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DAREX PROCESSING OF APPR FUEL: EFFECT OF ACIDITY AND GAS SPARGING ON RATE OF CHLORIDE REMOVAL FROM DISSOLVER PRODUCT DURING REFLUXING

B. C. Finney
F. G. Kitts

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CHEMICAL TECHNOLOGY DIVISION

Unit Operations Section

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ABSTRACT

The rate of chloride removal varied directly with HNO_3 concentration in an APPR-type Darex dissolver product containing 100 g/liter metal loading, 0.58 M initial chloride, and initial HNO_3 concentrations of 8, 9, 10, 12, and 14 M. The removal rate with 8 and 9 M HNO_3 was very low. After 6 hr refluxing, the chloride content decreased to 0.50 and 0.36 M, respectively. After refluxing for the same time with 10 to 14 M HNO_3, the product contained 0.064 to 0.0007 M (2270 to 25 ppm) chloride. The effect of air sparging was approximately equivalent to refluxing without sparging at a HNO_3 concentration 2 M higher. After 6 hr sparging and refluxing the chloride content varied from 0.034 to < 0.00014 M (1200 to < 5 ppm) for initial HNO_3 concentrations from 8 to 14 M.

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1.0 INTRODUCTION

The Darex head-end process is a means of converting stainless steel-uranium and stainless steel-UO_2 fuels to chloride-free nitrate solutions suitable for processing in existing solvent extraction equipment.[1,2] Chloride is necessary to effect dissolution of stainless steel in nitric acid but it must be removed to avoid corrosion of feed adjustment, solvent extraction, and waste handling equipment fabricated of stainless steel.

Small-scale chloride removal studies were made to determine the effect of nitric acid concentration and sparging on the rate of chloride removal from the dissolver product and to obtain data for use in designing larger scale feed adjustment experiments and in pilot plant installations. All results reported are strongly influenced by the scale of operation and must be verified on a larger scale, but they indicate the feasibility of the proposed techniques.

The Darex head-end process consists basically of three steps: (1) dissolution, (2) chloride removal, and (3) adjustment of the resulting solution to solvent extraction feed concentrations. These steps may be accomplished continuously, semicontinuously, or batchwise with nitric acid solutions from 61 to 95 wt % HNO_3 to volatilize and/or decompose the chloride. To remove chloride to the desired concentration of < 350 ppm in the solvent extraction feed, it may be desirable at some point in the various flowsheets to incorporate a reflux step.

In the ORNL reference flowsheet (Fig. 1) for APPR fuel reprocessing, provision is made for a refluxing step and an air sparge following the recovery of mixed acid (dilute aqua regia for the preparation of the next batch of dissolvent) and the batch addition of fresh 13.3 M HNO_3.[3,4] Excess nitric acid is removed after the reflux step by distillation, and the acidity in the solvent extraction feed is decreased to 2-3 M by dilution with water. The ultimate chloride content therefore cannot be specified for any run, but for acidities greater than 11 M there would probably be a further decrease in the reported values by a factor of at least 10.

