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SUBJECT: Nitric Acid Dissolution of Uranium in a Closed System

TO: F. L. Steahly

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FROM: A. E. Wible

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1.0 Introduction

The primary objectives of this work were to demonstrate on a small scale (8 kg. U) the feasibility of carrying out a uranium dissolution in a closed system using non-irradiated slugs and to recover the acidic gases (NO and NO_2) evolved in a form suitable for re-use.

Concurrent with demonstrating the process, data were obtained on the following:

U Dissolution -
- (a) Dissolution rates for W, W/2, and SR slugs in boiling 55% (Initial) HNO_3,
- (b) Average mols HNO_3 consumed/mol U dissolved,
- (c) Average off-gas composition,
- (d) Average residual gas composition and volume.

Al Jacket Removal-
- (a) Average Al penetration rate by 10% NaOH - 20% $NaNO_3$,
- (b) H_2 evolution,
- (c) U losses.

2.0 Summary

The dissolution of uranium in 55% nitric acid (initial concentration) at the boiling point in a closed system (see Fig. 5.1-1) presents no operational difficulties provided that:

(1) Dissolver freeboard is adequate (at least 200%) to prevent foam carry-over.
(2) Provisions are made to handle the initial off-gas surge.
(3) Self-priming centrifugal or positive displacement pumps are used for recirculating gas-holder solution.

The rates of reaction of W, W/2, and SR slugs (for dimensions and weights see Table 5.1-1) in boiling 55% nitric acid (initial concentration) are shown in Figure 5.2-2. An average of 4.3 mols nitric acid was consumed per mol U dissolved, and the acid concentration in the dissolver after 10 hours reaction time was, in general, less than 0.5 N. The off-gas composition from the condenser-absorber was approximately 83% NO, 15% NO_2, and 2% inerts. An average of 4.5 liters of inerts analyzing 88.2% N_2, 8.7% CO_2, 1.5% N_2, 1.3% CO and 0.3% H_2 were collected in the gas-holder per kilogram of uranium dissolved.

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The rate of penetration of the aluminum jackets by boiling 10% NaOH - 20% $NaNO_3$ averaged 0.1 inch/hr. At an initial molar ratio of NaOH/Al of 1.2, the de-jacketing solution showed an Al_2O_3 precipitate on standing overnight, while at higher ratios (greater than 1.65) no precipitation occurred. Average H_2 evolution at an NaOH/Al ratio of 1.65 was about 8 liters per kilogram of aluminum dissolved. Uranium losses averaged 0.014% in the de-jacketing step and 0.038% in the cold 3.5% nitric acid wash.

Based on data obtained, a flowsheet for the nitric acid dissolution of one metric ton of uranium is appended (Fig. 5.2-3).

3.0 Dissolving Procedure

I. Jacket Removal

The canned slugs were placed in the dissolver and covered with 10% NaOH - 20% $NaNO_3$ at the desired NaOH/Al ratio. This solution was brought to boiling and refluxed for 1-3 hrs., collecting the off-gas in the gas holder. The pot contents were then discharged, and the slugs washed with a 3.5% HNO_3 solution.

II. U Dissolution

An amount of water, sufficient to dilute the 70% HNO_3 to be added later to 55%, was then charged to the dissolver and refluxed to expel most of the air from the system. The gas holder was isolated, filled with H_2O, and oxygen added until a volume of H_2O equivalent to about 150% of the volume of residual gases expected (based on 4.5 liters inerts/kg. U dissolved) was displaced. Enough 70% HNO_3 was then added to the dissolver to dissolve one-third of the initial charge (based on 4.3 M HNO_3/M U). The 55% acid formed was brought to boiling at which time the off-gas vent valve was closed and the gas holder turned back into the system. The reaction was allowed to proceed (at the B. P.) for 10 hr. with the system pressure being controlled at atmospheric by manual addition of O_2 to the holder. The dissolver solution was sampled after the first, second and third hours operation in order to obtain rates of reaction for the various type slugs; the dissolution curves were then extrapolated to 100% (based on total U dissolved) at 10 hours. After 10 hrs. operation, the dissolver contents were cooled by the addition of H_2O and discharged with no attempt being made to control the uranium concentration in the dissolver solution; however, by the use of the following formula, the uranyl nitrate and nitric acid concentrations after 10 hrs. dissolution time (Table 5.1-3) can be calculated to any desired specific gravity:

$$\text{sp. gr.} = 1.001 + 0.318\ U\ (\underline{M}) + 0.031\ HNO_3\ (\underline{M}).$$

Approximately 6-9 kgs. U were dissolved per run.

