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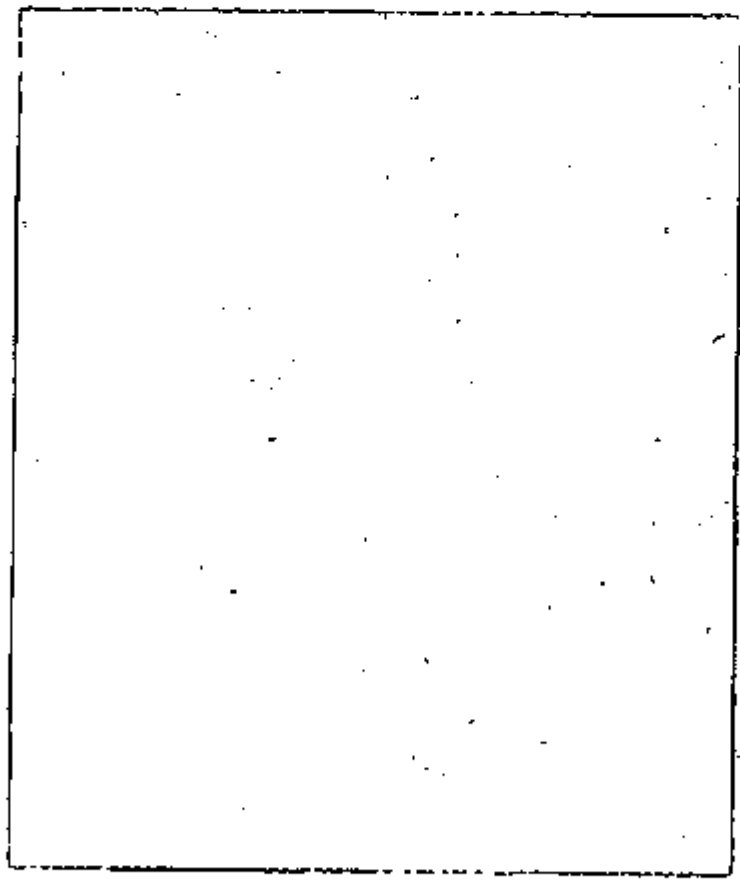
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TO: F. L. Culler  
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A PRELIMINARY STUDY OF PRE-SOLVENT EXTRACTION TREATMENT  
OF STAINLESS STEEL-URANIUM FUELS WITH DILUTE AQUA REGIA

F. G. Kitts and J. J. Perona

1.0 ABSTRACT

The continuous dissolution of 304 stainless steel and stainless steel-UO<sub>2</sub> alloy in dilute aqua regia was studied with subsequent stripping of the dissolver product to remove chloride ion.

The process has the advantage of producing, by means of a simple head end treatment, a solvent extract feed in a conventional nitric acid medium so that existing solvent extraction processes, materials of construction and waste disposal methods can be used.

The purposes of this study were (1) to investigate the variables affecting the dissolution process and to obtain dissolver scale-up data, and (2) to investigate the removal of chloride from the dissolver product and the variables affecting the stripping operation.

A continuous flooded pot dissolver was used in this investigation; it has the advantages of stability of operation and ease of control in comparison with column dissolvers and requires a minimum of mechanical processing prior to dissolution. Stripping of the dissolver product to remove chloride ion was studied in a 4-inch diameter Pyrex bubble-cap column containing 12 single bubble cap plates.

Continuous dissolution rates and dissolver product stainless steel loadings were correlated with aqua regia feed composition, acid feed rate and surface area exposed to reaction. Profiles of chloride concentration down the stripping column were obtained for various vapor to liquid mole ratios and for several nitric acid stripping vapor concentrations. Non-condensable off-gas compositions and rates were also measured.

2.0 SUMMARY

In 39 runs carried out in a continuous pot dissolver, dissolution rates varied from 10 to 50 mg/(cm<sup>2</sup>)(min) for type 304 stainless steel and stainless steel-UO<sub>2</sub> alloy (5.5 to 11% UO<sub>2</sub>) with aqua regia feed streams composed

of 5 M  $\text{HNO}_3$  - 2 M  $\text{HCl}$ , 5-1.5, 3-2 and 3-1.5 acid. Dissolution rates were expressed as a function of the ratio of acid feed rate to surface area of metal exposed to reaction. This ratio, which is analogous to a space velocity, was varied over the range of 0.18 to 1.65  $\text{cm}^3/(\text{cm}^2)(\text{min})$ . Dissolver product stream loadings varied from 20 to 140 g of metal/liter.

Nine stripping runs were carried out in a 4-inch bubble-cap column containing 12 plates. The chloride concentration in the metal-bearing stream from the dissolver was reduced to 50 ppm or below using 38.3 mole %  $\text{HNO}_3$  strip vapor for V/L ratios (vapor to liquid mole ratios) of 0.9 to 2.1. Using a strip vapor of 20 mole %  $\text{HNO}_3$ , chloride concentrations were reduced to 50 ppm or below with V/L ratios of 5.2 and 6.1, but were greater than 250 ppm for V/L ratios of 1.3 and 1.6.

Corrosion studies show that suitable materials of construction are titanium and tantalum, with high cobalt-containing alloys a possibility.

### 3.0 INTRODUCTION

The objectives of fuel reprocessing are the separation of fission product poisons from irradiated fuels and the conversion of recovered fuel to a reusable form. The technology of reprocessing Al, U, and Th containing fuels by nitric acid dissolution followed by organic extraction from the aqueous media is well developed, but many proposed power reactor fuels contain stainless steel, zirconium, niobium or molybdenum (rather than aluminum) as clad and alloying materials. An obvious approach to the reprocessing of power reactor fuels is the development of new head end processes for conversion of the fuels to a nitric acid media so that present solvent extraction techniques could be used for fission product removal. Such a head end process now under engineering development is the dissolution of stainless steel-uranium fuels in dilute aqua regia, followed by chloride removal from the dissolver product by stripping with concentrated nitric acid. The removal of chloride from the dissolver product stream would be desirable in that it would permit stainless steel to be used as a material of construction for equipment subsequent to the stripping column and for tanks storing waste from the first cycle solvent extraction.

### 4.0 PROCESS FLOWSHEET

A preliminary investigation has been carried out to obtain engineering scale-up data and to investigate the variables affecting the dissolution and stripping operations. A necessary addition to the stripper-dissolver flowsheet would be a feed adjustment tank to drive off excess nitric acid and the last traces of chloride ion prior to introduction to the solvent extraction system. If the vapors from the feed adjustment tank were returned to the stripping column for reuse, a material balance shows that a small amount of water, that added to the system with the  $\text{HCl}$  makeup plus the water

produced by the dissolution reactions, must be removed from the system to maintain steady state. This water removal could be accomplished by sending the vapors from the feed adjustment tank to a rectifying column. The resultant flowsheet is presented in Fig. 1. While it appears that the flowsheet could be simplified by rectifying the dilute aqua regia vapor leaving the top of the stripping column, experiments have shown that rectification of this stream in a useful composition range is not possible.<sup>1</sup>

The dissolution is carried out in a continuous flooded pot-type dissolver. Although a pot dissolver, having a well-mixed liquid phase, yields a lower reaction rate than a column dissolver, it has the advantages of more stable operation and easier product control because of the absence of channeling effects and variations in packing distribution. For most fuel shapes, such as multi-plate assemblies or long rods, the pot dissolver has the additional advantage of requiring less mechanical processing (e.g., chopping) of the fuel prior to dissolution.

The uranium and stainless steel-bearing stream from the dissolver passes down the stripping column where it is contacted countercurrently to a rising stream of concentrated nitric acid vapor which strips the chloride from the liquid into the vapor phase. The liquid stream leaving the bottom of the stripping column contains the dissolved uranium and stainless steel in a nitric acid medium in which the chloride content has been reduced to about 30 ppm.

Although only dissolution and stripping studies are reported here, bench scale studies of the feed adjustment tank operation have been completed and a loop composed of the four components is now under construction.

