{\text{Btu}}{\text{hr}\cdot\text{ft}^2\cdot{}^\circ\text{F}}$
V-8								
5.15	1.166	5.12	30.0	266.7	213.7	35	760	326
5.50	1.176	4.6	33.7	275.4	233.6	41.8	750	310
V-9								
4.34	1.140	4.5	33.4	270.5	229.9	40.6	788	324
4.60	1.148	3.17	47.8	283.8	232.7	51.1	777	363
4.93	1.158	2.75	55.6	295	237.2	57.8	770	371
6.05	1.193	2.58	61.0	305	240.8	64.2	730	347
6.95	1.219	2.17	74.1	311.7	243.5	68.2	700	380
V-10								
2.1	1.068	3.78	37.2	270.5	228.2	42.3	875	384
4.6	1.148	3.83	39.5	274.1	230.0	44.1	777	348
4.45	1.144	2.92	51.6	286.7	231.7	55.0	778	365
4.75	1.152	2.57	59.1	292.3	234.5	57.8	775	397
5.6	1.180	2.42	64.3	297.7	240.0	57.7	740	412
7.0	1.221	2.25	71.6	302.5	244.4	58.1	695	428
V-11								
1.85	1.060	4.17	33.6	268.3	228.2	40.1	885	371
4.3	1.139	3.58	42.0	277.5	230	47.5	788	349
4.45	1.144	2.75	55.0	289.5	232.7	56.8	778	376
4.85	1.156	2.38	64.1	293.7	235.4	58.3	771	424
5.65	1.181	2.40	65	297.1	240.8	56.3	740	427
7.00	1.221	2.30	70.1	302.5	244.4	58.1	695	419
V-12								
3.05	1.099	4.08	35.6	274.1	228.2	45.9	838	325
4.4	1.142	3.65	41.3	280.6	230.4	50.2	777	320
4.5	1.145	2.78	54.5	286.7	231.8	54.9	776	385
4.85	1.156	2.57	59.4	292.3	236.3	56.0	771	409
V-13								
4.4	1.142	5.6	26.9	258.8	228.2	30.6	777	342
4.2	1.136	4.75	31.6	266.7	230.0	36.7	790	340

8.0 BIBLIOGRAPHY

The information in this report is compiled from a number of sources. Included are all the pertinent and significant data from the following reports:

Chemical Technology Division Semiannual and Annual Reports

1. For Period Ending March 31, 1955, ORNL-1881.
2. For Period Ending Sept. 30, 1955, ORNL-2000.
3. For Period Ending March 31, 1956, ORNL-2079.
4. For Period Ending Aug. 31, 1956, ORNL-2169.
5. For Period Ending Aug. 31, 1957, ORNL-2392.
6. For Period Ending Aug. 31, 1959, ORNL-2788.
7. For Period Ending Aug. 31, 1958, ORNL-2576.

Power Reactor Fuel Processing Status Reports

8. Preliminary Report, ORNL-CF-56-5-48, May 14, 1956.
9. For June 1956, ORNL-CF-56-6-101.
10. For July 1956, ORNL-CF-56-7-101.
11. For August 1956, ORNL-CF-56-8-101 (Cf. EPS-X-258, RT-230, April 6, 1956).
12. For September 1956, ORNL-CF-56-9-101.
13. For October 1956, ORNL-2210.
14. For November 1956, ORNL-2228.
15. Status Report and Program Proposals for ORNL, ORNL-CF-56-12-95, (Dec. 29, 1956).

Chemical Technology Division Monthly Progress Reports

16. For January, 1957, ORNL-2251.
17. For February, 1957, ORNL-2270.
18. For March, 1957, ORNL-2307.
19. For April, 1957, ORNL-2324.

20. For May, 1957, ORNL-2361.

21. For June, 1957, ORNL-2362.

22. For July, 1957, ORNL-2385.

23. For August, 1957, ORNL-2406.

24. For September, 1957, ORNL-2416.

25. For October, 1957, ORNL-2417.

26. For November, 1957, ORNL-2447.

27. For December, 1957, ORNL-2468.

Chemical Technology Division, Unit Operations Section Monthly Progress Reports

28. For June 1956, ORNL-CF-56-6-177.

29. For July 1956, ORNL-CF-56-7-150.

30. For January 1958, ORNL-CF-58-1-137.

31. For February 1958, ORNL-CF-58-2-139.

32. For March 1958, ORNL-CF-58-3-71.

33. For April 1958, ORNL-CF-58-4-123.

34. For May 1958, ORNL-CF-58-5-50.

35. For June 1958, ORNL-CF-58-6-85.

36. For August 1958, ORNL-CF-58-8-59.

37. For September 1958, ORNL-CF-58-9-62.

38. For October 1958, ORNL-CF-58-10-90.

39. For November 1958, ORNL-CF-58-11-93.

40. For December 1958, ORNL-CF-58-12-35.

41. For January 1959, ORNL-CF-59-1-74.

42. For February 1959, ORNL-CF-59-2-45.

43. For March 1959, ORNL-CF-59-3-61.

44. For April 1959, ORNL-CF-59-4-47.

45. For May 1959, ORNL-CF-59-5-47.

46. For June 1959, ORNL-CF-59-6-63.

47. For July 1959, ORNL-CF-59-7-58.

48. For August 1959, ORNL-CF-59-8-76.

49. For September 1959, ORNL-CF-59-9-69.

50. For October 1959, ORNL-CF-59-10-77.

51. For November 1959, ORNL-CF-59-11-54.

52. For December 1959, ORNL-CF-59-12-49.

53. For January 1960, ORNL-CF-60-1-49.

54. For February 1960, ORNL-CF-60-2-56.

55. For April 1960, ORNL-CF-60-4-37.

56. For May 1960, ORNL-CF-60-5-58.

57. For June 1960, ORNL-CF-60-6-11.

58. For July 1960, ORNL-CF-60-7-46.

59. For November 1960, ORNL-CF-60-11-38.

60. For December 1960, ORNL-CF-60-12-28.

Topical Reports

61. R. E. Blanco, Processing of Power Reactor Fuels, *Nuclear Sci. Eng.* 1:409 (1956).

62. J. R. Flanary et al., Chemical Development of the 25-TBP Process, ORNL-1993, (Sept. 24, 1956).

63. F. L. Culler et al., An Analysis of Power Reactor Fuel Reprocessing, ORNL-2265 (March 7, 1957).

64. M. L. Hyman and J. J. Perona, Darex Process Demonstration by MIT Practice School Studends, ORNL-CF-57-3-91 (March 8, 1957)(Cf. EPS-X-299, KT-282, March 22, 1957).

65. H. E. Goeller, Bibliography: Nuclear Reactor Fuel Processing, ORNL-CF-57-3-153 (March 12, 1957).

66. K. J. Fritz, Preliminary Aqua Regia Dissolution Studies, ORNL-CF-57-7-32 (July 10, 1957).

67. R. J. Beaver et al., Specifications for Army Package Power Reactor (APPR-1) Fuel and Control Rod Components, ORNL-2225 (July 24, 1957).

68. R. E. Blanco and C. D. Watson, Reactor Handbook, Vol. IV, Fuel Reprocessing. Chapter 3, Headend for Solid Fuels (ORNL-CF-57-9-38, September 1957).

69. M. L. Hyman, Laboratory Development of the Darex Process, ORNL-2239 (Sept. 18, 1957).

70. W. E. Clark and A. H. Kibbey, Darex Flowsheet (Batch Operations), ORNL-CF-57-9-73 (Sept. 18, 1957).

71. F. G. Kitts, A Continuous Darex Process Flowsheet, ORNL-CF-57-10-89 (Oct. 10, 1957).

72. F. G. Kitts and J. J. Perona, Preliminary Study of Pre-Solvent Extraction Treatment of Stainless-Steel-Uranium Fuels with Dilute Aqua Regia, ORNL-CF-57-6-125 (Rev)(Oct. 11, 1957).

73. J. R. Flanary and J. H. Goode, Darex Flowsheet (Batch Operations). Parts V and VI. Solvent Extraction, ORNL-CF-57-11-77 (Nov. 5, 1957).

74. R. C. Reid et al., Vapor-Liquid Equilibria of Dilute Nitric, Hydrochloric Acid-Nitric Acid-Water Solutions, Ind. Eng. Chem., 49:1307-10 (1957).

75. P. D. Miller et al., Evaluation of Container Materials for Zircex and Darex Nuclear Fuel Recovery Processes, BMI-1242 (Dec. 11, 1957).

76. L. P. Bupp, Monthly Report, Chemical Research and Development Operation, HW-54760C (January 1958).

77. J. R. Flanary and J. H. Goode, Darex Process: Batch Dissolution and Chloride Removal Steps for Yankee Atomic Fuel, ORNL-CF-58-2-135 (Feb. 21, 1958).

78. J. R. Flanary and J. H. Goode, Preparation of Solvent Extraction Feeds from Irradiated Yankee Atomic Fuel Specimens by the Batch Darex and Sulfex Processes, ORNL-CF-58-4-110 (April 1958).

79. T. A. Gens, Chlorine Removal from the Darex Off-Gas, ORNL-CF-58-9-83 (Sept. 17, 1958).

80. F. L. Culler and R. E. Blanco, Dissolution and Feed Preparation for Aqueous Radiochemical Separation Processes, P/1930, Proc. 2nd UN International Conf. on the Peaceful Uses of Atomic Energy, Geneva, 1958, Vol. 17, p. 259, UN, New York.

81. J. R. Flanary and J. H. Goode, Sand Filtration of Foreign Research Reactor Feed Solutions, ORNL-CF-58-10-113 (Oct. 3, 1958).

82. F. C. Kitts and B. C. Finney, Development of Batchwise and Semi-continuous Flowsheets Using 61 wt % HNO_3, ORNL-CF-58-11-106 (Nov. 19, 1958).

83. F. C. Kitts, B. C. Finney, and J. H. Goode, The Darex Process: Progress since the 1958 Geneva Conference, ORNL-CF-58-11-82 (November 1958).

84. J. J. Shefcik and A. M. Platt, Preliminary Darex Flowsheet, HW-58600 (Dec. 18, 1958).

85. J. R. Flanary and J. H. Goode, Recovery of Enriched Uranium from UO_2-Stainless Steel Fuel Elements by Solvent Extraction, Ind. Eng. Chem. 51:23 (1959)(ORNL-CF-58-4-2).

86. F. R. Bruce, R. E. Blanco, and J. C. Bresee, Recent Developments in Feed Preparation and Solvent Extraction, presented at 5th Nuclear Congress, Cleveland, Ohio, April 7, 1959 (ORNL-CF-58-11-91).

87. B. C. Finney and F. G. Kitts, Darex Processing of APPR Fuel: Effect of Acidity and Gas Sparging on Rate of Chloride Removal from Dissolver Product during Refluxing, ORNL-2753 (July 20, 1959).

88. C. L. Peterson, P. D. Miller, J. D. Jackson, and F. W. Fink, Construction Materials for Various Head-End Processes for the Aqueous Reprocessing of Spent Fuel Elements, BMI-1375 (Aug. 28, 1959).