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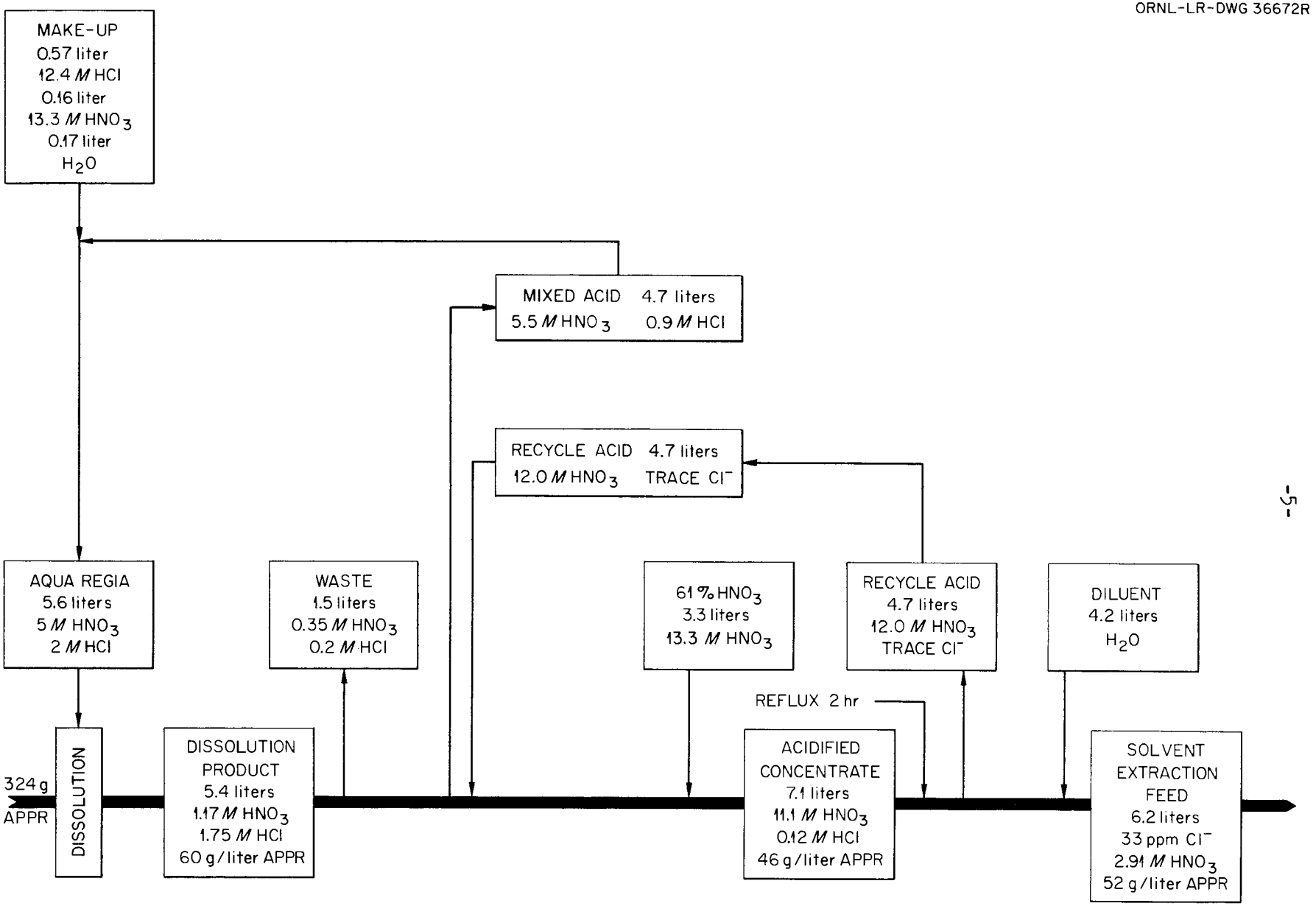

Fig. 1. Darex Process: Reference Flowsheet for Batch Operation with 61 wt % HNO_3 (Data from Run APPR-52).

2.0 VARIABLES AFFECTING CHLORIDE REMOVAL

2.1 Nitric Acid Concentration and Refluxing Time

For a given reflux time the chloride concentration in the dissolver product varied inversely with the initial nitric acid concentration (Fig. 2). Very low chloride concentrations were reached (< 100 ppm) by decomposition during 6 hr of reflux with initial nitric acid concentrations of 12 M or greater. Below an initial HNO_3 concentration of 10 M there was only a very slow change in the chloride concentration with reflux time.

Higher nitric acid concentrations increased the chloride decomposition rate and decreased the chloride in equilibrium with the liquid phase. Initially, chloride removal rates were high for acidities above 10 M, but the lower slopes of the removal curves indicated either the approach to an equilibrium chloride concentration or a gradual decrease in acidity and total removal rate. However, the experimental data (Table 1, Appendix) indicate that the nitric acid concentration did not decrease significantly in any run, so that a pseudo-equilibrium chloride content which varies with acidity is probably approached in the refluxing step.