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4.0 Discussion

I. Jacket Removal

Jackets have been removed from X, W, W/2, and SR slugs. Wall thicknesses, depending on the type of slug used, varied from 0.02 to 0.05 inches and ends from 0.2 to 0.4 inch; however, two Hanford W slugs (origin unknown) meeting over-all dimension requirements were found to have end pieces approximately 0.8 inch thick. It should be stressed that over-size Al end pieces on production slugs cannot be tolerated since the end pieces have been observed to drop off during jacket removal and could create quite a problem by plugging transfer lines.

Penetration rates could not be determined by chemical analysis since the jacket wall, which constitutes 80-90% of the aluminum to be removed, is essentially dissolved in the first half-hour. The estimate of the penetration rate (0.1 inch per hour) was deduced from measurements made on the end pieces of partially de-jacketed slugs at various reaction time intervals. Visual observations made on the extent of jacket removal from W, W-2, X and SR slugs by the 10% NaOH - 20% $NaNO_3$ solution are given in Table 5.1-2.

One run made, using 15% NaOH, increased the reaction rate slightly, but this work was dropped since the dimensions of the dissolver required an excessive NaOH/Al ratio to completely cover the slugs.

The NH_3 given off during the course of the reaction was absorbed in the condenser and returned to the dissolver. A condensate sample at the end of a run analyzed 8.3N basic. Based on holder gas analyses, samples in duplicate from three runs gave an average H_2 evolution of 8 liters per kilogram of aluminum dissolved.

Uranium losses in the jacket removal step varied from 0.002 to 0.036% and in the nitric acid wash varied from 0.033 to 0.060%.

II. Uranium Dissolution

A. Dissolver

Curves showing comparative dissolution rates for the first dissolving of a series (200% heel) and for the second dissolving (100% heel) of W, W/2, and SR slugs are shown in Figs. 5.2-2a and b. A curve, representing the third dissolving (200% heel) of a series using W slugs, is shown in Fig. 5.2-2c. After 4-1/2 dissolvings, in a series using W slugs, approximately 5% of the initial charge remained as small (cigarette size) slugs with extremely jagged ends. (Figs. 5.2-2d).

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The superficial surface per unit weight ratio apparently has little significance relative to the dissolving rate. This ratio for the SR slugs is 20 to 30% greater than the W or W/2, but its initial dissolution rate is approximately the same as the W and 50% that of the W/2. Excessive attack on the ends of some slugs has been noted where the apparent dissolution rate is about 3 to 4 times that on the sides, while in other cases the rates appear to be about the same. This indicates that the dissolving rate may be dependent on the metallurgical treatment of the slugs.

There is a definite lag in the reaction rate during the second hour of the second dissolving (100% heel). This anomaly has occurred in 4 out of 5 second dissolvings and has not been observed in either the first or third dissolvings. Although not shown on Fig. 5.2-2b, the amount of U dissolved during the second hour is relatively small.

B. Condenser-Absorber

The condenser reflux was essentially constant throughout a run at 80-100 ml/min. Changes in the HNO_3 and HNO_2 concentrations in the reflux during the course of a run (W slugs) are shown in Fig. 5.2-4. Based on HNO_3 analyses of the dissolver contents and condenser reflux throughout the run, the overall NO_2 absorption efficiency for the down-draft condenser was calculated to be about 90%.

The ratio of NO/NO_2 in the off-gas from the condenser at the end of 1 hr. varied from 65/35 to 85/15, and after that time, a ratio of ca. 85/15 is indicated (spot analyses). By using the following two equations and the average experimental value of 4.3 mols HNO_3/mol U, a ratio of NO/NO_2 of 80/20 is calculated, which is in reasonable agreement with the above analytical value:

$$U + 4\ HNO_3 \longrightarrow UO_2\ (NO_3)_2 + 2\ NO + 2\ H_2O$$

$$U + 8\ HNO_3 \longrightarrow UO_2\ (NO_3)_2 + 6\ NO_2 + 4\ H_2O$$

A down-draft condenser was used to provide more wetted area and greater contact time for the absorption of NO_2 in the off-gas from the dissolver, since a standard reflux (up-draft) condenser of the same area does not utilize its upper portion, thus reducing both area and contact time materially.