89. O. R. Klemens, Corrosion of Titanium in the System: HNO_3-HCl-H_2O, IDO-14479 (Oct. 2, 1959).

90. R. E. Blanco et al., Chemical Processing of Power and Research Reactor Fuels at ORNL in Proceedings of the AEC Symposium for Chemical Processing of Irradiated Fuels, Richland, Washington, October 1959, TID-7583 (also ORNL-CF-59-12-70).

91. L. M. Ferris, A. H. Kibbey, and K. S. Warren, Dissolution of Insolubles from Darex and Sulfex Processes, ORNL-CF-60-6-70, (June 1960).

92. C. Orr, Jr., M. C. Kordecki, and C. T. Young, A Study of Equilibria Involved Between Darex Off-Gases and Solutions, Georgia Inst. Tech., Final Technical Report Project No. A427 (July 1960).

93. A. F. Messing and O. C. Dean, Removal of Silica from Darex Dissolver Solutions, ORNL-3000 (Dec. 27, 1960).

94. T. A. Gens, Measurements of Hazardous Components of Darex Process Off-Gas, ORNL-3022 (April 1961).

95. J. H. Goode, Disposition of Boron "Poison" During Darex Dissolution and Chloride Removal, ORNL-CF-61-11-36 (November 1961).

9.0 APPENDIX

Table A.1. Batch Chloride Removal Runs with 95 wt % HNO_3 by the Reflux Flowsheet

APPR Prototype Fuel

APPR	Dissolution Product			Acid Waste			22.5 M HNO_3	Mixed Acid			22.5 M HNO_3	Acidified Concentrate			Re-flux	HNO_3 Recovery (Trace Cl^-)		Solvent Extraction Feed		
Run No.	Vol, ml	H^+, M	Cl^-, M	Vol, ml	HNO_3, M	Cl^-, M	Added, ml	Vol, ml	HNO_3, M	Cl^-, M	Added, ml	Vol, ml	HNO_3, M	Cl^-, M	Time, hr	Vol, ml	HNO_3, M	Vol, ml	HNO_3, M	Cl, ppm
1	940	2.97	1.65	150	0.26	0.09	0	530	2.22	0.86	200	400	11.1	1.87	0	200	16.06	650	2.90[a]	0.24 M
2	1000	3.30	1.77	150	0.29	0.12	0	625	2.94	0.92	225	~440	-	-	2	200	15.7	800	0.68	291
4	1000	2.44	1.76	600	1.3	0.57	250	300	12.9	0.17	-	-	-	-	-	-	-	1000	0.75	0.21 M
5	1000	2.44	1.76	200	0.37	0.14	200	760	7.13	0.88	200	~340	8.8[b]	0.014	3	-	-	1000	2.92	36
6	970	2.44	1.76	175	0.40	0.12	100	650	5.22	1.12	200	~420	10.16[b]	0.02	3	-	-	720	4.45	35
7	960	3.09	1.66	-	-	-	150	860	4.67	1.0	200	~440	10.9[b]	0.01	2	-	-	1000	3.34	35
8	960	3.09	1.66	-	-	-	170[c]	870	4.35	0.96	180[c]	~450	9.1	1.24	2	-	-	1000	3.41	44
9	980	3.05	1.74	-	-	-	170	870	5.10	0.99	180	~430	9.7	0.90	2	-	-	850	4.88	8
10	960	3.05	1.74	-	-	-	170	870	4.92	1.19	180	~400	10.1	0.32	2	-	-	835	4.83	6
11	1900	3.14	1.66	-	-	-	300	1700	4.93	0.87	300	~730	10.3	1.42	2	-	-	1900	3.24	400
14	1940	3.2	1.7	-	-	-	300	1720	4.9	1.3	300	~715	10.4	0.43	2[d]	-	-	2230	2.9	148
39	980	3.03	1.74	-	-	-	225[e]	800	5.0	1.2	175[e]	~570	10.0	1.07	2[f]	75	14.1	1120	3.47	35
41	980	3.03	1.74	-	-	-	225[g]	800	4.97	1.13	165[g]	~570	9.82	1.06	2[f]	75	13.5	1120	3.21	160

[a] Added 450 ml of 2.5 M HNO_3

[b] After 1 hr reflux

[c] C.P. HNO_3 21.2 M

[d] Downdraft condenser

[e] 92-1/2 wt % HNO_3 (21.85 M)

[f] 0.25 scfh air sparge during reflux

[g] 90 wt % HNO_3 (21.3 M)

Table A.2. Semicontinuous Chloride Removal Runs by the Reflux Flowsheet with 95 wt % HNO_3

APPR	Dissolution Product				22.5 M	HNO_3	Mixed Acid Recovery						Vol	Acidified Concentrate			Re-flux	Solvent Extraction Feed		
	Vol	Composition		Vol Me-	Vol	Vol	Concurrent W/DP			After HNO_3 Addition			22.5 M HNO_3							
Run No.	Chgd, ml	H^+, M	Cl^-, M	tered, ml	Chgd, ml	Added, ml	Vol, ml	HNO_3, M	Cl^-, M	Vol, ml	HNO_3, M	Cl^-, M	Add, ml	Vol, ml	HNO_3, M	Cl^-, M	Time, hr	Vol, ml	HNO_3, M	Cl^-, ppm
13	1250	2.77	1.64	2450	250	350	2700	3.3	1.15	600	11.9	0.38	600	1400	10.36	0.73	2	3700	2.9	25
12	1250	2.78	2.25	2550	250	350[a]	2600	2.8	1.1	850	10.3	0.6	600	1320	12.3	1.66	2	3700	1.93	0.09 M
15	1200	3.32	1.74	2630	240	360	2725	3.6	1.3	740	11.3	0.4	600	1320	9.61	0.66	2	3500	2.91	150
16	850	3.51	1.52	1905	170	255	2070	3.4	1.1	410	12.65	0.25	425	950	b		2	3130	2.90	35
17	930	3.28	1.74	1770	186	270	1950	3.4	1.15	400	11.7	0.4	480	1140	10.85	0.82	2	3130	3.35	600

[a] Continuous addition after all dissolution product added.

[b] Not sampled.

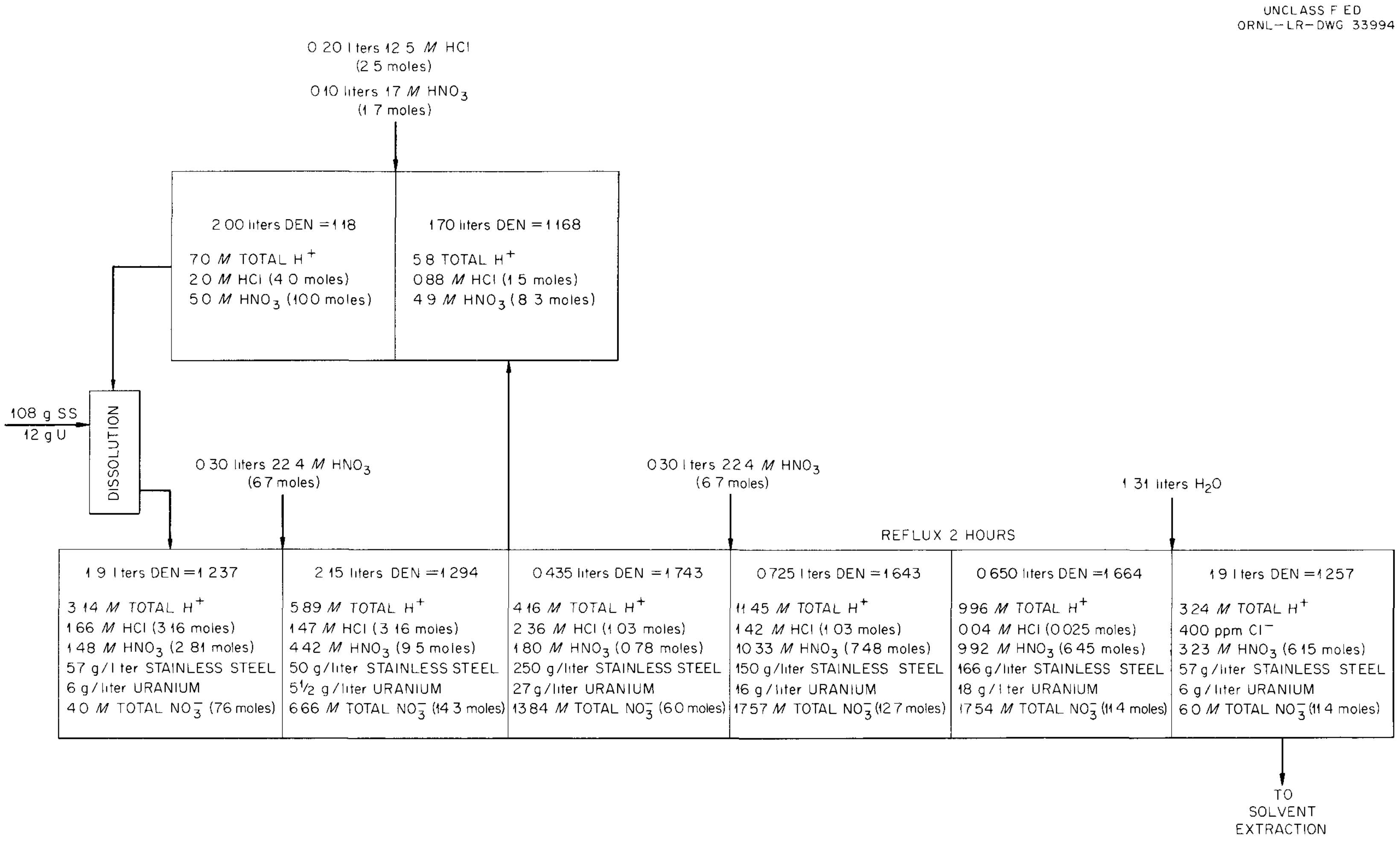

Fig. A.1. Data for batch Darex Run APPR-11.