Five runs were made with an arbitrarily selected dissolver product containing 100 g of APPR metal per liter, 0.58 M initial chloride, and initial HNO_3 concentrations of 8, 9, 10, 12, and 14 M.

2.2 Sparging

Air sparging increased both the rate of chloride removal and the total amount removed (Fig. 3). For example, after 2 hr refluxing and sparging of a solution with an initial HNO_3 concentration of 10 M, the chloride concentration was approximately 0.01 M (355 ppm) as compared to 0.3 M without sparging.

Use of the sparge was approximately equivalent to an additional 2 moles of HNO_3 per liter without sparging. With an initial dissolver product HNO_3 concentration of 8 M, the chloride concentration after 6 hr was 0.034 M as compared to 0.064 M with an initial HNO_3 concentration of 10 M without air sparging. With initial HNO_3 concentrations of 12 and 14 M it was possible to obtain chloride concentrations of less than 10 ppm with

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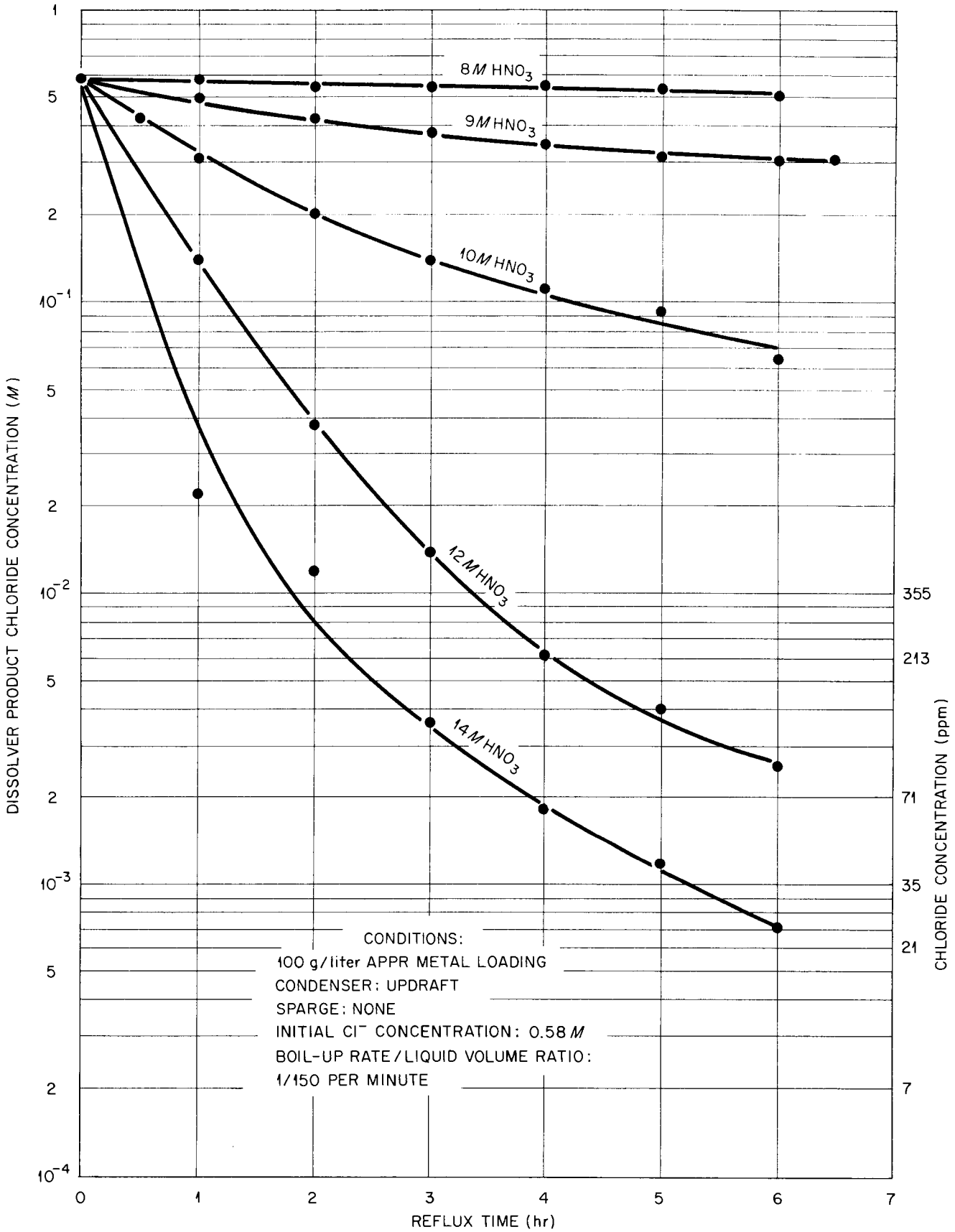