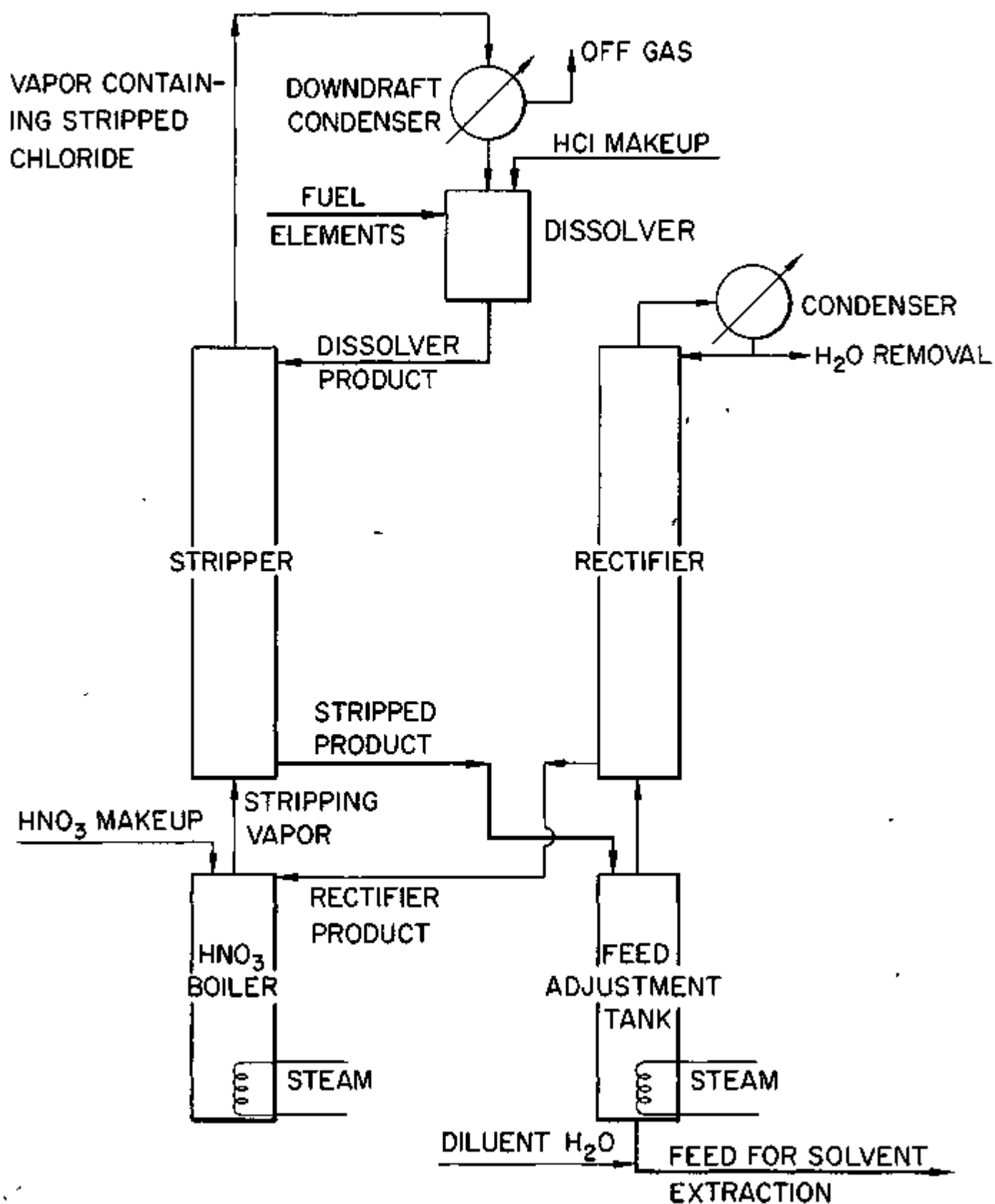
## 5.0 CONTINUOUS DISSOLUTION

### 5.1 Equipment

Continuous dissolution studies were carried out on 1-inch type 304 stainless steel tubing and on stainless steel- $UO_2$  strips (5.5 to 11%  $UO_2$ ). Aqua regia of the desired composition was premixed and fed by gravity through a rotameter to the acid preheater, where it was heated to 105°C. The acid then flowed into the dissolver. The dissolver was equipped with a reflux condenser and a product stream cooler.

Acid level in the dissolver was maintained by an internal standpipe. The metal tube or strip undergoing dissolution stood on end in the dissolver, partly submerged in the liquid phase. As the end of the metal dissolved, the tube or strip continuously sank into the liquid, maintaining the area of metal exposed to dissolution approximately constant.

<sup>1</sup> Refer to Chemical Technology Division Monthly Progress Report, September 1957, ORNL-2416.



Flowsheet for Processing SS-U Fuels with Dilute Aqua Regia

## 5.2 Results

Reaction rates were measured with acid feed compositions of 5 M  $\text{HNO}_3$  - 2 M  $\text{HCl}$ , 5 M  $\text{HNO}_3$  - 1.5 M  $\text{HCl}$ , 3 M  $\text{HNO}_3$  - 2 M  $\text{HCl}$  and 3 M  $\text{HNO}_3$  - 1.5 M  $\text{HCl}$  and correlated with acid feed rate to surface area ratio (F/S ratio) (Figs. 2, 3, 4, 5). The effect of low percentages of  $\text{UO}_2$  in stainless steel (5.5 to 11%) on reaction rate was negligible except for 3 M  $\text{HNO}_3$  - 1.5 M  $\text{HCl}$  acid feed, where the reaction rates were about 50% higher for the  $\text{UO}_2$ -containing metal. For F/S ratios of less than 0.5 cm/min, the reaction rates for stainless steel-containing  $\text{UO}_2$  were approximately the same for the four acid feed composition; however, at higher F/S ratios the reaction rates leveled off more quickly for the more dilute acid feed compositions.

The usefulness of the correlation of reaction rate with F/S ratio stems from its independence of dissolver size and fuel element geometry. This correlation should apply to any continuous pot dissolver, provided the liquid phase is well-mixed in all cases. The high rate of gas evolution associated with the chemical system assures good mixing.

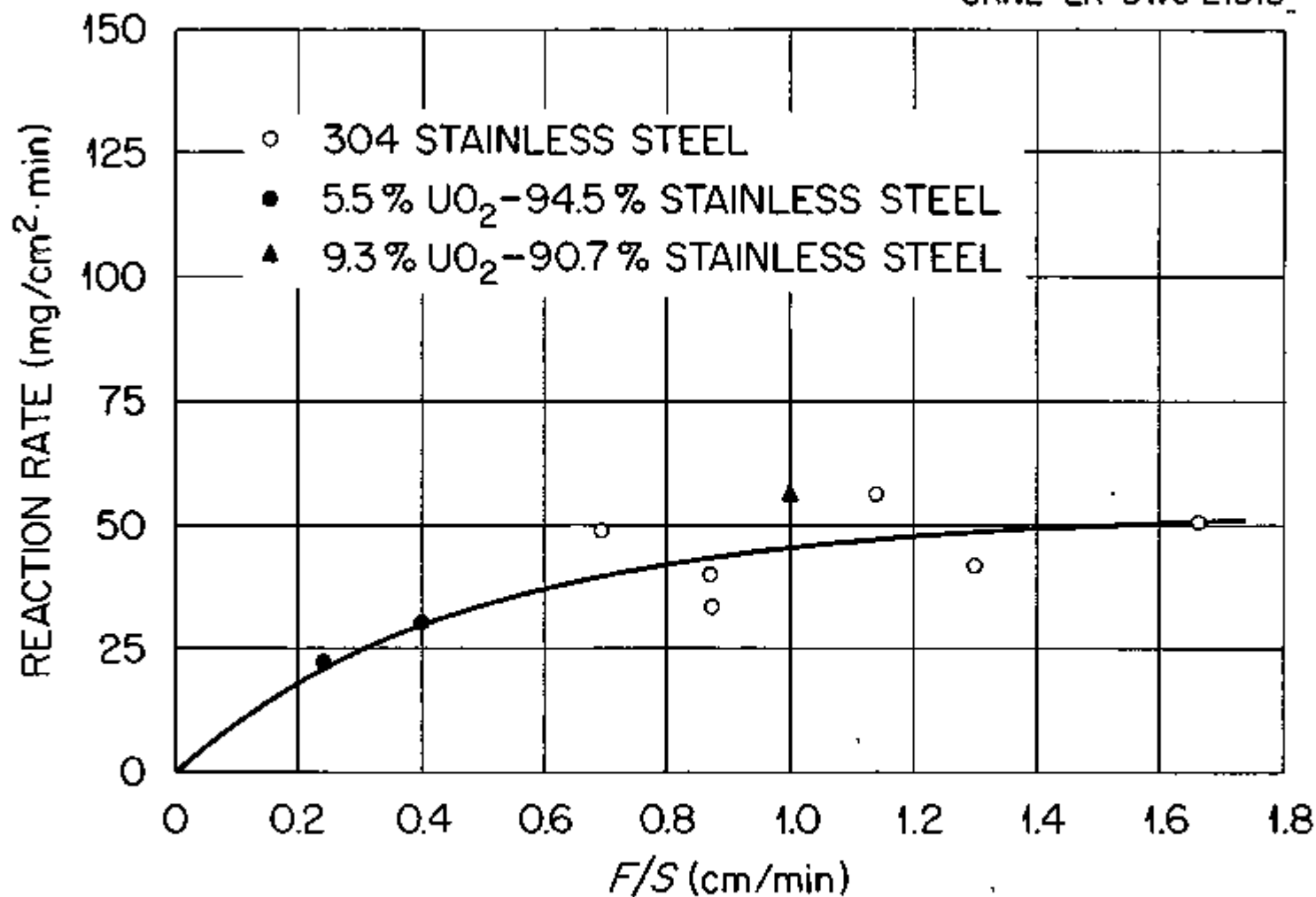
The F/S ratio is directly analogous to the space velocity term commonly used as a characteristic of heterogeneous reactions taking place in flow reactors containing packed beds of the solid phase. Space velocity is usually expressed as the ratio of feed rate to reactor volume (F/V) or feed rate to weight of solid phase (F/W) because the surface area of the packed bed is not easily measured. In the use of conventional space velocity the assumption is made that the interfacial surface area is directly proportional to the volume or weight of the solid phase. This assumption is not necessary since the interfacial area was known, at least superficially.