Table A.3. Semicontinuous Chloride Removal Runs by the Reflux Flowsheet with 61 wt % HNO_3

APPR	Dissolution Product			Acid Waste			13.3 M HNO_3	Mixed Acid			13.3 M HNO_3	Acidified Concentrate			Re-flux		Mixed Acid (Trace Cl^-)		Solvent Extraction Feed		
Run No.	Vol, ml	H^+, M	Cl^-, M	Vol, ml	HNO_3, M	Cl^-, M	Added, ml	Vol, ml	HNO_3, M	Cl^-, M	Added, ml	Vol, ml	HNO_3, M	Cl^-, M	Time, hr	7-ℓ/hr Sparge	Vol, ml	HNO_3, M	Vol, ml	HNO_3, M	Cl^-, ppm
20	2000	~2.6	1.65	450	0.4	0.1	300	1450	4.85	0.95	800	1175	7.07	1.65	4	-	300	10.2	2300	2.07	3100
21	1955	~3.0	1.75	450	0.6	0.25	475	1500	5.45	1.05	800	~1200	8.58	0.87	2	-	200	10.3	2250	3.6	3800
22	2000	~3.00	1.75	-	-	-	400	1970	4.15	1.05	1000	~1400	~9.0	0.95	2	-	-	-	2300	5.5	4300
23	1400	3.05	1.75	200	0.68	0.47	280	1100	3.9	1.1	600	~900	8.66	0.37	2	O_2	200	10.6	1600	3.42	172
24	1400	3.05	1.75	300	0.64	0.26	350	1070	4.7	1.0	600	~900	9.28	0.30	2	Air	200	10.8	1600	3.8	150

Table A.4. Batch Chloride Removal Runs by the Reflux Flowsheet with 61 wt % HNO_3

APPR	Dissolution Product			Acid Waste			13.3 M HNO_3	Mixed Acid			13.3 M HNO_3	Acidified Concentrate			Re-flux	Air Sparge	Mixed Acid (Trace Cl^-)		Solvent Extraction Feed		
Run No.	Vol, ml	H^+, M	Cl^-, M	Vol, ml	HNO_3, M	Cl^-, M	Added, ml	Vol, ml	HNO_3, M	Cl^-, M	Added, ml	Vol, ml	HNO_3, M	Cl^-, M	Time, hr	Rate, ℓ/hr	Vol, ml	HNO_3, M	Vol, ml	HNO_3, M	Cl^-, ppm
25	1400	3.05	1.75	300	0.52	0.15	350	1090	4.85	1.2	600	~900	9.52	0.06[a]	1.5	7	~250	-	1600	-	250
26	1400	3.05	1.75	300	0.5	0.2	300	1060	4.75	1.2	600	~900	~9.0	0.4	2	7	220	11.0	1600	3.49	149
27	1400	3.05	1.75	250	0.35	0.35	250	1000	3.75	1.3	600	~900	9.16	0.38	2	7	300	10.5	1600	2.80	218
28	1400	3.05	1.75	250	0.4	0.2	250	1060	4.2	1.27	600	~915	~9.0	0.05[b]	2	7	250	11.0	1600	3.26	125
29	1200	3.05	1.75	250	0.79	0.19	500	1100	5.95	0.95	900	~1200	11.1	0.007	1	7	900	13.0	1370	1.1	50
34	1400	3.19	1.73	400	0.35	0.15	850[c]	1250	6.95	0.95	-	~560	6.5	0.75	2	-	-	-	1600	2.34	5000
38	980	3.01	1.66	175	0.3	0.2	595	800	5.0	1.1	-	~600	8.1	0.086	2	7	100	9.1	1120	3.20	580
45	900	2.92	1.75	200	0.55	0.35	800[c]	800	5.65	1.1	530	~1220	11.8	0.12	2	7	830	12.2	990	3.75	35
46	900	2.92	1.75	200	0.4	0.2	820[d]	820	4.88	0.97	550	~1240	11.46	0.06	2	7	820	12.0	1000	4.08	37

[a] After 0.5 hr reflux.

[b] After 1 hr reflux.

[c] Continuous addition.

[d] Continuous addition of 12.2 M HNO_3.

Table A.5. Batch Chloride Removal Runs by the Reference Flowsheet in 4-in.-dia Pyrex

No Air Sparge

Run No.	Condenser	Dissolution Product[c]			Acid Waste			At Constant Level: 12 M HNO_3 Added, ℓ	At Constant Level: Aqua Regia Recycle			13.3 M HNO_3 Added, ℓ	Acidified Concentrate			Reflux Time, hr	Recycle HNO_3 (trace Cl^-)		Solvent Extraction Feed		
		Vol, ℓ	H^+, M	Cl^-, M	Vol, ℓ	HNO_3, M	Cl^-, M		Vol, ℓ	HNO_3, M	Cl^-, M		Vol, ℓ	HNO_3, M	Cl^-, M		Vol, ℓ	HNO_3, M	Vol, ℓ	HNO_3, M	Cl^-, ppm
APPR-51	UPDR	5.4	2.92	1.75	1.5	0.45	0.20	4.7	4.7	5.6	1.2	3.0	6.8	11.0	0.19	2	4.7	12.0	6.2	2.33	28
APPR-52	UPDR	5.4	2.92	1.75	1.5	0.35	0.20	4.7	4.7	5.55	0.9	3.3	7.1	11.1	0.12	2	4.7	12.0	6.2	2.91	33
APPR-53	UPDR	5.4	2.92	1.75	1.5	0.47	0.20	4.7	4.7	5.7	1.1	3.3	7.1	11.3	0.10	-	4.6	12.0	6.2	3.04	51
APPR-54	UPDR	5.4	2.92	1.75	1.5	0.40	0.25	4.7	4.7	5.8	1.0	3.3	7.1	11.3	0.10	-	4.7	12.1	6.2	2.29	48
APPR-55	UPDR	5.4	2.92	1.75	1.5	0.41	0.22	4.7	4.7	5.8	1.0	3.3	7.1	11.3	0.12	-	4.7	12.1	6.2	2.40	40
APPR-56	UPDR	5.4[a]	2.92	1.75	1.5	0.35	0.20	4.7	4.7	5.7	1.0	3.3	7.1	9.9	0.20	-	4.7	12.1	6.2	3.07	39
APPR-65	UPDR	5.4	2.92	1.75	1.5	0.35	0.25	4.7	4.7	5.35	1.05	3.3	7.1	11.1	0.12	-	4.7	11.6	6.2	3.52	154
APPR-67[b]	UPDR	5.4	2.92	1.75	1.5	0.37	0.23	4.7	4.7	5.55	1.1	3.3	7.1	11.3	0.062	-	4.7	11.7	6.2	3.93	70
								Batch 13.3 M HNO_3													
V-5	DWNDR	6.0	4.31	1.65	-	-	-	3.5	5.2	4.0	1.1	-	4.0	9.7	0.004	-	-	-	12.0	3.23	40
V-6	DWNDR	6.0	4.31	1.65	-	-	-	2.6	4.5	3.4	1.4	-	4.0	8.4	0.006	-	-	-	12.0	2.80	71
V-7	DWNDR	6.0	4.31	1.65	1.0	1.18	1.17	3.0	5.0	5.18	0.92	-	2.75	9.1	0.004	-	-	-	8.3	3.03	~40

[a] Added 80 ml of sodium silicate solution equivalent to 400 g of SiO_2 per liter.

[b] Titanium present in vapor phase.

[c] Contained ~60 g per liter total metals.

Table A.6. Batch Chloride Removal Runs by the Reflux Flowsheet with 13.3 M HNO_3 in 4-in.-dia Pyrex

APPR Run No.	Condenser Operation	Dissolution Product[e]			Waste Acid			13.3 M HNO_3 Added, ℓ	Air Sparge Rate, ℓ/min	Mixed Acid			13.3 M HNO_3 Added, ℓ	Acidified Concentrate			Reflux Time, hr	Mixed Acid (trace Cl^-)		Solvent Extraction Feed		
		Vol, ℓ	H^+, M	Cl^-, M	Vol, ℓ	HNO_3, M	Cl^-, M			Vol, ℓ	HNO_3, M	Cl^-, M		Vol, ℓ	HNO_3, M	Cl^-, M		Vol, ℓ	HNO_3, M	Vol, ℓ	HNO_3, M	Cl^-, ppm
30	UPDR	10.0	3.04	1.75	1.8	0.48	0.32	1.8	-	7.5	4.3	1.5	4.3	6.5	8.43	0.09[a]	1.5	1.8	10.4	11.5	3.1	960
31	UPDR	10.0	3.34	1.66	2.0	0.64	0.50	1.8	1[b]	7.5	4.55	1.1	4.0	6.1	8.99	0.67	2	1.6	11.0	11.5	2.77	135
32	DWNDR	10.0	3.17	1.67	2.0	0.75	0.45	1.8	1[b]	7.5	4.2	1.2	4.0	6.1	8.91	0.58	2	1.7	11.3	11.5	2.81	330
33	DWNDR	10.0	3.19	1.73	2.0	0.53	0.32	1.8	-	7.5	4.43	1.57	4.0	6.1	9.08	0.58	2	1.7	11.2	11.5	2.92	565
35	DWNDR	10.0	2.98	1.74	2.0	0.48	0.22	1.8	1[c]	7.5	4.18	1.37	4.0	5.1[d]	7.76	0.41	2	2.0	10.2	11.5	2.43	1200
37	DWNDR	10.0	3.01	1.66	2.0	0.35	0.25	1.8	2[c]	7.5	4.15	1.45	4.3	6.3	9.15	0.76	2	1.9	10.4	11.5	3.18	480
44	UPDR	10.0	2.92	1.75	2.0	0.50	0.25	1.8	2[c]	7.5	4.25	1.70	4.0	6.1	9.36	0.58	2	1.8	10.7	11.5	2.92	200
47	UPDR	10.0	2.92	1.75	2.0	0.40	0.25	1.8	2[c]	7.5	4.10	1.45	4.0	6.1	9.21	0.56	2	1.9	10.9	11.5	2.87	225
42	UPDR	10.0	2.92	1.75	2.0	0.35	0.25	1.8	1[c]	7.5	4.17	1.53	4.0	6.1	8.97	0.80	2	2.0	10.2	11.5	2.8	309
43	UPDR	10.0	2.92	1.75	2.0	0.47	0.20	1.8	-	7.5	4.15	1.55	4.0	6.1	8.88	0.83	2	1.9	10.8	11.5	3.1	351
48	UPDR	10.0	2.92	1.75	2.0	0.45	0.25	1.8	-	7.5	4.35	1.45	4.0	6.1	9.26	0.82	2	1.9	10.7	11.5	2.9	510
49	UPDR	10.0	2.92	1.75	2.0	0.45	0.25	1.8	-	7.5	4.2	1.50	4.0	6.1	8.98	0.80	2	1.9	10.6	11.5	2.9	590
50	UPDR	10.0	2.92	1.75	2.0	0.43	0.27	1.8	-	7.5	4.15	1.45	4.0	6.1	8.77	0.62	2	1.9	10.7	11.5	2.7	320

[a] After 1.5 hr reflux.

[b] During mixed acid withdrawal and reflux.

[c] During reflux.

[d] One liter of mixed acid (trace Cl^-) withdrawn prior to reflux.

[e] Contained ~60 g per liter total metals.