III. Gas Holder (Spray Chamber)

The inert gases present in the off-gas from the condenser were concentrated in the spray chamber by reacting the NO-NO_2 with O_2 and absorbing in H_2O. Regardless of the NO/NO_2 ratio, the mols of O_2 consumed per mol of U dissolved will be 1.5, viz:

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$$U + 4\ HNO_3 \longrightarrow UO_2(NO_3)_2 + 2\ NO + 2\ H_2O$$
$$U + 8\ HNO_3 \longrightarrow UO_2(NO_3)_2 + 6\ NO_2 + 4\ H_2O$$
$$2\ NO + 1.5\ O_2 + H_2O \longrightarrow 2\ HNO_3$$
$$6\ NO_2 + 1.5\ O_2 + 3\ H_2O \longrightarrow 6\ HNO_3$$

$$2\ U + 3\ O_2 + 4\ HNO_3 \longrightarrow 2\ UO_2(NO_3)_2 + 2\ H_2O$$

Appreciable HNO_2 was formed in the absorbing water regardless of the partial pressure of O_2 in the vapor space. HNO_2 concentrations up to 0.15 N were observed at HNO_3 concentrations of 1 N with subsequent pump failure due to gassing. Use of a self-priming pump is recommended to alleviate this situation.

Good operational control was achieved throughout the runs by operating the gas holder with O_2 in the holder amounting to 4% of the total gas evolution. The over-all vapor space, including the dissolver, condenser, spray chamber and associated lines, was approximately 8% of the total gas evolved per run. Invariably, however, at the start of a run the pressure in the system increased, probably due to a time lag in the oxidation-absorption step. The time cycle for the gradual increase from 0 to 4" (avg.) Hg pressure and decrease to 0 was about 15 minutes. At no time, other than when an attempt was made to operate the holder at 2% free space (based on total off-gas), did the initial pressure increase require dumping H_2O from the holder in order to acquire additional free space and prevent excessive pressure build-up (> 8" Hg) in the system.

In order to reduce the NO, NO_2, O_2 concentrations in the residual gas, an attempt was made to run O_2 into an NO-NO_2 atmosphere instead of vice versa. Pressure surges (constant volume - variable pressure gas holder), with flash-over from the dissolver, resulted during this run due to the time lag (induction period) in the oxidation-absorption step.

Recommended design and operation for a scaled-up process would include:

(1) Operation of the dissolver at the boiling point.
(2) A variable-volume constant-pressure type combination gas-holder and spray-chamber should be used with a maximum volume of about 30% the total volume of off-gas expected.
(3) Oxygen in the holder at the start of a dissolving equivalent to 10% of the total off-gas.
(4) Controlled oxygen addition to maintain liquid level in the gas-holder constant after the initial surge.
(5) When reaction is 90% complete, stop oxygen flow and collect remainder of gas by displacement.
(6) Titrate holder contents with oxygen to minimum volume at end of dissolving.

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To determine the feasibility of (6), the gas remaining in the holder at the end of one run was titrated with O_2:

	NO	NO_2	O_2	Inerts
Initial (%)	21.0	5.5	0	73.5
Final (%)	0.2	1.9	6.2	91.7

Presumably, the NO-NO_2-O_2 concentrations can be reduced even further using better control methods.

A. E. Wible

A. E. Wible

AEW/rcp

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5.0 Appendix

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5.1 Tables

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Table 5.1-1

Slug Dimensions and Compositions

Slug Type	Slug Dimensions (in.)	Type of Bonding	End Pieces (in.)	Al Bonding (g/slug)	Uranium (g/slug)
Hanford 8" (W)	8 x 1.36 dia.	Triple dip*	0.40	110 ± 5	3590 ± 10
Hanford 4" (W/2)	4 x 1.36 dia.	Triple dip	0.20	57 ± 3	1780 ± 10
Savannah River (SR)	8 x 1.00 dia.	Triple dip	0.20	62 ± 2	1910 ± 10
ORNL (X)	4 x 1.00 dia.	None	0.20	27 ± 3	1160

* Triple dip: bronze at 710°C, 40 secs;
tin at 595°C, 40 secs;
Al-Si at 590°C, 5 secs.