Metal loadings in the dissolver product stream decreased as F/S ratio increased for the acid feed compositions studied (Figs. 6, 7, 8, 9). For a given value of F/S ratio, metal loadings decreased as the acid feed composition decreased. Although metal loadings exceeding 100 g/liter are reported, there was evidence that loadings above 40 to 50 g/liter contained some metal in suspension rather than in true solution; however, no buildup of solids, except for silica, was observed in the stripping column.

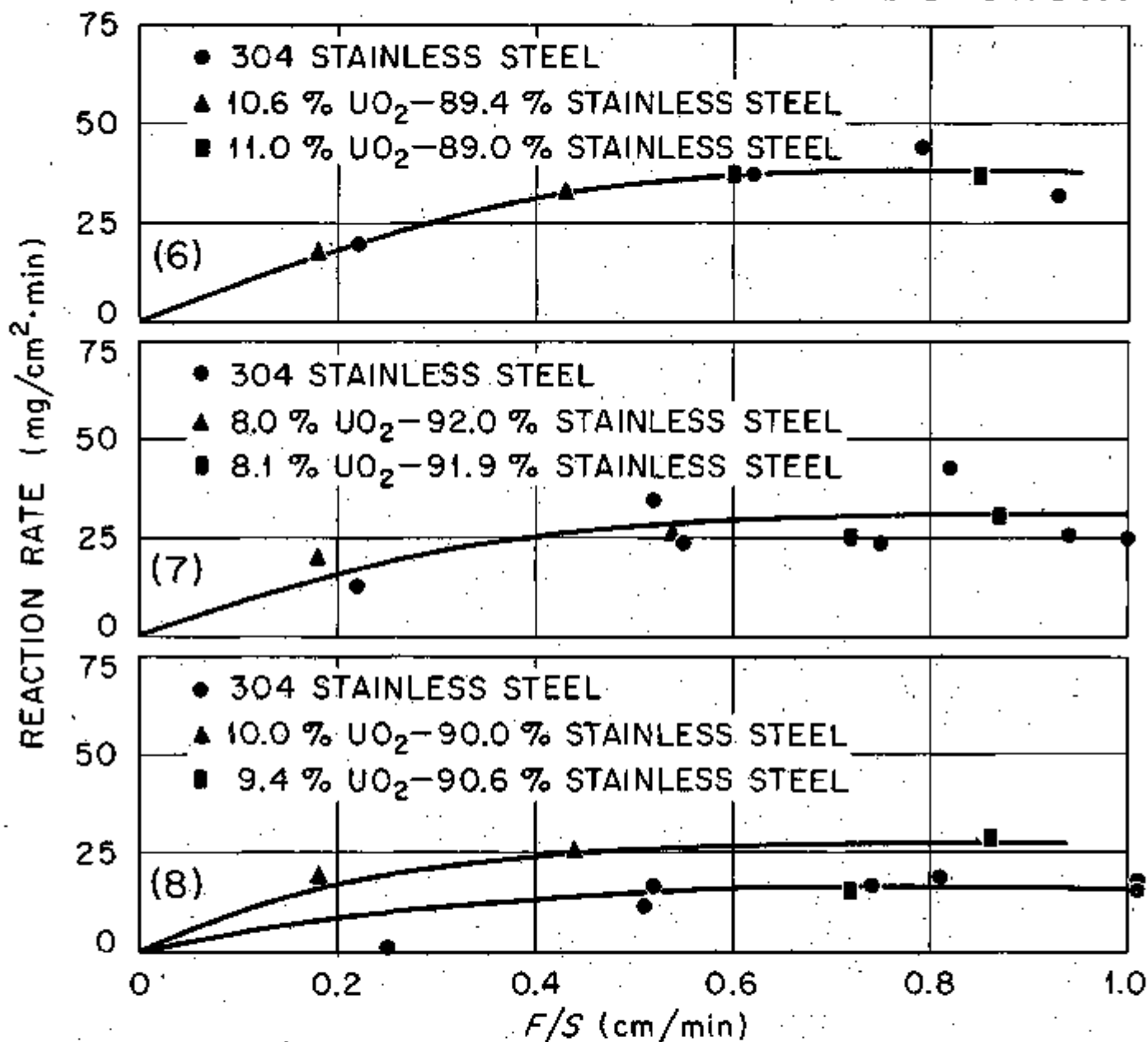
For the runs in which stainless steel alone was dissolved, metal dissolution rate was plotted as a function of  $\text{H}^+$  consumption rate and  $\text{NO}_3^-$  consumption rate (Figs. 10 and 11). From the reciprocal slopes of Fig. 10 it was calculated that 3.90 moles of  $\text{H}^+$  were consumed per mole of stainless steel dissolved. Since no detectable amounts of  $\text{H}_2$  were observed in the off-gases, most of the  $\text{H}^+$  consumed resulted in the formation of water.

The plot of stainless steel dissolution rate as a function of  $\text{NO}_3^-$  consumption rate was best represented by two lines, one for 5-2 and 3-1.5 acid composition from which a  $\text{NO}_3^-$  consumption of 1.41 moles per mole of stainless steel dissolved was calculated, and the other line for 5-1.5 and 3-2 acid feed compositions from which a ratio of 0.35 moles of  $\text{NO}_3^-$  consumed per mole of stainless steel dissolved was calculated. Nitrate decomposition to  $\text{NO}$ ,  $\text{NO}_2$  and  $\text{N}_2$  was the principal source of non-condensable off-gases.