Fig. 2. Darex Dissolver Product Chloride Concentration as a Function of Reflux Time for Various Initial Nitric Acid Strengths.

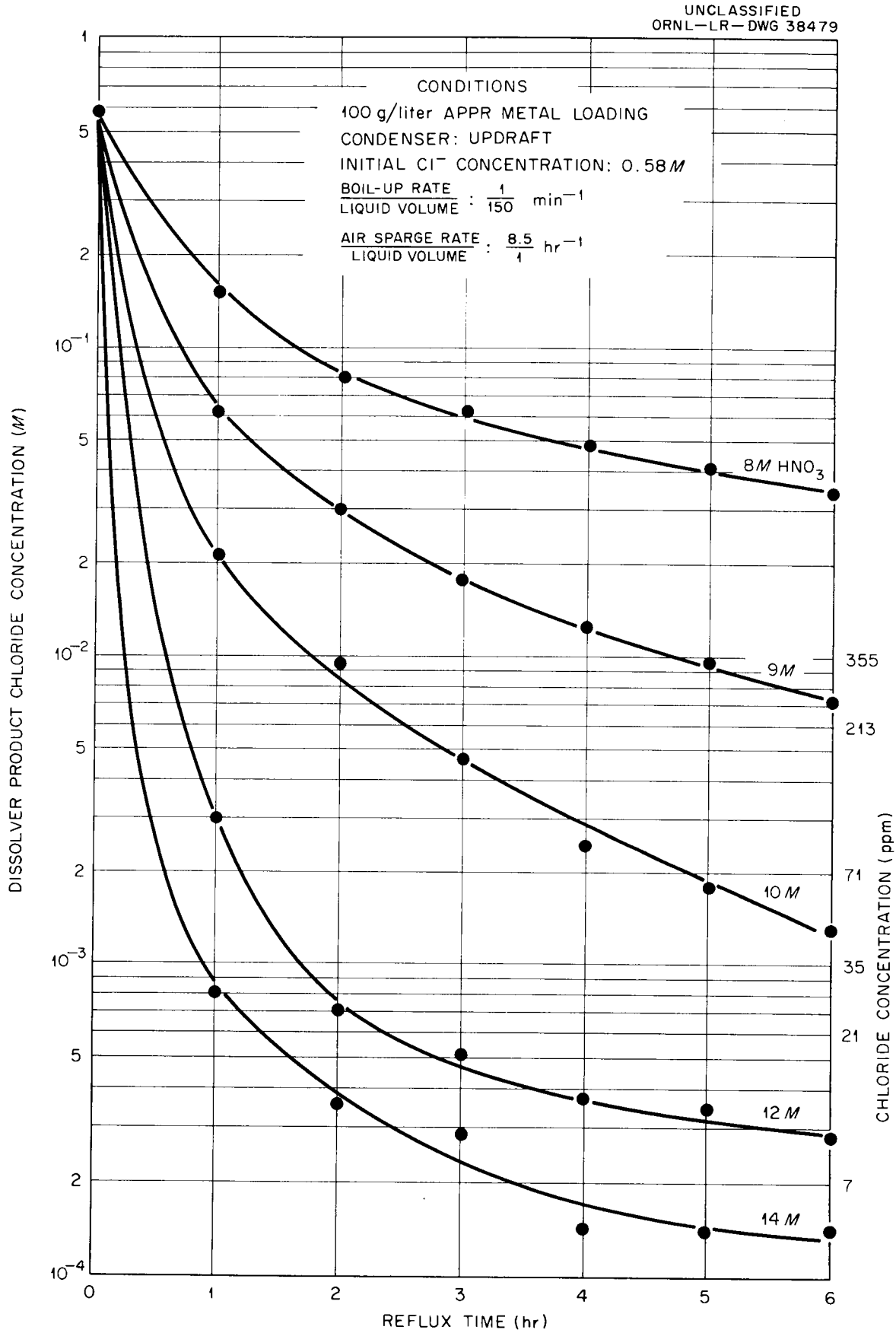

Fig. 3. Darex Dissolver Product Chloride Concentration as a Function of Reflux Time for Various Initial Nitric Acid Concentrations Using an Air Sparge.

sparging. These five runs were made with the same type of Darex dissolver product used previously (Sec. 2.1) containing 100 g of APPR metal per liter, 0.58 M initially in chloride and 8, 9, 10, 12, and 14 M in HNO_3.

One run was also made to determine the rate of chloride removal from a dissolver product at room temperature (~ 25°C) using an air sparge (Fig. 4). There was a very slow reduction in the chloride concentration (0.65 M to 0.41 M) after 12 hr refluxing. Room temperature sparging with 12.7 M HNO_3 was approximately as effective as refluxing with 8 M HNO_3 with no sparging (Fig. 2).

In one scouting run, refluxing with nitrogen as a sparge gas was more effective than refluxing with no sparge but was not so effective initially as refluxing with air (Fig. 5). The over-all rates for chloride removal with air and nitrogen were approximately equal after 6 hr.

It was concluded that refluxing and sparging is a useful and effective method of removal of chloride from the dissolver product of the Darex process for APPR fuel. The use of an air sparge made it possible to remove chloride rapidly when the acidity was over 9 M. With refluxing alone, chloride was removed very slowly from 9 M HNO_3. It is recommended that provisions for refluxing and sparging be incorporated in the final pilot plant design for APPR fuel processing. The use of reflux and sparge would increase the flexibility of any flowsheet which depended on distillation alone for chloride removal.