Table A.7. Chloride Removal by the Reference Flowsheet in a 10-in.-dia Titanium Vessel

									At Constant Level													
	Dissolution Product					Acid Waste				Aqua Regia Recycle				Acidified Concentrate				Recycle HNO_3 (trace Cl^-)		Solvent Extraction Feed		
Run No.	Vol, ℓ	H^+, M	Cl^-, M	U, g/ℓ	SS, g/ℓ	Vol, ℓ	HNO_3, M	Cl^-, M	12 M HNO_3 Added, ℓ	Vol, ℓ	HNO_3, M	Cl^-, M	13.3 M HNO_3 Added, ℓ	Vol, ℓ	HNO_3, M	Cl^-, M	Reflux Time, hr	Vol, ℓ	HNO_3, M	Vol, ℓ	HNO_3, M	Cl^-, ppm
APPR Fuel																						
APPR-57	10.8	2.92	1.75	5.5	55	3.0	0.45	0.15	9.4	9.4	5.7	0.65	6.6	~14.4	11.9	0.07	-	9.4	11.9	12.4	3.72	423
APPR-58	10.8	2.92	1.75	5.5	55	3.0	0.92	0.33	8.7	8.7	6.8	0.70	6.6	~14.4	11.0	0.06	-	9.4	12.1	12.4	2.32	206
APPR-59	10.8	2.92	1.75	5.5	55	3.0	0.63	0.27	9.4	9.4	5.68	0.67	6.6	~14.4	11.13	0.14	-	9.4	12.0	12.4	3.23	235
APPR-60	8.7	2.92	1.75	5.5	55	2.4	0.50	0.25	7.5	7.5	5.7	0.75	5.3	~11.6	10.86	0.30	-	7.5	11.9	9.8	3.53	845
APPR-63	8.7	2.92	1.75	5.5	55	2.4	0.55	0.20	7.5	7.5	5.9	0.65	5.3	~11.6	11.44	0.18	2	7.5	11.9	9.8	4.04	730
APPR-64	10.8	2.92	1.75	5.5	55	3.0	0.55	0.25	9.4	9.4	5.65	0.65	6.6	~14.4	11.28	0.16	-	9.4	12.0	12.4	3.18	306
APPR-66	8.7	2.92	1.75	5.5	55	2.4	0.40	0.20	7.5	7.5	5.35	0.70	5.3	~11.6	11.02	0.22	2[a]	7.5	11.6	9.8	3.27	70
Yankee Atomic and NSS Fuel																						
YA-61	10.8	2.3	1.1	130	35	3.0	0.25	0.10	9.4	9.4	5.47	0.53	5.0	~12.8	11.12	0.14	-	9.4	12.2	10.8	1.38	440
YA-62	10.8	3.07	1.25	149	40	3.0	0.75	0.25	9.4	9.4	6.55	0.55	5.45	~13.25	11.0	0.076	-	9.4	12.3	10.8	2.02	1410
YA-68	10.8	4.35	1.54	211	58	3.0	1.85	0.60	8.0	8.0	7.15	0.55	5.5	~13.3	10.26	0.185	2[a]	9.4	12.15	10.8	1.15	64
NSS-69	10.8	1.50	1.66	130	60	3.0	0.28	0.10	9.4	9.4	5.55	0.55	5.5	~13.3	9.56	0.20	2[b]	9.4	12.0	10.8	1.05	68

[a] 1.6 liters/min air sparge during reflux and recycle acid recovery.

[b] 1.33 liters/min air sparge during reflux and recycle acid recovery.

Table A.8. Chloride Removal from Special Stainless Steel Dissolution Product

	Dissolution Product[g]			Waste Acid				Mixed Acid				Acidified Concentrate				Solvent Extraction Feed				
Run No.	Vol, ℓ	H^+, M	Cl^-, M	Vol, ℓ	HNO_3, M	Cl^-, M	13.3 M HNO_3 Added, ℓ	Vol, ℓ	HNO_3, M	Cl^-, M	13.3 M HNO_3 Added, ℓ	Vol, ℓ	HNO_3, M	Cl^-, M	Reflux Time, hr	Vol, ℓ	HNO_3, M	Cl^-, ppm	Steam Pressure psig	HNO_3 Loss, moles
V-8	6.0	4.15	1.65	-	-	-	2.6[a]	4.5[b]	3.42	1.13	-	4.1	8.5	0.1	-	11.0	3.36	1400	14-31	-1.3
V-9	6.0	4.15	1.65	1.0	1.07	0.92	3.0[c]	5.2[b]	3.85	1.25	-	3.0	7.25	0.11	-	11.0	1.98	1060	20-65	13.5
V-10	6.0	4.15	1.65	1.3	1.1	1.0	3.7	5.4[b]	4.3	1.0	-	3.0	7.25	0.016	-	11.0	1.98	160	25-55	21
V-11	6.0	4.15	1.65	1.0	1.0	0.85	3.0	5.0[b]	3.4	1.1	-	3.0	7.0	0.14	-	11.0	1.90	1400	26-55	16
V-12	6.0	4.15	1.65	-	-	-	2.5[d]	4.4[b]	2.7	1.25	-	4.1	6.5	0.21	2	11.0	2.16	1780	25-45	13
V-13	6.0	4.15	1.65	-	-	-	2.0	4.0	3.15	1.15	1.0	5.0	8.15	0.036	2[e]	11.0	3.34	< 25	20-30	6.3
V-14	6.0	4.15	1.65	-	-	-	2.0	4.0	3.1	1.0	1.0	5.0	8.3	0.017	2[f]	11.0	3.50	100	20	5.0

[a] At constant level as mixed acid was removed.

[b] Recycle not possible, cannot be adjusted to 5 M HNO_3-2 M HCl in 6.0 liters.

[c] 1 liter batchwise, then 2 liters at constant level.

[d] 0.5 liter batchwise, then 2 liters at constant level.

[e] Air sparged at unknown rate.

[f] Air sparged at 0.18 liters air per min-liter solution.

[g] Contained ~60 g per liter total metals.

Table A.9. Continuous Feed Adjustment Runs in Engineering-scale Equipment

			Feed[a]						Overhead					Concentrated Product							Solvent Extraction Feed					
Run No.	Temp, °C	Length of Run, hr	Vol, ℓ	Den. g/ℓ	SS g/ℓ	HNO_3, M	H_2O, moles	Cl^-, ppm	Vol, ℓ	Den, g/ℓ	HNO_3, M	H_2O, M	Cl^-, ppm	Vol, ℓ	Den, g/ℓ	SS, g/ℓ	HNO_3, M	H_2O, moles	Cl^-, ppm	H_2O Added, ℓ	Vol, ℓ	Den, g/ℓ	SS, g/ℓ	HNO_3, M	H_2O, moles	Cl^-, ppm
4-I	125	16	1.00[b]	1.45	41.55	13.36	24.1	170	0.754	1.407	15.0	19.5	90	0.254	1.655	167.3	6.47	7.94	170	0.254	0.508	1.328	83.6	3.24	22.04	105
-II	125	5.5	1.00	1.45	34.1	11.8	31.4	114	0.748	1.38	13.68	21.51	68	0.257	1.636	155	6.0	10.0	224	0.257	0.514	1.318	77.5	3.0	24.28	139
8	125	2	1.63	1.445	34.0	13.64	40.2	-	1.30	1.40	15.2	32.5	-	0.34	1.64	163	7.0	9.6	-	0.41	0.75	1.29	73.9	3.2	32.4	-
10	130	6	1.00	1.536	21.7[c]	13.7	23.4	30	0.786	1.386	15.3	18.5	26	0.223	1.970	92.2	7.54	4.9	22	0.617	0.84	1.267	24.5	2.0	39.2	9
11	135	7	1.00	1.536	21.7[c]	13.7	23.4	30	0.867	1.385	15.05	21.0	26	0.127	2.778	171	5.12	3.4	23	0.198	0.325	1.696	66.8	2.0	14.4	15
14	132	6.25	1.00	1.511	19.1[d]	13.4	24.5	23	0.826	1.39	15.0	20.4	13	0.167	2.256	121	4.28	5.3	30	0.576	0.743	1.317	27.0	2.0	36	12
15	132	7.25																								
16	132	4																								

[a] In all runs the feed was introduced at rates of 130-150 ml/min.

[b] In all runs except No. 8 the basis of calculation was 1.00 liter of feed. In run No. 8 it was one mole (55.4 g) of stainless steel.

[c] In runs 10 and 11 the feed also contained 96.7 g U/liter.

[d] In runs 14-16 the feed also contained 87.5 g U/liter.

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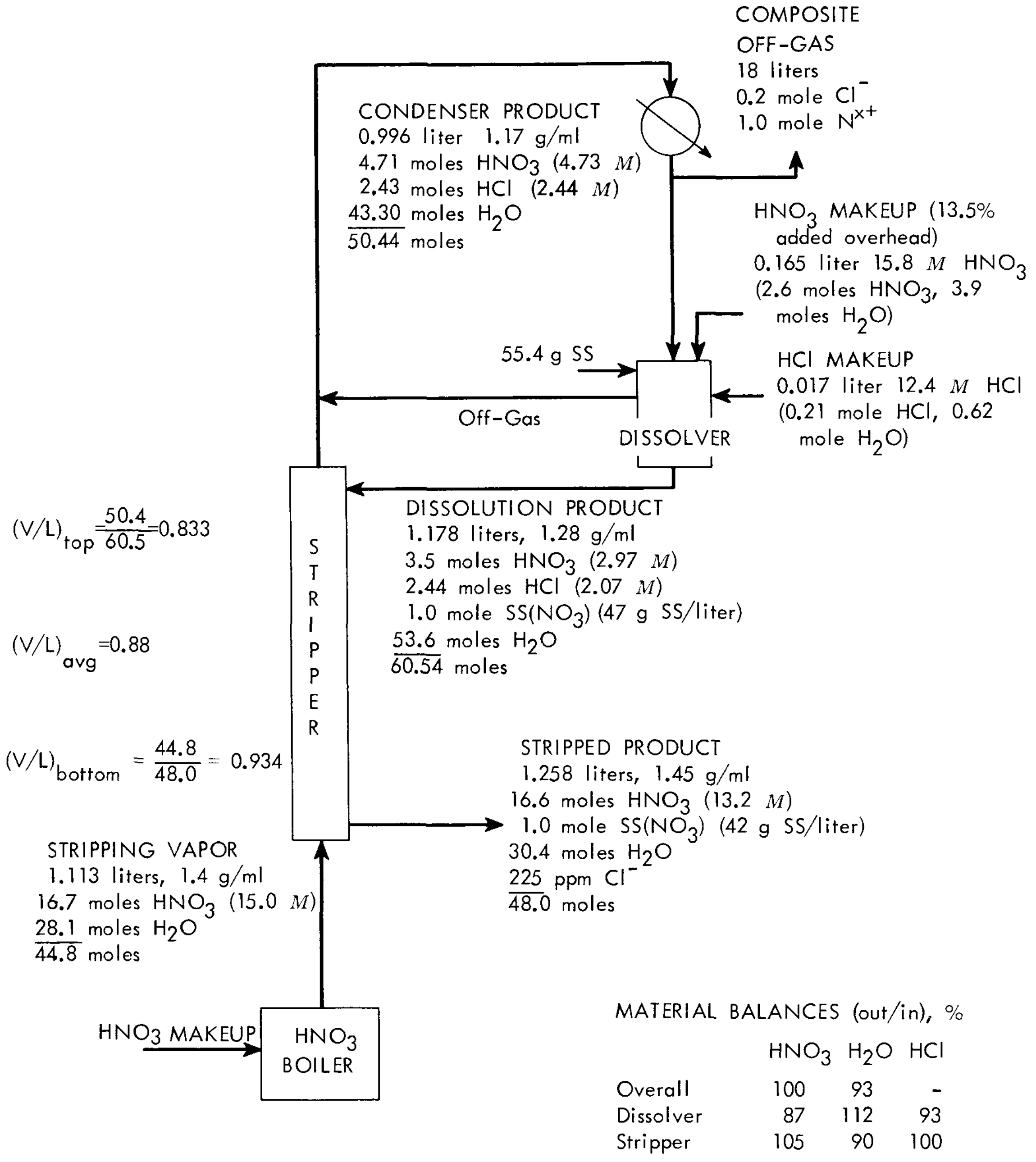

MATERIAL BALANCES (out/in), %

	HNO_3	H_2O	HCl
Overall	100	93	-
Dissolver	87	112	93
Stripper	105	90	100

Fig. A.2. Material balance for run 45. Basis: 1 mole (55 g) of stainless steel dissolved; time required: 9.05 min.