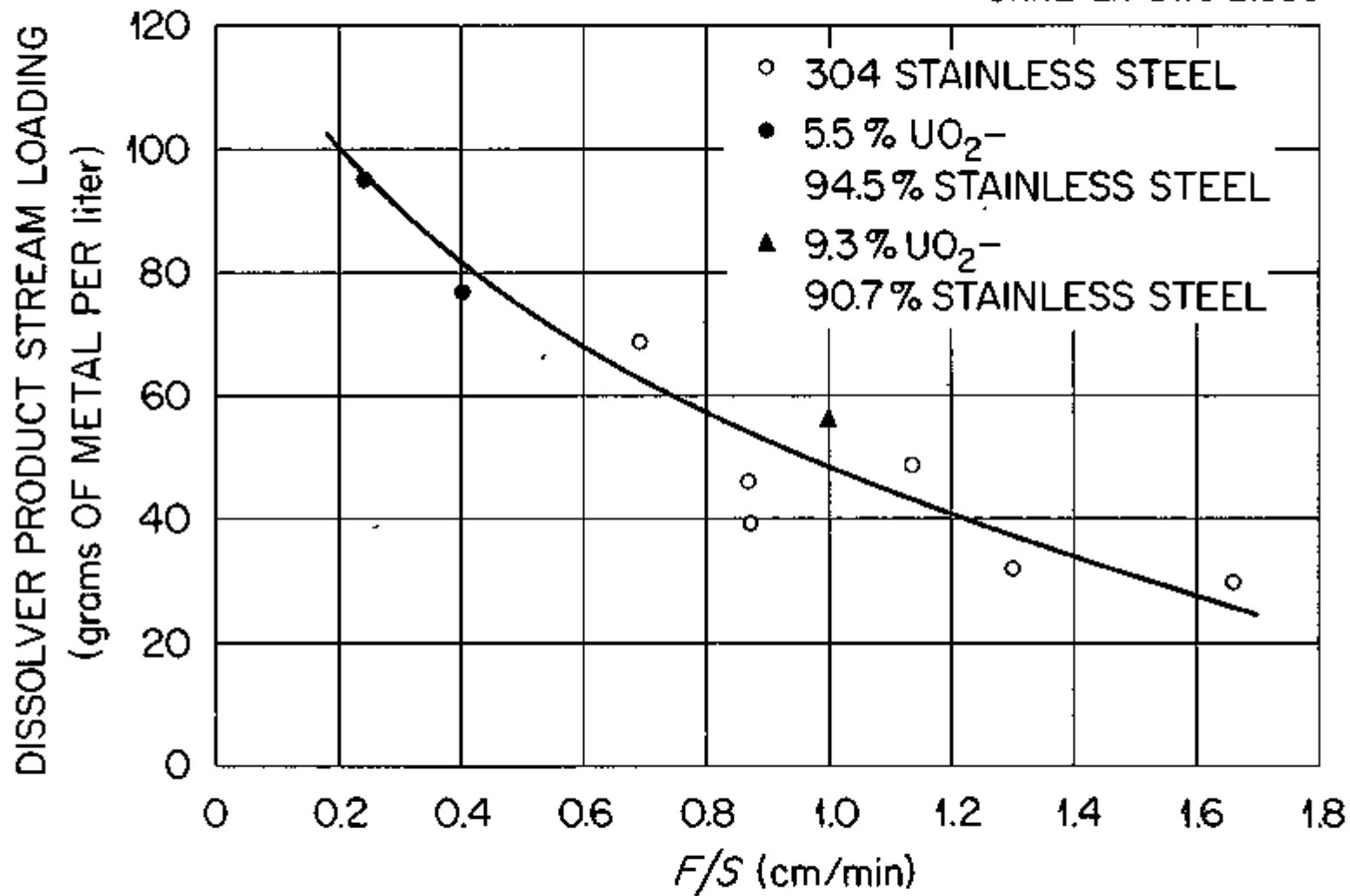




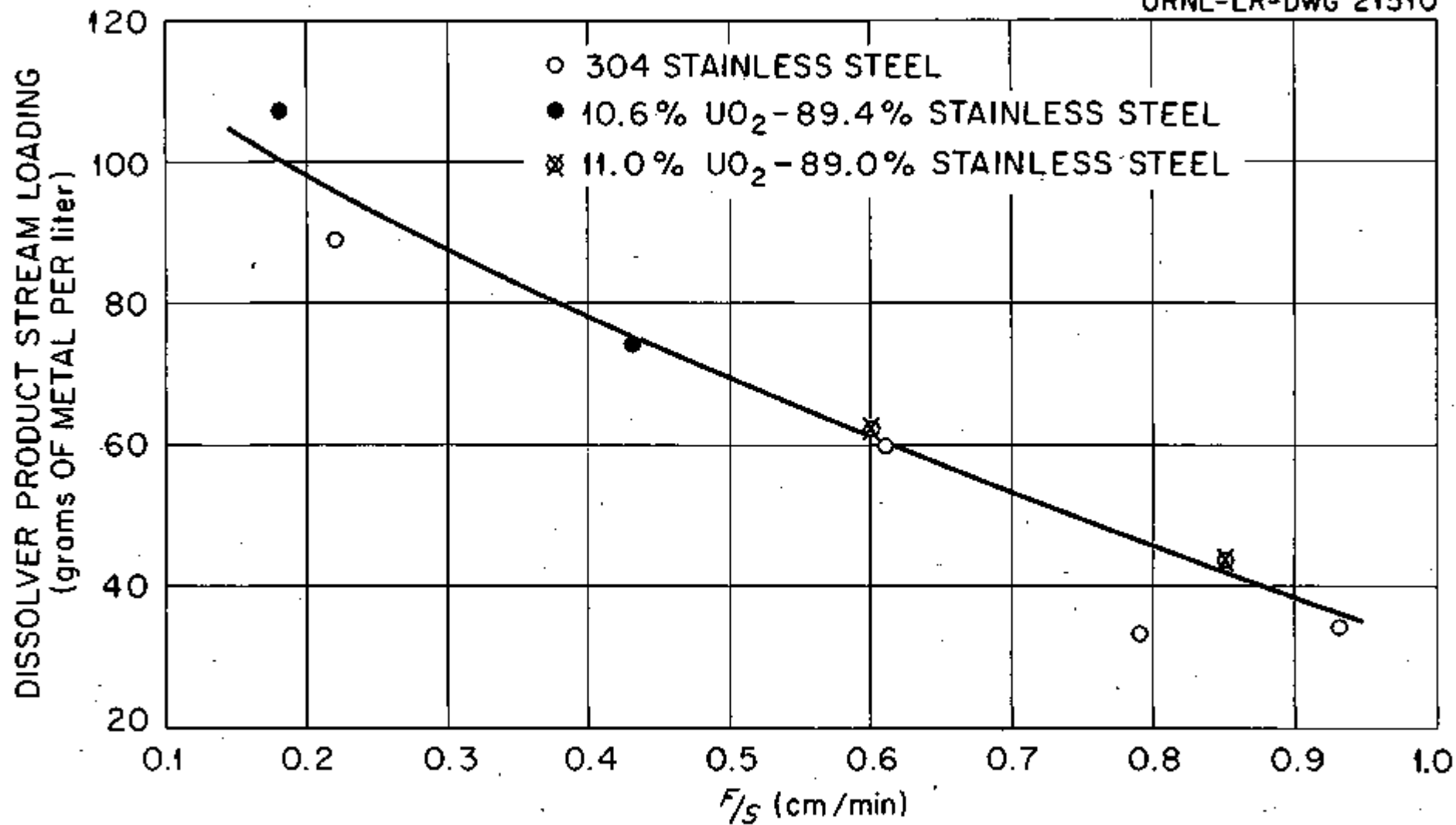
Reaction Rate as a Function of Acid Feed Rate to Surface Area Ratio for an Acid Feed Composition of 5M HNO<sub>3</sub>-2M HCl.



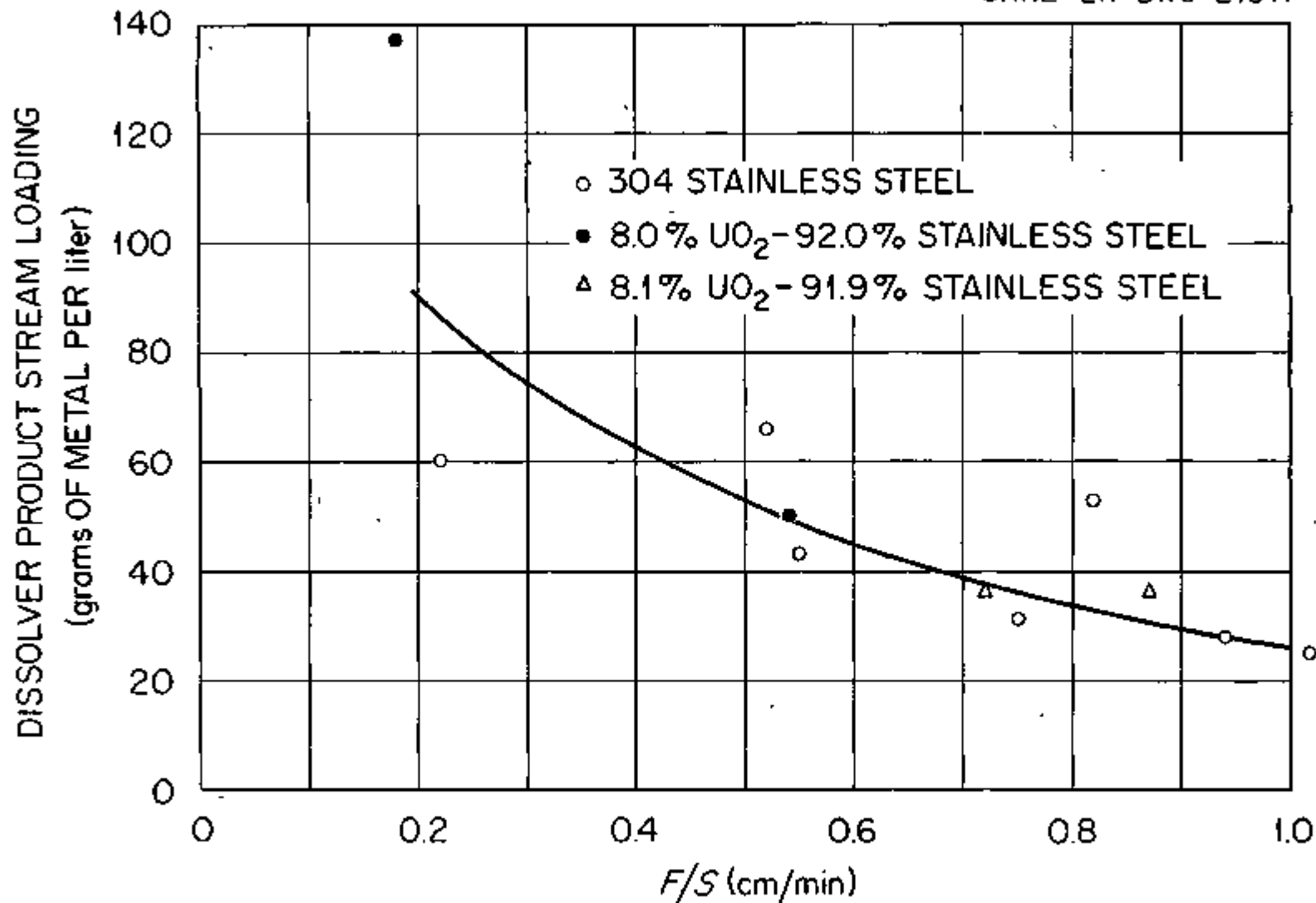
Reaction Rate as a Function of Acid Feed Rate to Surface Area Ratio for Acid Feed Compositions of (6) 5 M HNO<sub>3</sub>-1.5 M HCl; (7) 3 M HNO<sub>3</sub>-2 M HCl; and (8) 3 M HNO<sub>3</sub>-1.5 M HCl.