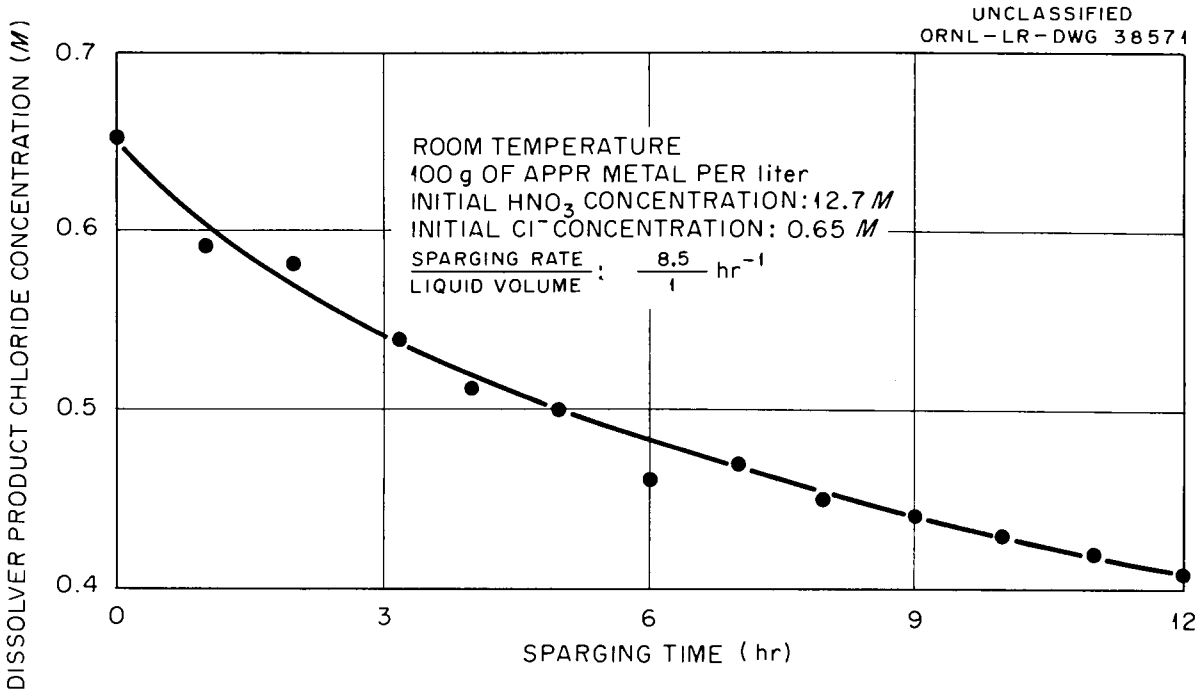

Fig. 4. Chloride Concentration in Darex Dissolver Product as a Function of Air Sparging Time.