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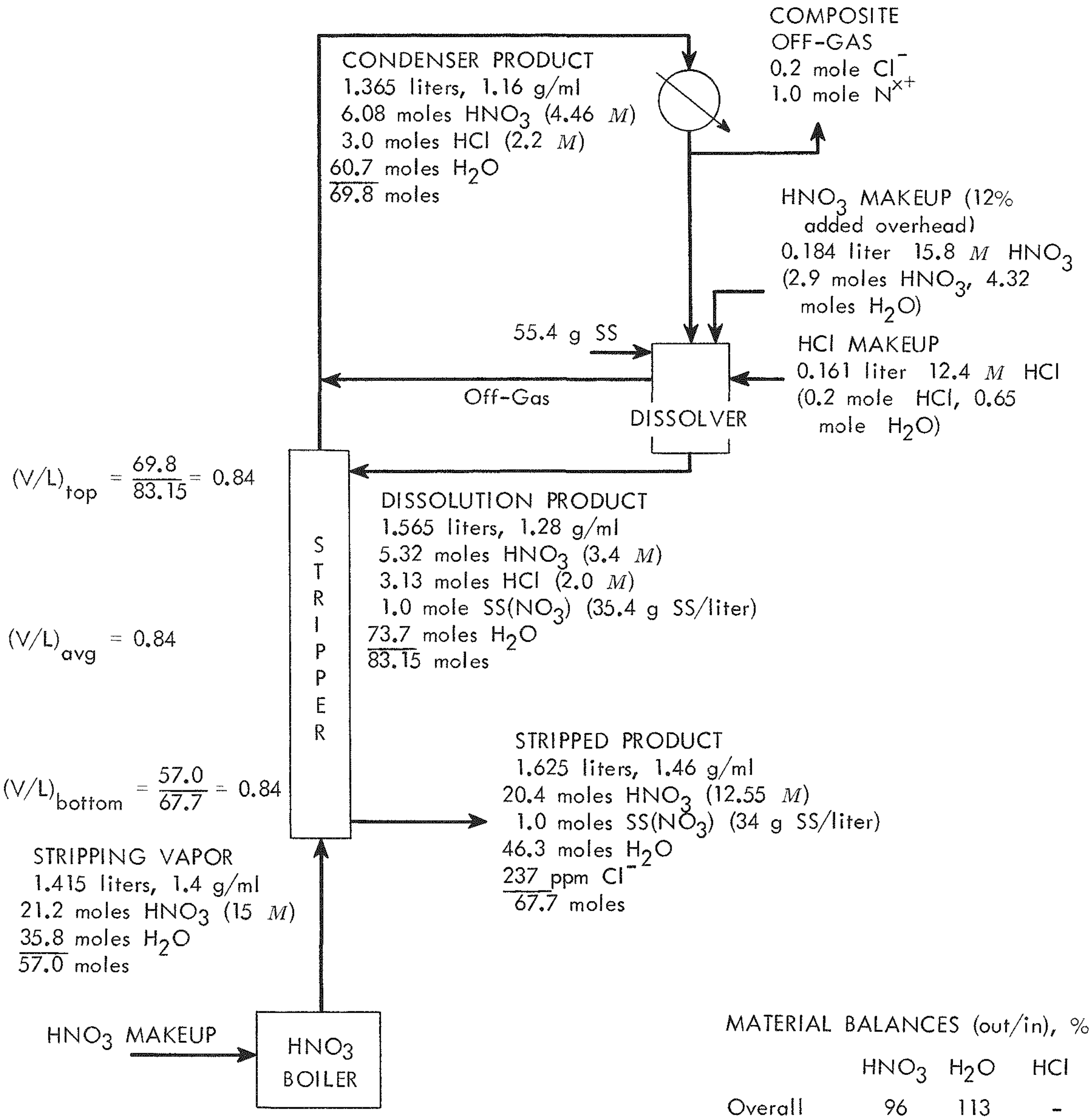

MATERIAL BALANCES (out/in), %

	HNO_3	H_2O	HCl
Overall	96	113	-
Dissolver	91	112	98
Stripper	100	98	96

Fig. A.3. Material balance for run 47, part I. Basis: 1 mole (55.4 g) of stainless steel dissolved; time required: 12.4 min.

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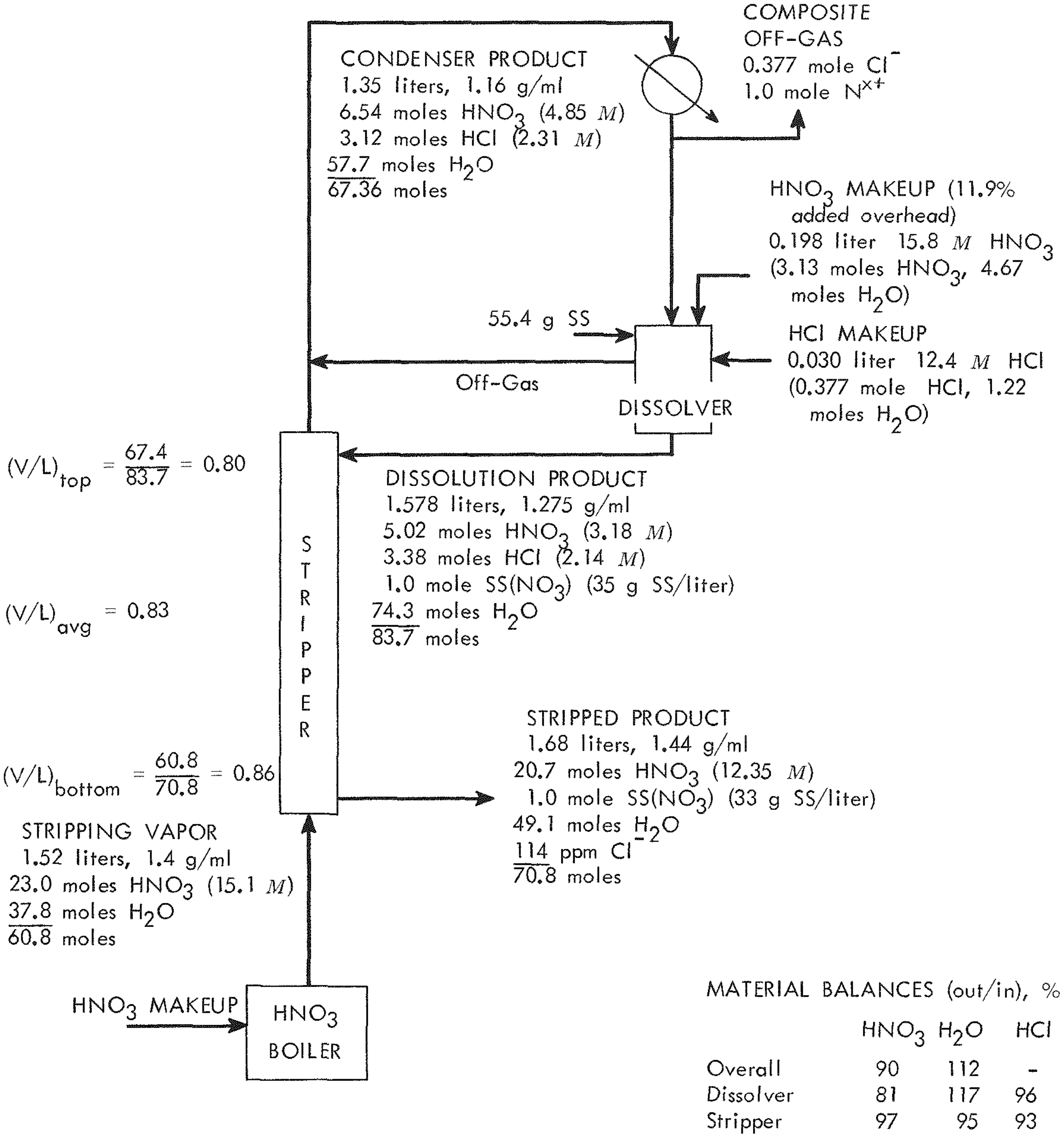

MATERIAL BALANCES (out/in), %

	HNO_3	H_2O	HCl
Overall	90	112	-
Dissolver	81	117	96
Stripper	97	95	93

Fig. A.4. Material balance for run 47, part II. Basis: 1 mole (55.4 g) of stainless steel dissolved; time required: 13.1 min.

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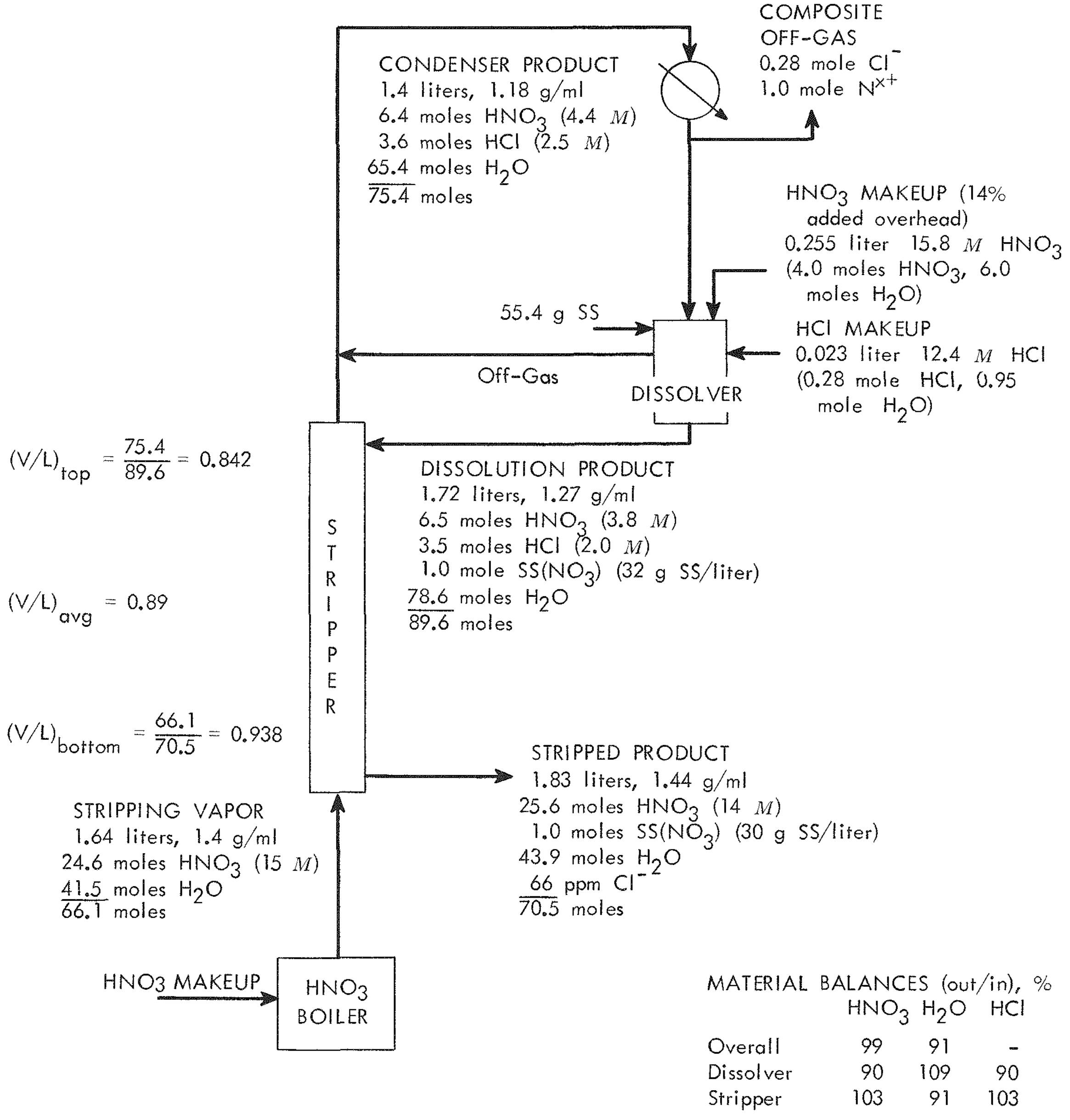

MATERIAL BALANCES (out/in), %

	HNO_3	H_2O	HCl
Overall	99	91	-
Dissolver	90	109	90
Stripper	103	91	103

Fig. A.5. Material balance for run 47, part III. Basis: 1 mole (55.4 g) of stainless steel dissolved; time required: 13.5 min.