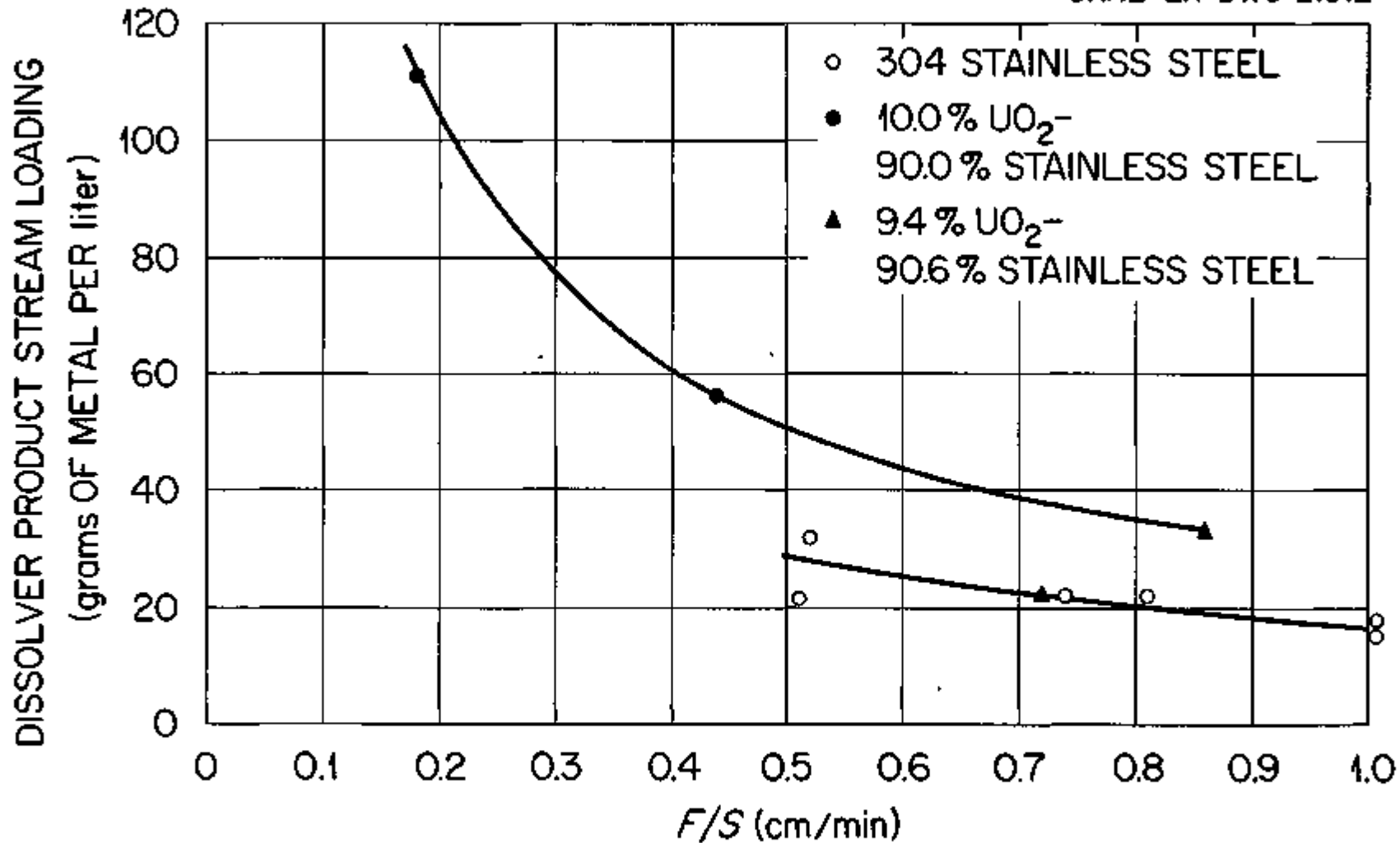
Dissolver Product Stream Loading as a Function of Acid Feed Rate to Surface Area Ratio for Acid Feed Composition 5M HNO<sub>3</sub>-2M HCl.



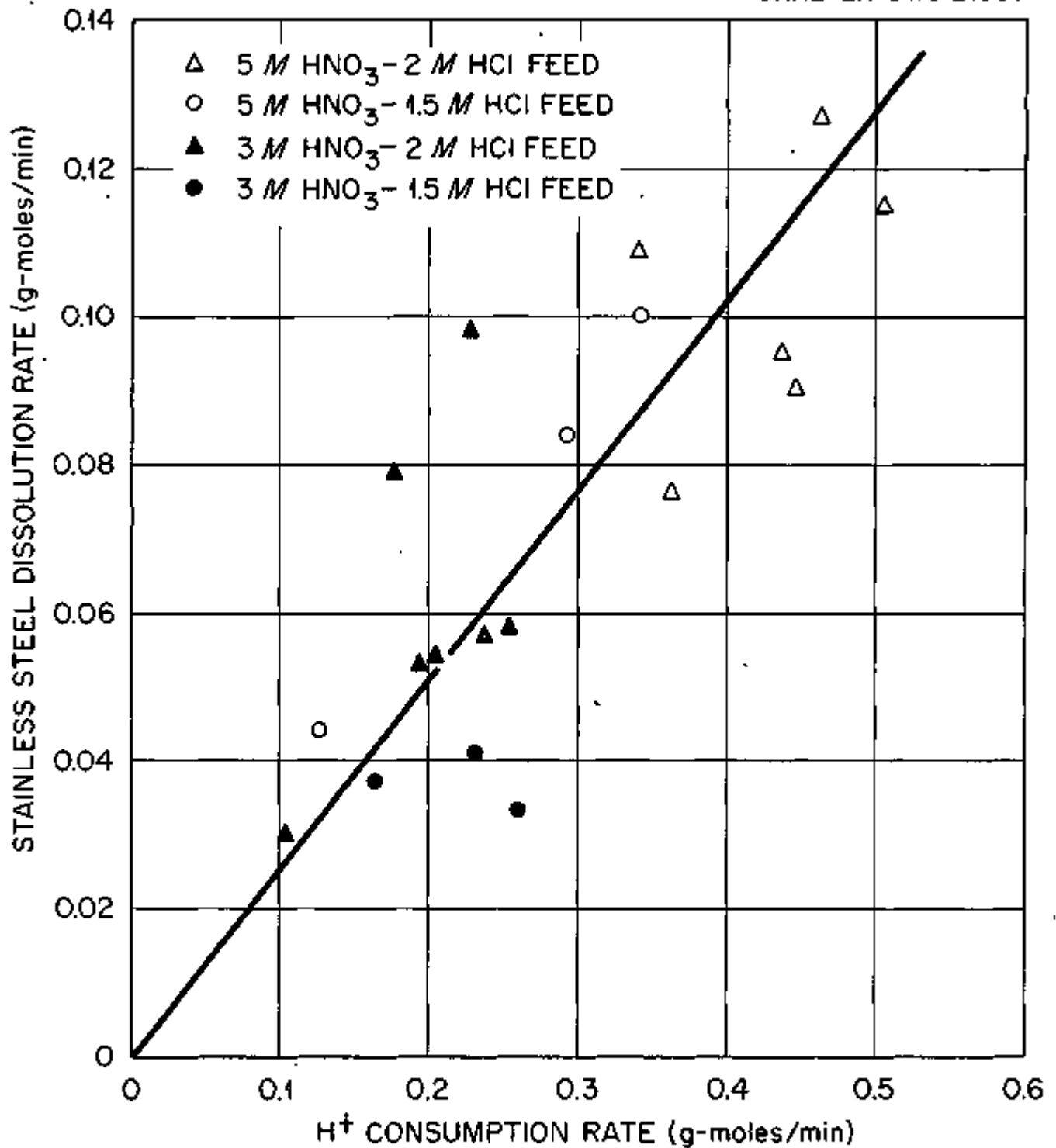
Dissolver Product Stream Loading as a Function of Acid Feed Rate to Surface Area Ratio for Acid Feed Composition 5 M HNO<sub>3</sub>-1.5 M HCl.



Dissolver Product Stream Loading as a Function of Acid Feed Rate to Surface Area Ratio for Acid Feed Composition 3 M HNO<sub>3</sub> - 2M HCl.