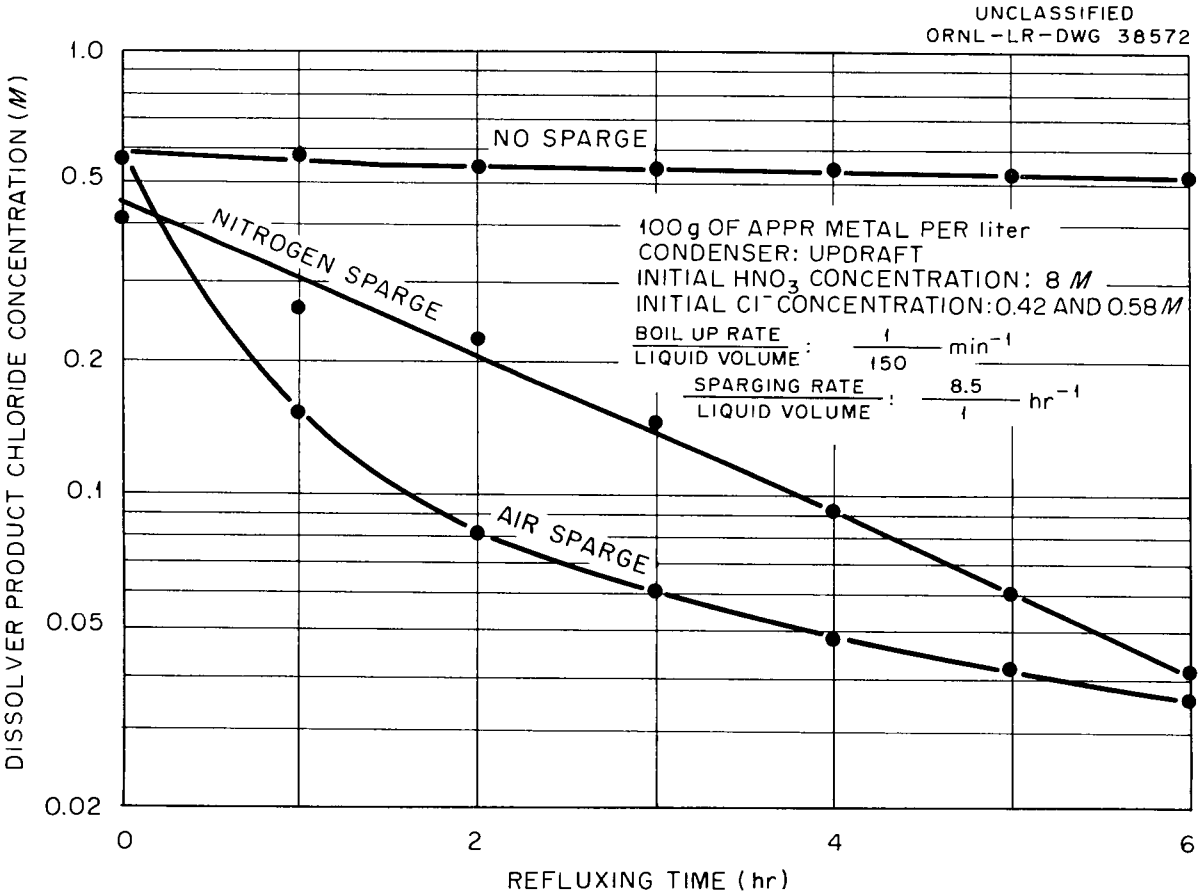

Fig. 5. Chloride Concentration in Darex Dissolver Product as a Function of Refluxing Time.