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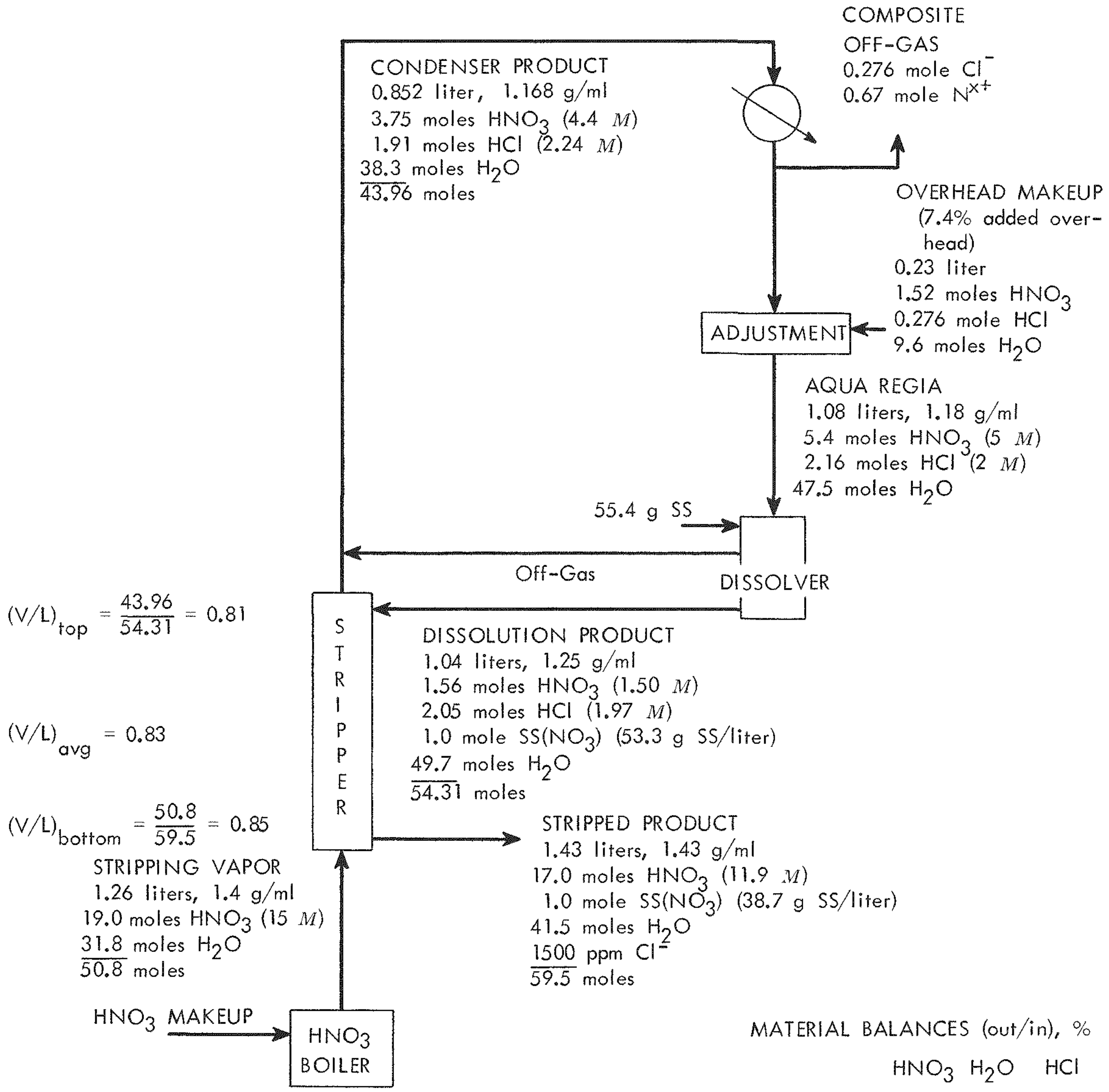

MATERIAL BALANCES (out/in), %

	HNO_3	H_2O	HCl
Overall	97	100	-
Dissolver	82	105	95
Stripper	101	98	96

Fig. A.6. Material balance for run 50. Basis: 1 mole (55.4 g) of stainless steel dissolved; time required: 11.7 min.

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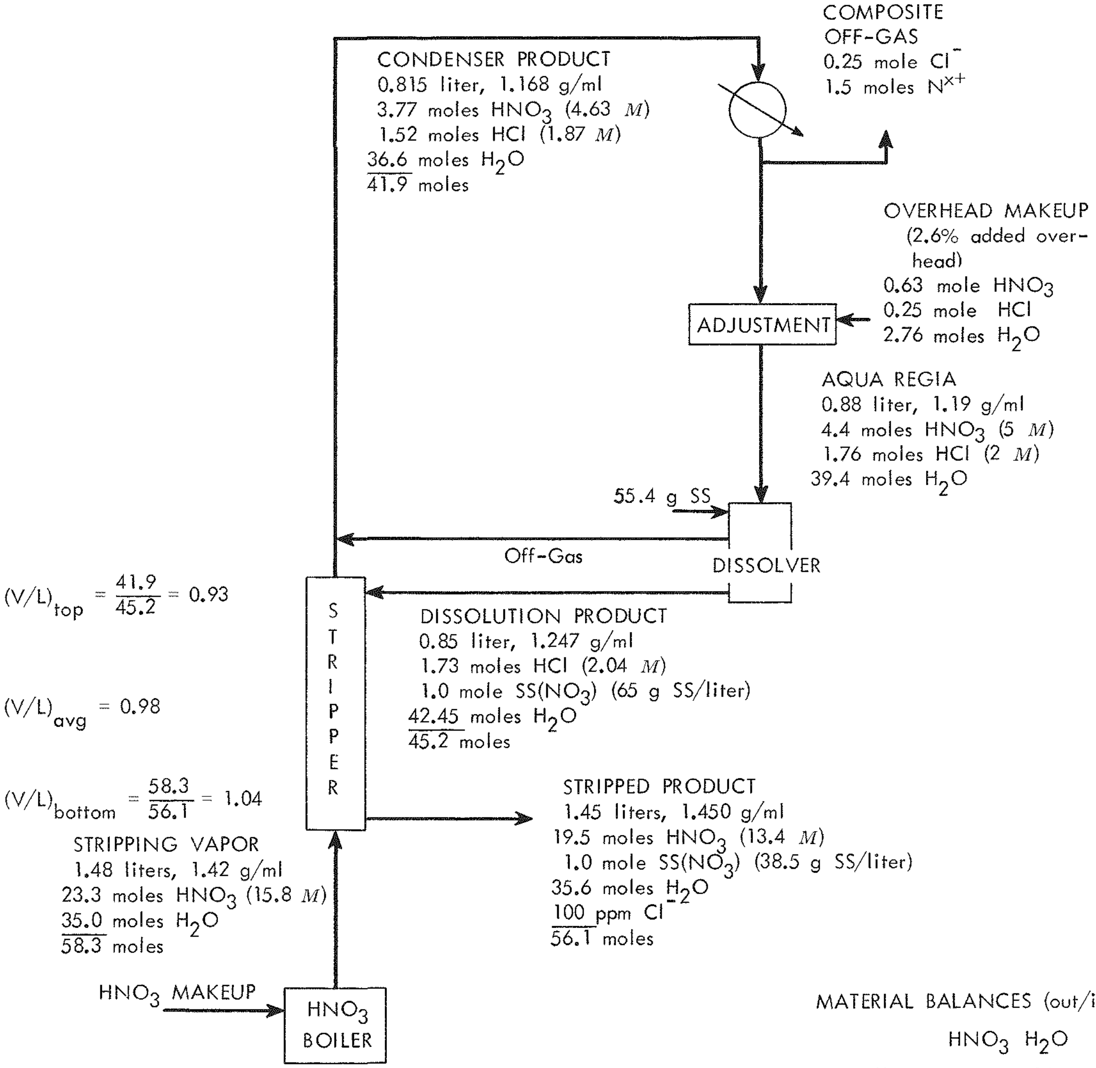

MATERIAL BALANCES (out/in), %

	HNO_3	H_2O	HCl
Overall	94	94	-
Dissolver	65	108	98
Stripper	100	93	88

Fig. A.7. Material balance for run 53. Basis: 1 mole (55.4 g) of stainless steel dissolved; time required: 13 min.