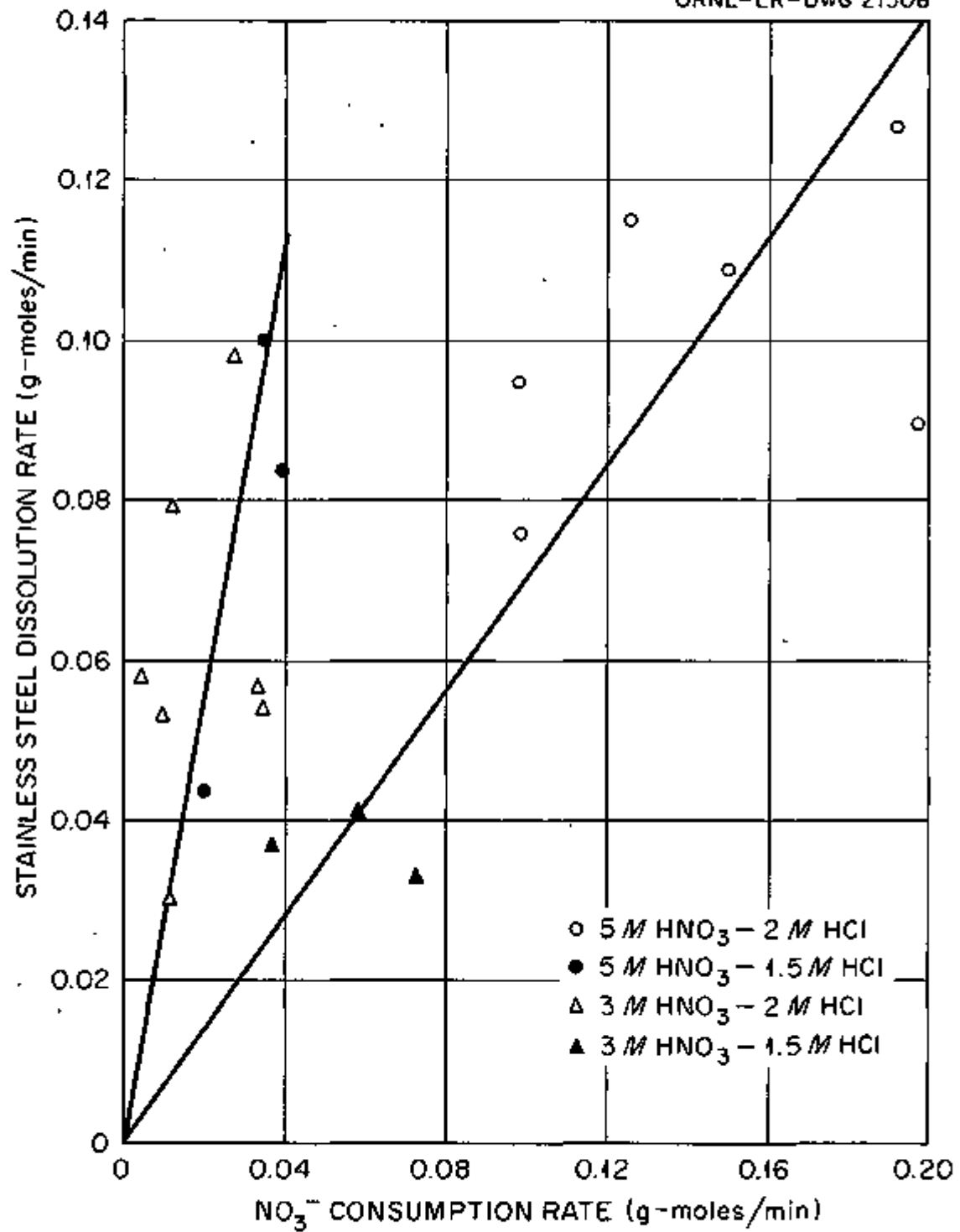


Dissolver Product Stream Loading as a Function of Acid Feed Rate to Surface Area Ratio for Acid Feed Composition 3M HNO<sub>3</sub>-1.5M HCl.

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Stainless Steel Dissolution Rate as a Function  
of H<sup>+</sup> Consumption Rate.

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Stainless Steel Dissolution Rate as a Function of  
NO<sub>3</sub><sup>-</sup> Consumption Rate.



Non-condensable off-gas compositions were not appreciably affected by small fractions of  $UO_2$  (5.5 to 11%) in the stainless steel, except for the 5-2 acid feed where it suppressed chloride loss to some extent (Table 1).

Chloride losses ranged from 0.2 to 4.6% and nitrogen losses ranged from 8.6 to 28.3%.

## 6.0 STRIPPING

### 6.1 Equipment

The stripping apparatus consisted primarily of a 4 in. Pyrex column, a reboiler and condenser (Fig. 12). The column contains 12 "Vycor" glass single bubble cap plates with 6 in. long sections of 4 in. flanged Pyrex pipe secured between the bubble cap plates and sealed with Teflon envelope gaskets. The plates are designed so that samples may be withdrawn from both the liquid on the plate and the vapor below the plate without seriously disturbing column operation (Fig. 13). A Teflon gasket seals the Pyrex down-comer to the plate.

The reboiler is a steam-jacketed, glass-lined vessel provided with a sight glass for level control. The condenser is a 13.5 ft<sup>2</sup> Pyrex single-pass heat exchanger suspended vertically and operated as an updraft condenser. The feed was metered by a glass rotameter using a weighted plastic bob and by a Pulsafeeder pump with a Kel F diaphragm and a ceramic and Teflon head. All the materials used in parts of the system subjected to appreciable  $Cl^-$  concentrations at operating temperatures were of either Vycor, Pyrex, Fluorothene or Teflon.

### 6.2 Procedure

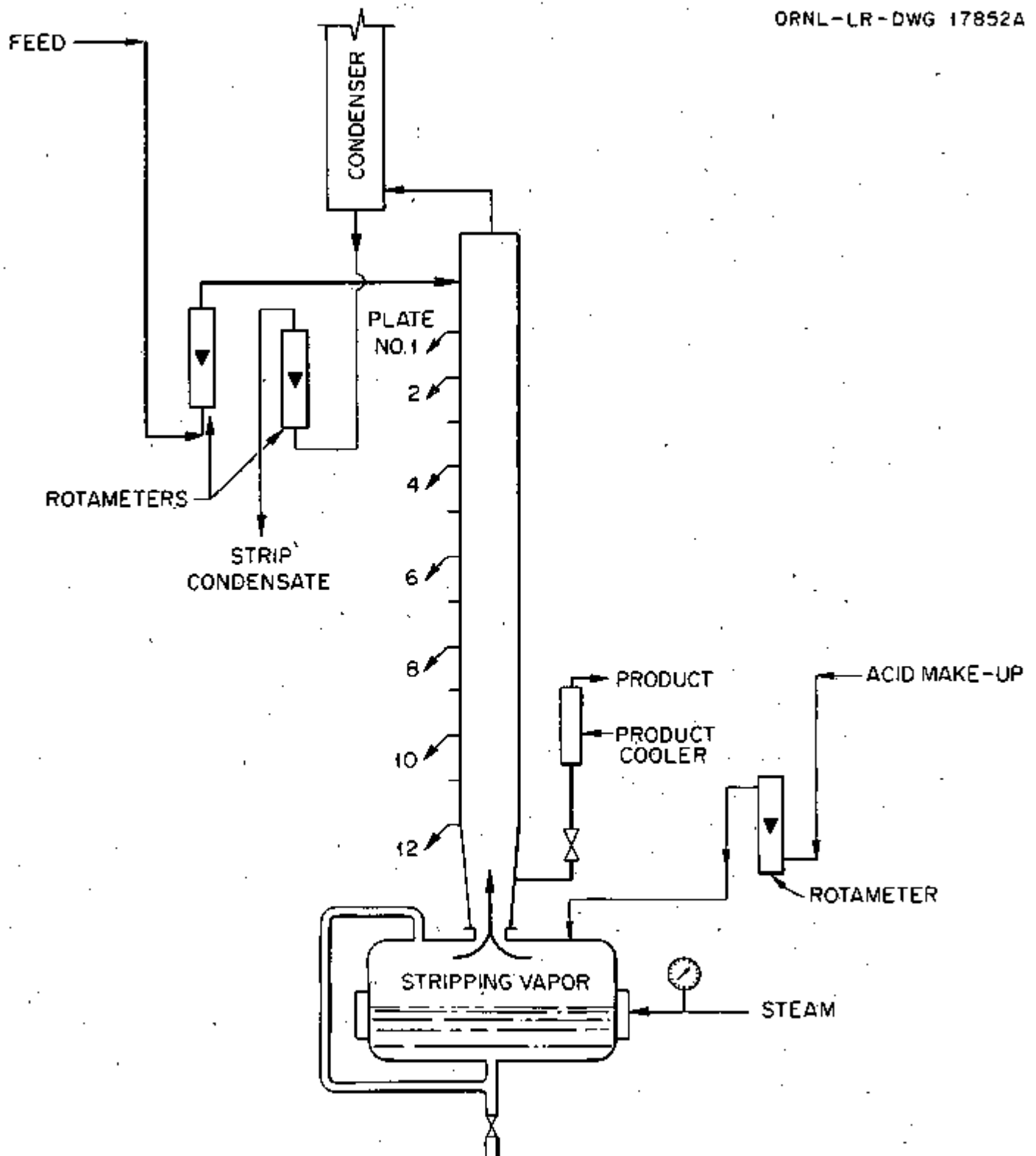
To operate the equipment over a range of values of  $V/L$ , (moles of vapor flowing upward/moles of liquid flowing downward) the vapor rate  $V$  was kept relatively constant while the liquid rate  $L$  was varied by changing feed rates. The vapor rate from the reboiler was kept constant by regulating the steam pressure while the vapor rate at the top of the column was obtained by measuring the overhead condensate rate. This measurement allowed adjustment of  $V/L$  without waiting for lab results since feed compositions varied only slightly throughout the nine runs.