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4.0 APPENDIX

4.1 Procedure

The test solutions were prepared by concentrating a single batch of product from chloride removal and feed adjustment runs made in the 4-in.-i.d. Pyrex feed adjustment tank using 61 wt % HNO_3 with a reflux flowsheet.[3] Hydrochloric acid, nitric acid, and water were added to obtain solutions with 100 g of APPR metal per liter and the various chloride and nitric acid concentrations indicated. A run was made by charging 900 ml of adjusted dissolver product to a 2-liter distillation flask and boiling the solution at total reflux using an updraft condenser. Constant boil-up was maintained at a boil-up/liquid volume ratio of approximately 1/150 per minute. The sparging rate was also maintained constant at a sparging rate/liquid volume ratio of approximately 8.5 per hour. The sparge gas was dispersed by a 1-in.-dia glass frit mounted horizontally and centered about 2 in. below the undisturbed surface level.

4.2 Summary of Data and Calculated Values

In Table 1 are shown the experimental results of all chloride removal runs. Most of the data are presented graphically in Figs. 2-5.

Table 1. Comparison of Chloride Concentration in APPR Darex Dissolver Product as a Function of Reflux Time and Various HNO_3 Concentrations, with and without Air Sparging

Dissolver product: 100 g APPR metal per liter, 0.58 *M* initial Cl^-, and 8-14 *M* initial HNO_3

Condenser: updraft with total reflux

$$\frac{\text{Boil Up Rate}}{\text{Liquid Volume}} \approx \frac{1}{150}\ \text{min}^{-1}$$

$$\frac{\text{Air Sparge Rate}}{\text{Liquid Volume}} \approx \frac{8.5}{1}\ \text{hr}^{-1}$$

Reflux Time, hr	8 *M* Initial HNO_3				9 *M* Initial HNO_3				10 *M* Initial HNO_3				12 *M* Initial HNO_3				14 *M* Initial HNO_3			
	HNO_3 Content, *M*		Cl Content, *M*		HNO_3 Content, *M*		Cl Content, *M*		HNO_3 Content, *M*		Cl Content, *M*		HNO_3 Content, *M*		Cl Content, *M*		HNO_3 Content, *M*		Cl Content, *M*	
	Sparge	No Sparge	Sparge	No Sparge	Sparge	No Sparge	Sparge	No Sparge	Sparge	No Sparge	Sparge	No Sparge	Sparge	No Sparge	Sparge	No Sparge	Sparge	No Sparge	Sparge	No Sparge
1	7.60	7.79	0.15	0.57	8.73	8.9	0.062	0.50	9.69	10.0	0.0215	0.31	11.34	11.16	0.0013	0.14	13.01	13.19	0.0008	0.022
2	7.61	8.03	0.08	0.54	8.90	8.9	0.03	0.42	9.71	10.0	0.0093	0.20	10.96	11.22	0.0007	0.04	13.19	12.9	0.00035	0.012
3	7.71	8.03	0.062	0.54	8.83	9.0	0.0176	0.38	9.78	9.79	0.0047	0.15	11.55	11.18	0.00051	0.0146	13.16	12.62	<0.00028	0.0037
4	7.65	8.01	0.048	0.54	8.87	8.89	0.0124	0.34	9.74	9.81	0.0024	0.11	11.60	11.03	0.00037	0.006	13.41	12.71	<0.00014	0.0018
5	7.63	8.09	0.0415	0.53	8.82	8.95	0.0095	0.31	9.51	9.71	0.0018	0.092	11.74	11.08	0.00034	0.004	13.57	12.75	<0.00014	0.0012
6	7.62	8.07	0.034	0.50	8.90	8.92	0.0072	0.30	9.53	9.70	0.0013	0.064	11.66	11.00	0.00028	0.0025	13.36	12.95	<0.00014	0.0007

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