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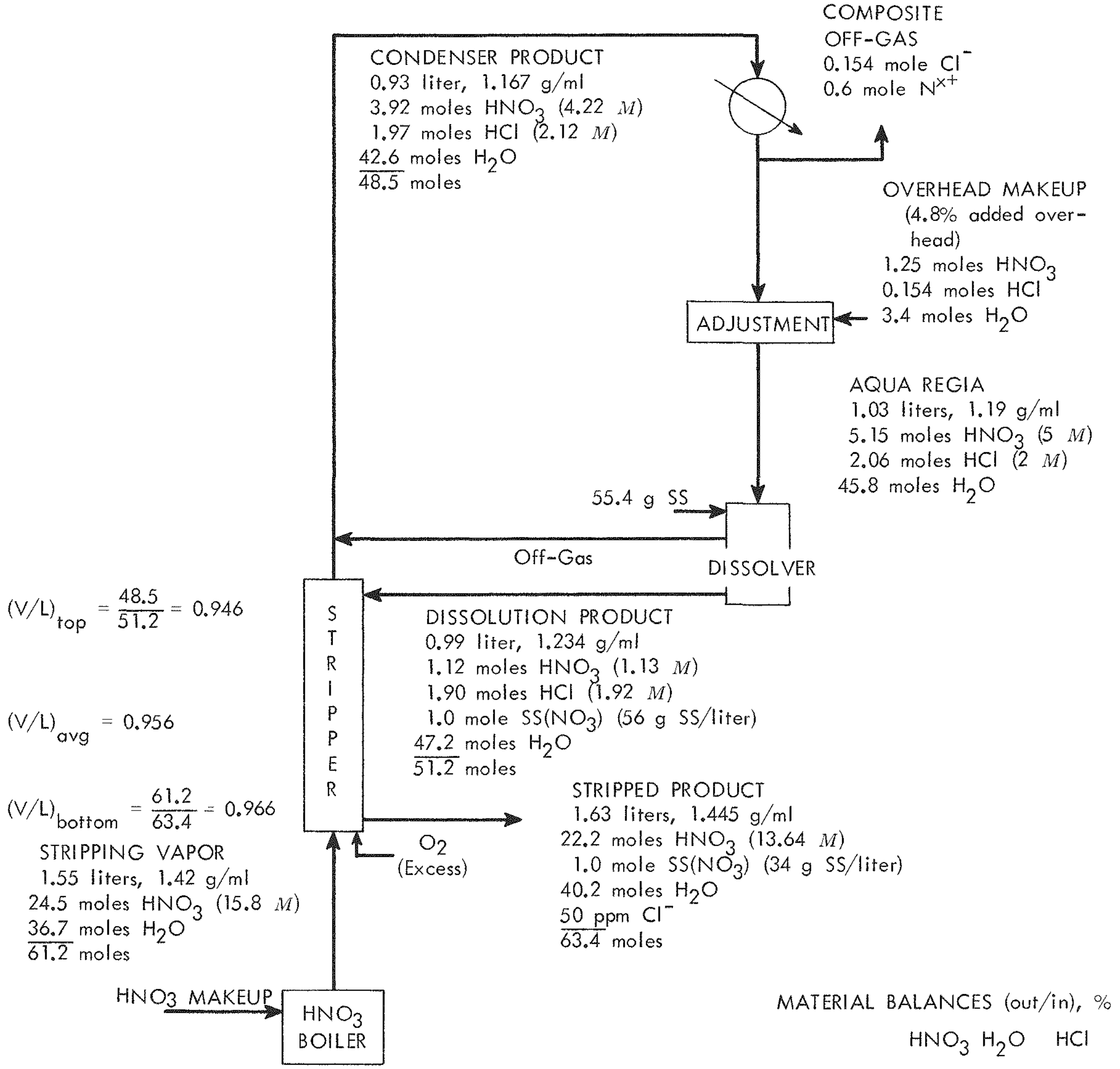

MATERIAL BALANCES (out/in), %

	HNO_3	H_2O	HCl
Overall	97	100	-
Dissolver	77	103	92
Stripper	102	99	104

Fig. A.8. Material balance for run 54. Basis: 1 mole (55.4 g) of stainless steel dissolved; time required: 11.1 min.

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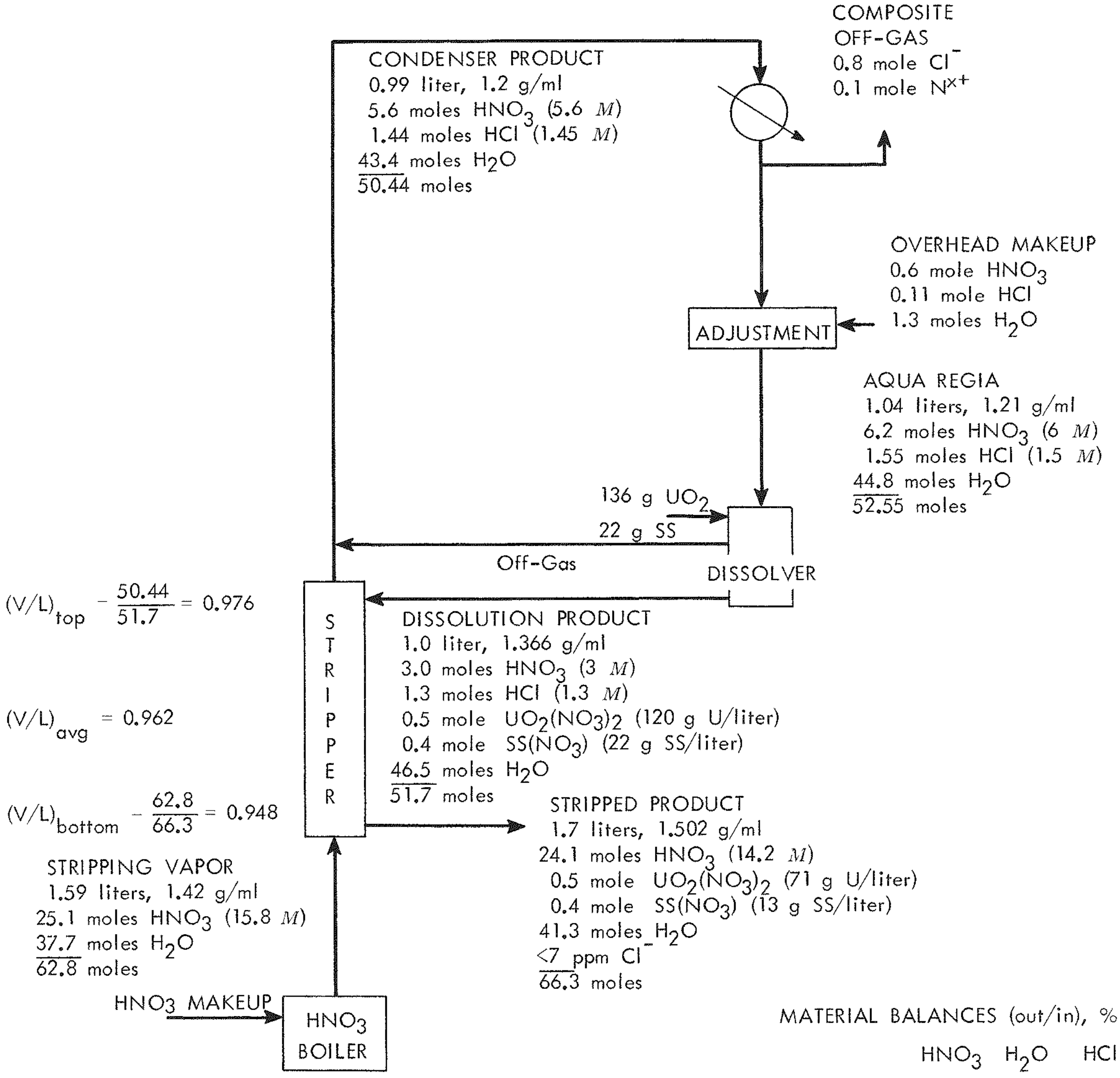
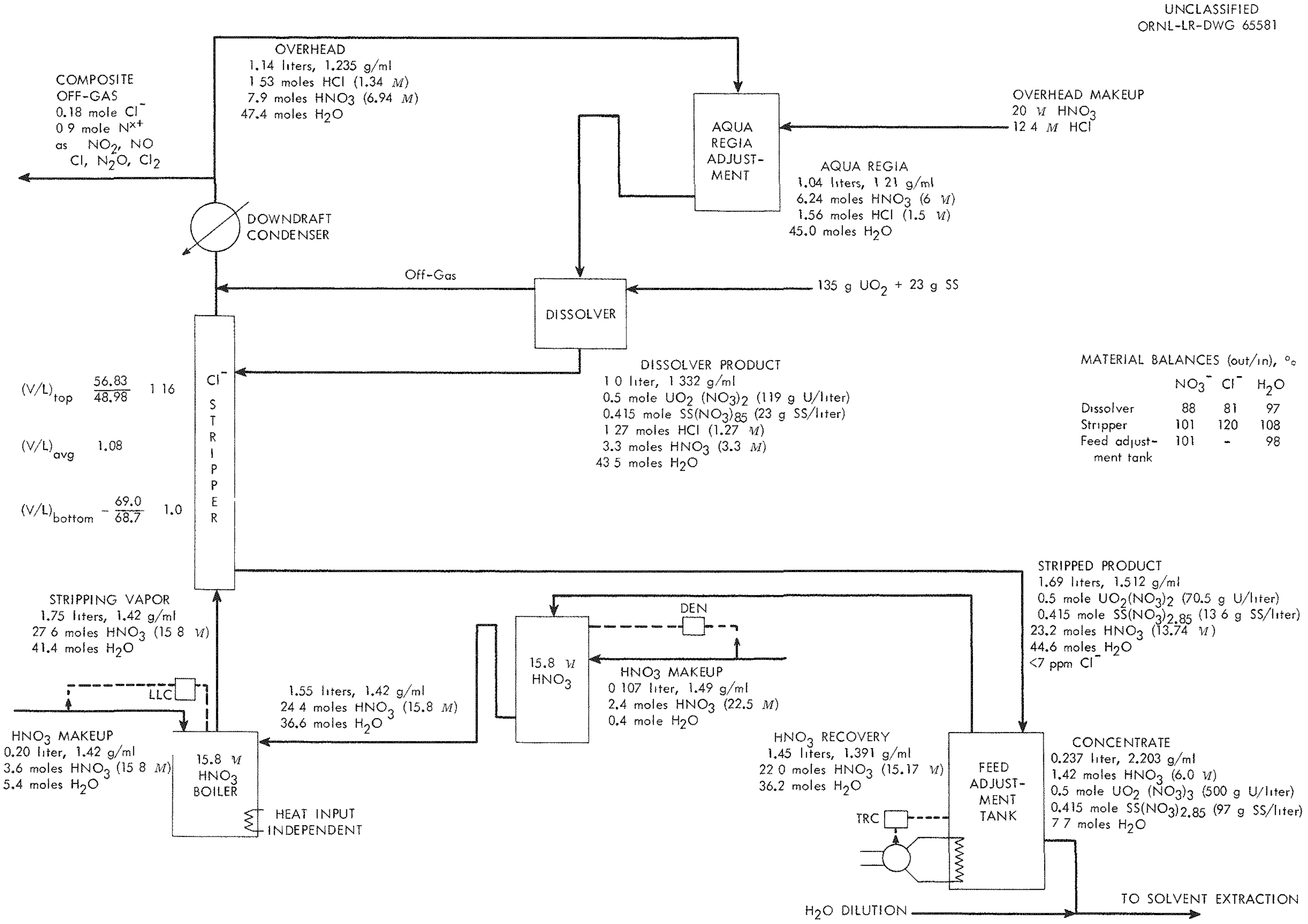


MATERIAL BALANCES (out/in), %

	HNO_3	H_2O	HCl
Overall	105	106	-
Dissolver	83	104	84
Stripper	106	101	111

Fig. A.9. Material balance for run 60. Basis: 1 liter of dissolution product in 15 min.



MATERIAL BALANCES (out/in), %

	NO_3^-	Cl^-	H_2O
Dissolver	88	81	97
Stripper	101	120	108
Feed adjustment tank	101	-	98

Fig. A.10. Material balance for run 61. Basis: 12.67 min. of system operation.