The stripped product was drawn out of the column directly from the twelfth or bottom plate thus isolating the reboiler from the  $Cl^-$  containing part of the system. Thus, by keeping the volume of the  $Cl^-$  containing part of the system low, steady state operation could be reached in about two hours. An average run was two hours in duration with samples withdrawn after 1/4, 1 and 1-3/4 hours of operation; sample points included the strip, feed, reboiler, product, plates Nos. 1, 2, 4, 6, 8, and 10 and the off-gas line.

TABLE I  
DISSOLVER OFF-GAS COMPOSITIONS AND RATES

ACID FEED COMPOSITION	Wt. % UO <sub>2</sub> IN STAINLESS STEEL	OFF-GAS COMPOSITION (%)				Cl LOSS (%)	N LOSS (%)
		CHLORIDE*	NO <sub>2</sub>	NO	N <sub>2</sub>		
5 M HNO <sub>3</sub> - 2 M HCl	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

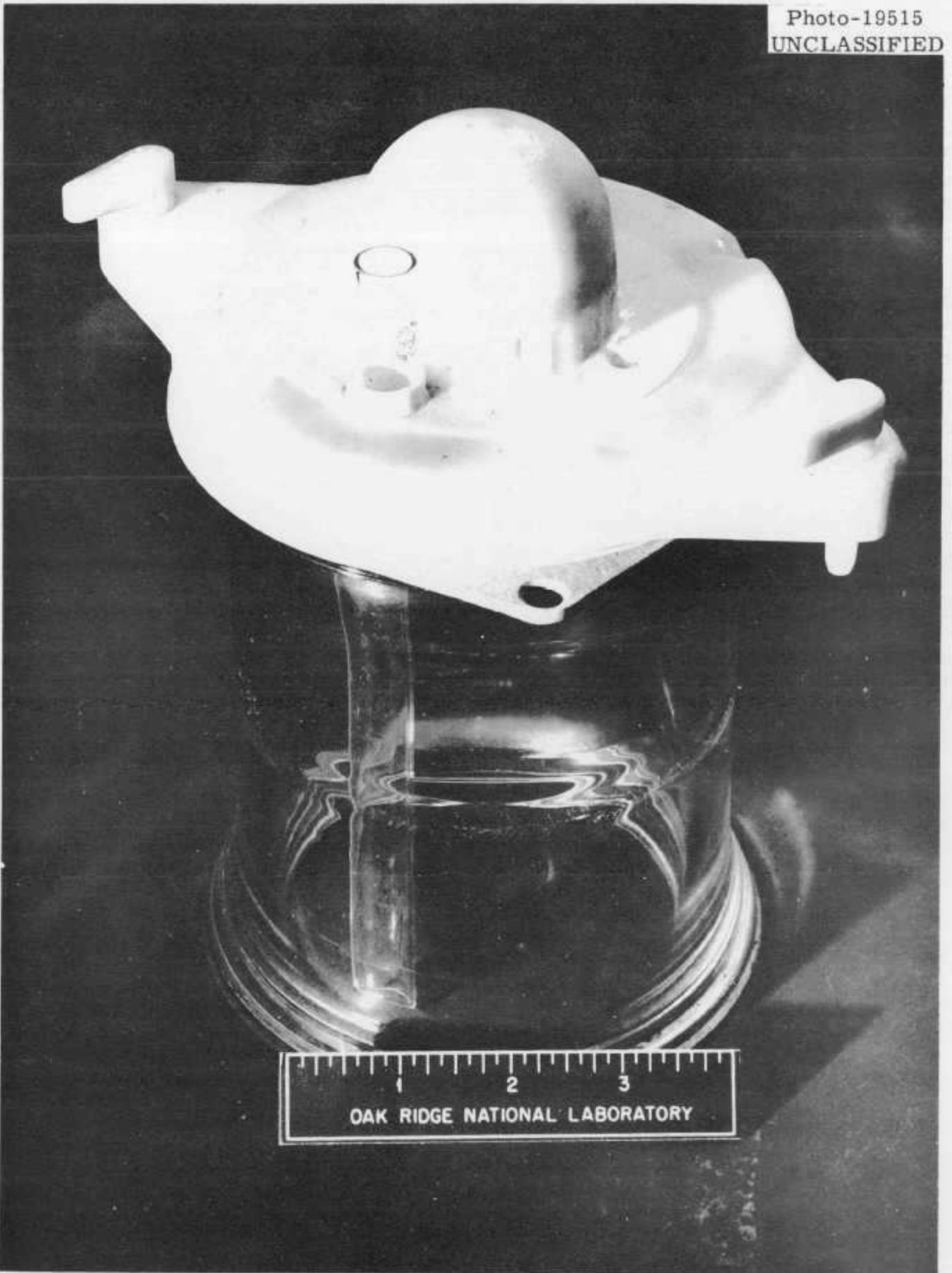
\*NOT ANALYZED BY MOLECULAR SPECIES BUT AS TOTAL CHLORIDE.



Apporatus for HCl Distillation.

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The number of moles/liter of each stream was calculated from laboratory analyses of the samples; this number multiplied by the volume of the stream collected during the run gave the total moles of that stream, the liquid or vapor rates required in V/L calculations. The V/L's tabulated are averages of the V/L at the top of the column calculated from the feed and  $\text{Cl}^-$  containing strip condensate streams, and the V/L at the bottom calculated from the product stream and the  $\text{HNO}_3\text{-H}_2\text{O}$  stripping vapor. The feeds for all runs were prepared by dissolving 50-60 g/liter  $30^4$  stainless steel in 5 N  $\text{HNO}_3$  - 2 N  $\text{HCl}$ ; the feed for runs Nos. 1 and 2 also contained about 12 g/liter natural uranium. The uranium apparently had no effect on the  $\text{Cl}^-$  stripping.

### 6.3 Results

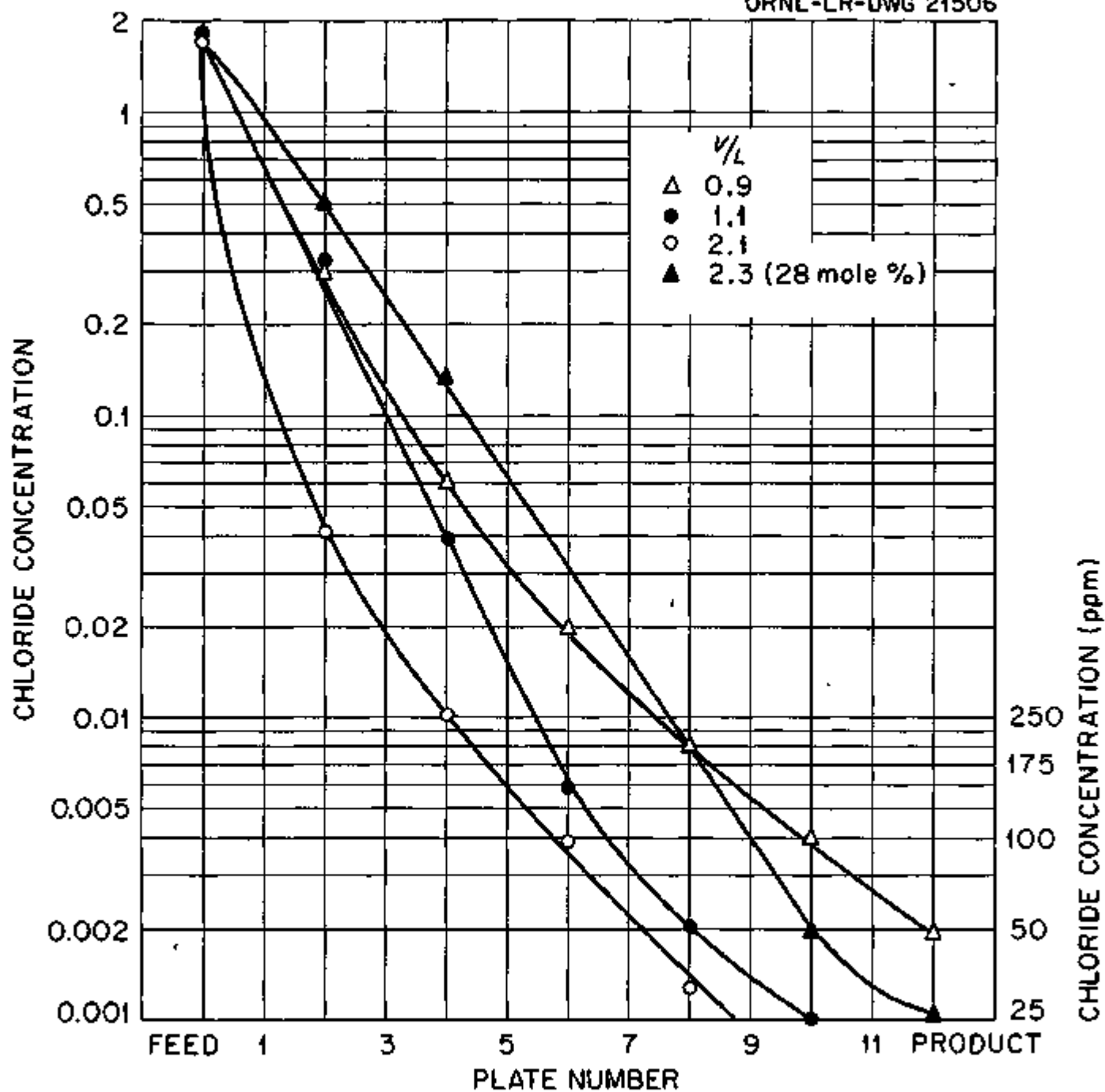
The results of the nine stripping runs showed that the  $\text{Cl}^-$  concentration in the stripped product could be reduced to 50 ppm or below by stripping with  $\text{HNO}_3\text{-H}_2\text{O}$  vapor ranging from 20 mole %  $\text{HNO}_3$  to 38.3 mole %  $\text{HNO}_3$  (azeotrope). A V/L as low as 0.9 was effective using azeotrope while a value somewhat in excess of 1.7 was required with 20 mole % stripping vapor (Table 2). From these data it may be seen that the higher the  $\text{HNO}_3$  concentration of the strip vapor the more effective the  $\text{Cl}^-$  removal and for a given concentration, the higher the V/L the more effective the removal (Figs. 14 and 15). This result is as would be expected but yields no information about the method of  $\text{Cl}^-$  removal. It may also be observed that the higher the  $\text{HNO}_3$  concentration the higher the  $\text{Cl}^-$  loss in the form of non-condensable gases. This property as well as most of the other properties of the system can best be discussed as a function of V/L at a specific stripping vapor composition. At 20 mole % stripping vapor, as the V/L increased, the  $\text{Cl}^-$  loss decreased, the  $\text{NO}_2$  in the overhead increased and the  $\text{NO}_2$  in the bottoms product did not change appreciably. At 38.3 mole %, as V/L increased, the  $\text{Cl}^-$  loss increased, the  $\text{NO}_2$  in the overhead increased, and the  $\text{NO}_2$  in the bottoms product changed only slightly. The trend in  $\text{Cl}^-$  loss was the only one which reversed with the change in stripping vapor concentration.

### 6.4 Plate Efficiency

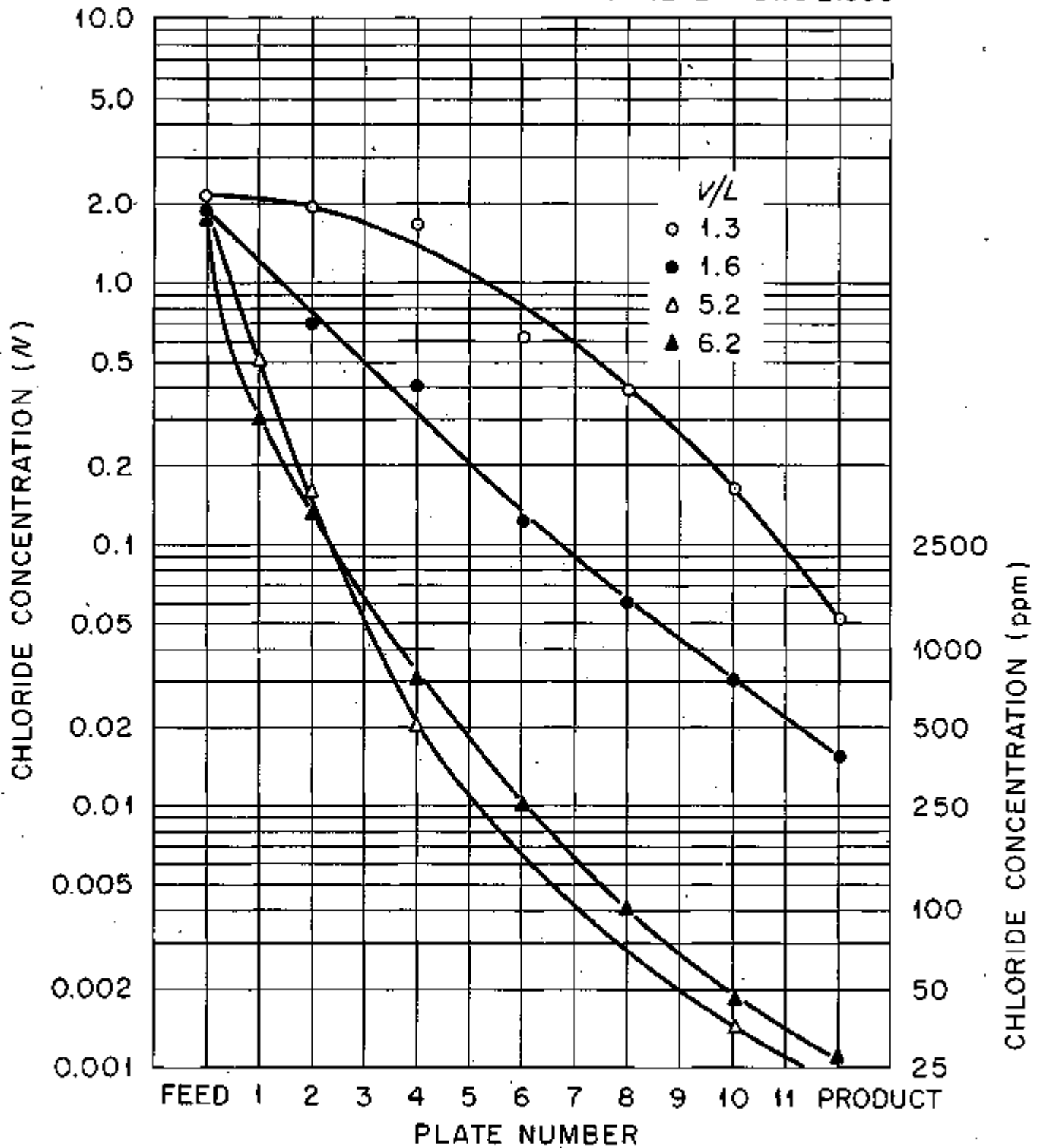
Direct calculation of plate efficiency was not possible due to the lack of vapor-liquid equilibrium data for aqua regia solutions of stainless steel salts. The plate efficiency for the rectification of 65%  $\text{HNO}_3$  in the stripping column was found to be about 30%. Hence the number of theoretical stages to carry out the separations reported was probably about three to four.

## 7.0 MATERIALS OF CONSTRUCTION

The dissolver-stripper-feed adjustment tank-rectifier flowsheet presents a variety of conditions to be withstood by materials of construction. In the dissolver, the corrosive environment changes from boiling dilute

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Chloride Concentration Profile in DAREX Stripping Column  
Azeotropic Stripping Vapor.

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Chloride Concentration Profile in DAREX Stripping Column. 20 mole % stripping vapor.

Table 2  
EFFECT OF V/L AND STRIPPING VAPOR CONCENTRATION ON Cl<sup>-</sup> REMOVAL

Stripping Vapor Mole % HNO <sub>3</sub>	V/L	Cl <sup>-</sup> Loss %	NO <sub>3</sub> <sup>-</sup> in Overhead N	NO <sub>3</sub> <sup>-</sup> in Product N	Cl <sup>-</sup> in Product (ppm)
20	1.3	38	1.75	12.3	1300
20	1.6	35	3.36	12.2	375
20	5.2	5	7.6	12.6	17
20	6.1	5	7.2	11.8	27
38.3	0.9	65	4.56	15.0	27
38.3	1.1	75	7.16	14.7	12
38.3	2.1	90	12.9	15.9	16
38.3	2.1	90	12.9	16.2	10



aqua regia to a solution of metal ions in depleted acid, with oxides of nitrogen and chlorine-containing species in the vapor phase. The dissolver product stream in the top of the stripping column is in equilibrium with dilute aqua regia vapor and non-condensable gases produced by decomposition reactions, while the solution at the bottom is in equilibrium with azeotropic  $\text{HNO}_3$ . Corrosion is not a serious problem for the feed adjustment tank and rectifier due to the absence of chloride ion.

Corrosion tests under simulated batch and continuous dissolver conditions and stripping column conditions are being conducted by Battelle Memorial Institute for Oak Ridge National Laboratory. For batch dissolution conditions tantalum, titanium 75, zirconium and Haynes 21 have corrosion rates below 2 mils per month. For the conditions of continuous dissolution tantalum, titanium, and Haynes 21 appear sufficiently resistant. Tantalum and titanium are satisfactory for the stripping column, while Haynes 21 is not suitable.