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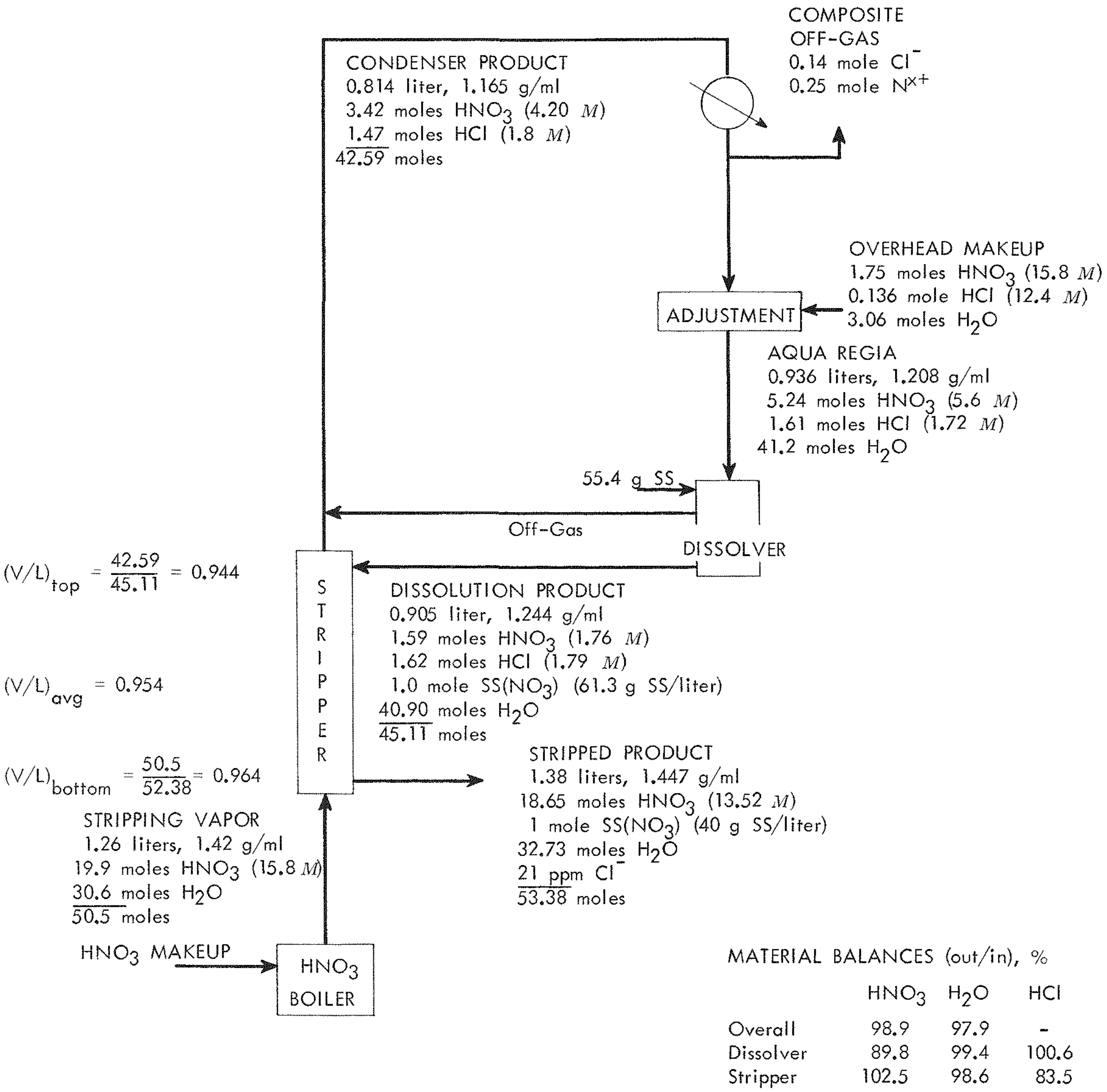

MATERIAL BALANCES (out/in), %

	HNO_3	H_2O	HCl
Overall	98.9	97.9	-
Dissolver	89.8	99.4	100.6
Stripper	102.5	98.6	83.5

Fig. A.11. Material balance for run 70. Basis: 1 mole of stainless steel dissolved in 9 min.

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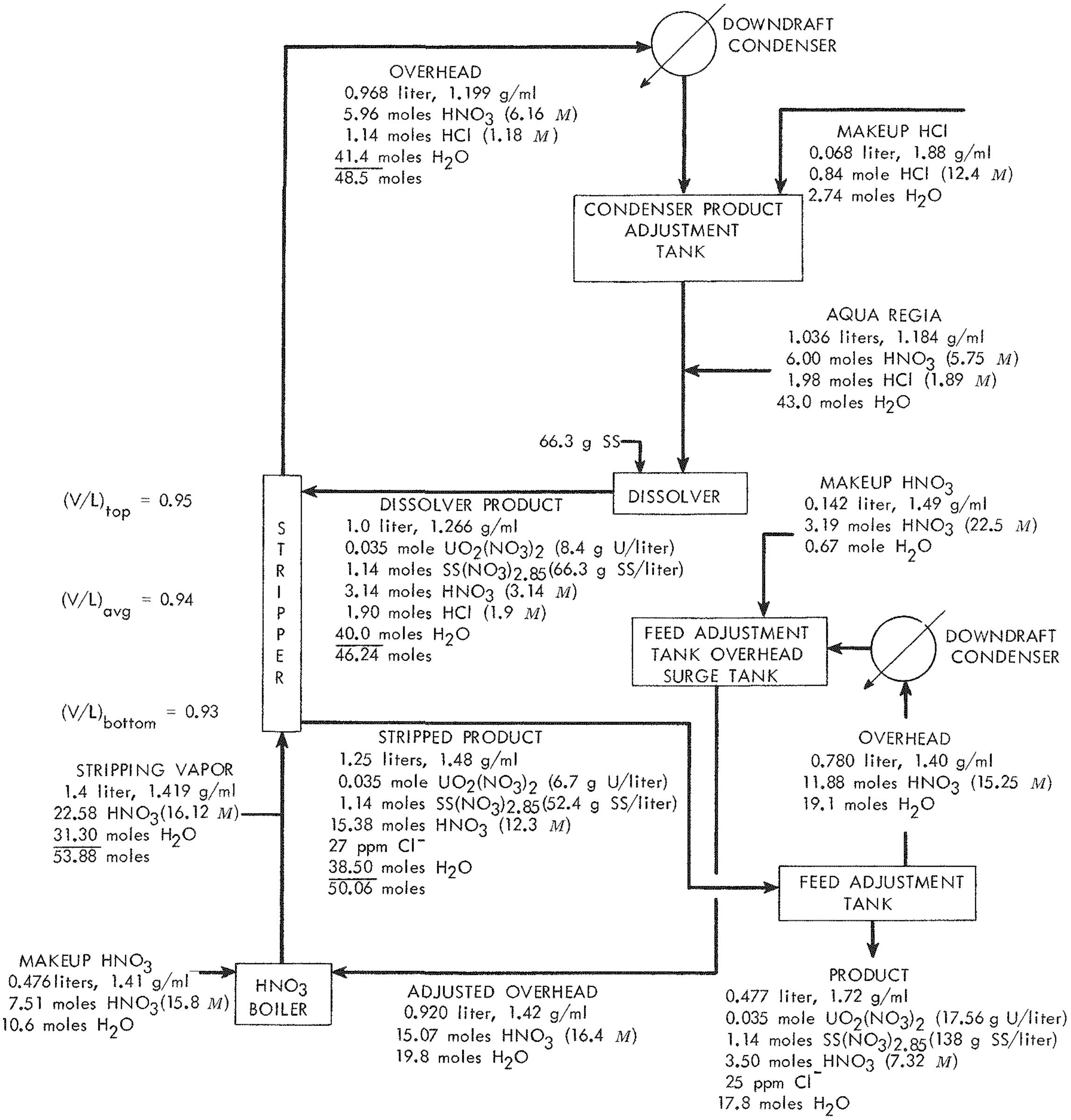

Fig. A.12. Material balance for run 72. Basis: 1 liter of dissolver product.

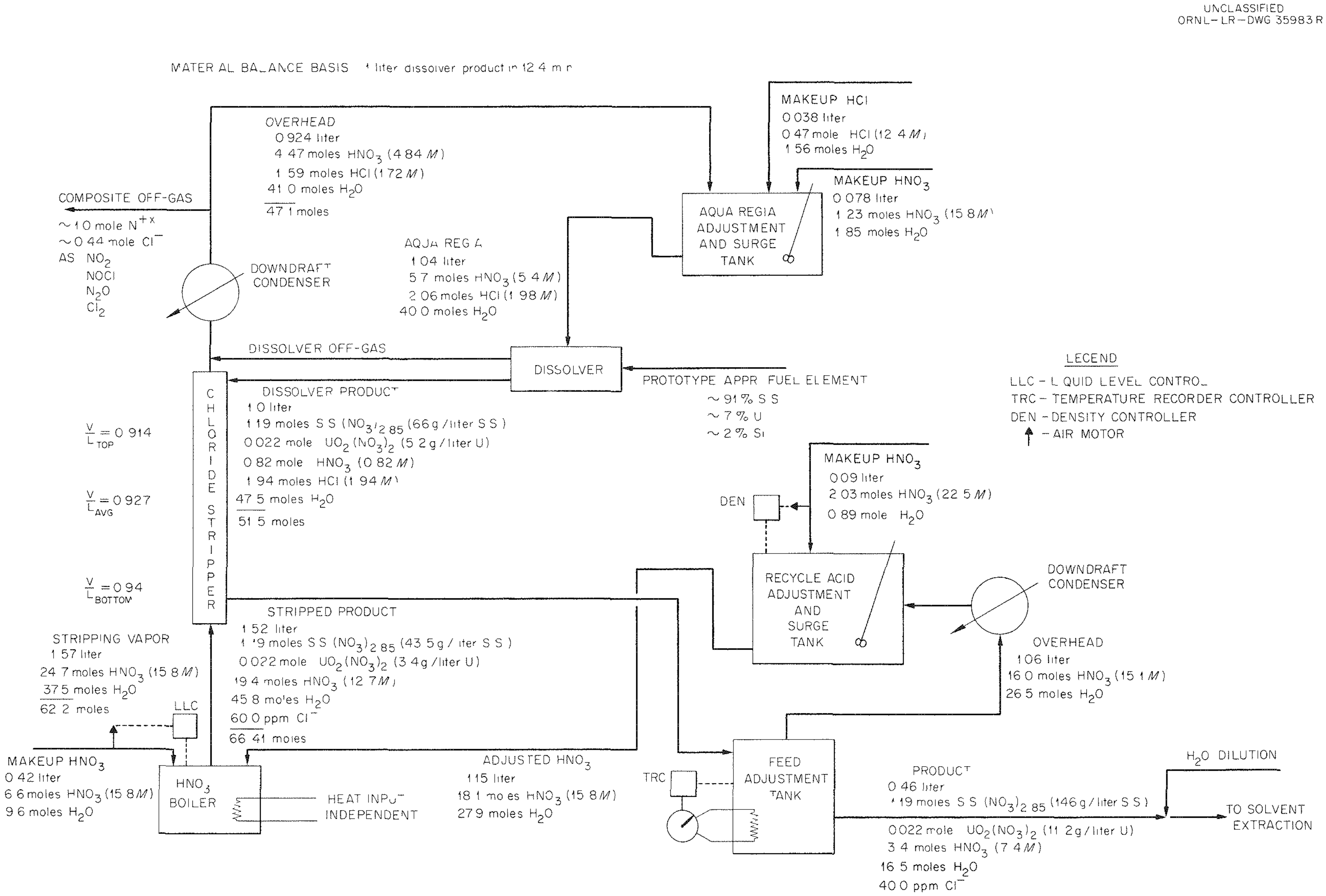

Fig. A.13. Continuous Darex Process Equipment and Control Flowsheet Including Material Balance.

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