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Table 5.1-2

Data on Aluminum Jacket Removal

Dissolution reagent: 10% NaOH - 20% $NaNO_3$

No. and type of slugs	NaOH/Al mole ratio	Dissolving Time (hr.)	Total Amt. of Al dissolved (g)	Percentage of Al dissolved (estimated by visual inspection)	
				From walls	From ends
6 Hanford 4"	0.80*	2	360	100	50
	0.80*	1	320	95	50
8 Hanford 4"	0.80*	2	430	100	50
6 Hanford 4"	1.15*	2	330	100	100
	1.15*	1	350	100	100
5 Hanford 8"	0.60	2	420	100	50 - 75
	1.12	2	570	100	50 - 75
	1.12	3	not determined	100	100
	1.69	2	510	100	95
10 ORNL	1.52	2	240	100	50
	2.20	2	290	100	100
5 Savannah River	1.11	3	300	100	100
	1.11	3	not determined	100	100
	1.66	3	319	100	100
	1.66	1.5	304	100	95
	2.22	3	314	100	100

* Dissolution reagent in these runs was 10% NaOH - 13% $NaNO_3$.

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Table 5.1-3

Date on Uranium Dissolution

Run No.	Slug Type	Dissolution Time (hr.)	Initial HNO_3 (%)	U (kg) Dissolved	U (kg) Heel	Moles HNO_3 per Mole U	Product Solution U (M)	Product Solution Uranyl Nitrate (%)	Product Solution HNO_3 (M)	Vol. Residual Gas (a) (liters (STP)/kg U dissolved) CO_2	N_2O	CO	H_2	N_2
1	U rod	8	48	5.06	6.91	3.7	1.71	41.0	3.75	0.51	0.22	0.14	0	X
2	U rod	11.3	48	6.56	6.37	3.6	2.52	53.0	2.75	0.24	0.06	0	0	3.02
3	U rod	13	58	10.94	11.65	4.1	2.73	56.2	2.0	0.16	0.07	0	0.02	1.08
4	W	6	55	8.07	17.95	3.8	1.53	40.4	0.63	0.33	0.02	0.01	0	3.64
5-A	W	10	55	8.04	16.51	4.18	2.88	59.2	0.13	0.21	0.27	0	0	3.76
B	W	10	55	8.20	8.31	4.04	2.46	54.1	0.25	---	---	---	---	---
C	W	10	55	7.81	15.79	4.17	2.36	53.0	0.13	0.28	0.02	0.008	0.04	3.11
D	W	8	55	6.34	9.45	3.59	1.85	43.6	2.63					
E	W	8	48	7.34	17.10	3.47	1.81	43.9	1.50	0.08	0.02	0.04	0.04	3.14
6-A	W	10	55	7.51	16.83	4.39	1.60	41.6	0.25	0.40	X	0.09	0.009	5.05
B	W	10	55	7.64	9.19	4.39	1.60	41.7	0.13					
7-A	W	10	55	8.52	16.18	4.53	1.95	47.4	0.0	0.56	0.01	0.09	0	2.34
8-A	W/2	10	55	7.55	13.85	4.04	2.00	48.2	0.13 (b)	0.49	0	0.25	0.03	3.43
B	W/2	10	55	7.35	6.50	4.11	1.92	46.6	0.06	0.54	0.07	0.04	0	4.48
9-A	X	10	55	7.59	15.65	---	1.70	---	---	0.37	0.02	0.08	0	6.23
B	X	10	55	7.92	7.73	4.23	3.42 (c)	---	0.19 (b)	0.56	0	0	0	4.84
10-A	W	10	55	9.46	19.20	4.18	1.40	38.2	0.12 (b)	0.26	X	0.04	0.42	3.31
B	W	10	55	9.24	9.96	4.03	1.70	43.4	0.05					
11-A	SR	10	55	6.02	13.05	4.47	1.66	42.7	0.16					
B	SR	9	55	5.85	7.20	4.44	1.51	39.9	0.36					
12-A	SR	10	55	6.52	12.55	4.43	2.68	56.6	0.45					
B	SR	10	55	5.60	6.95	4.64	1.79	44.4	0.64					
											average			
										0.36	0.064	0.056	0.011	3.64
											% of total			
										8.7	1.5	1.3	0.3	88.2

(a) NO_2 - NO - O_2 free basis
(b) Basic
(c) Frozen
X deleted
--- not analyzed

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5.2 Figures

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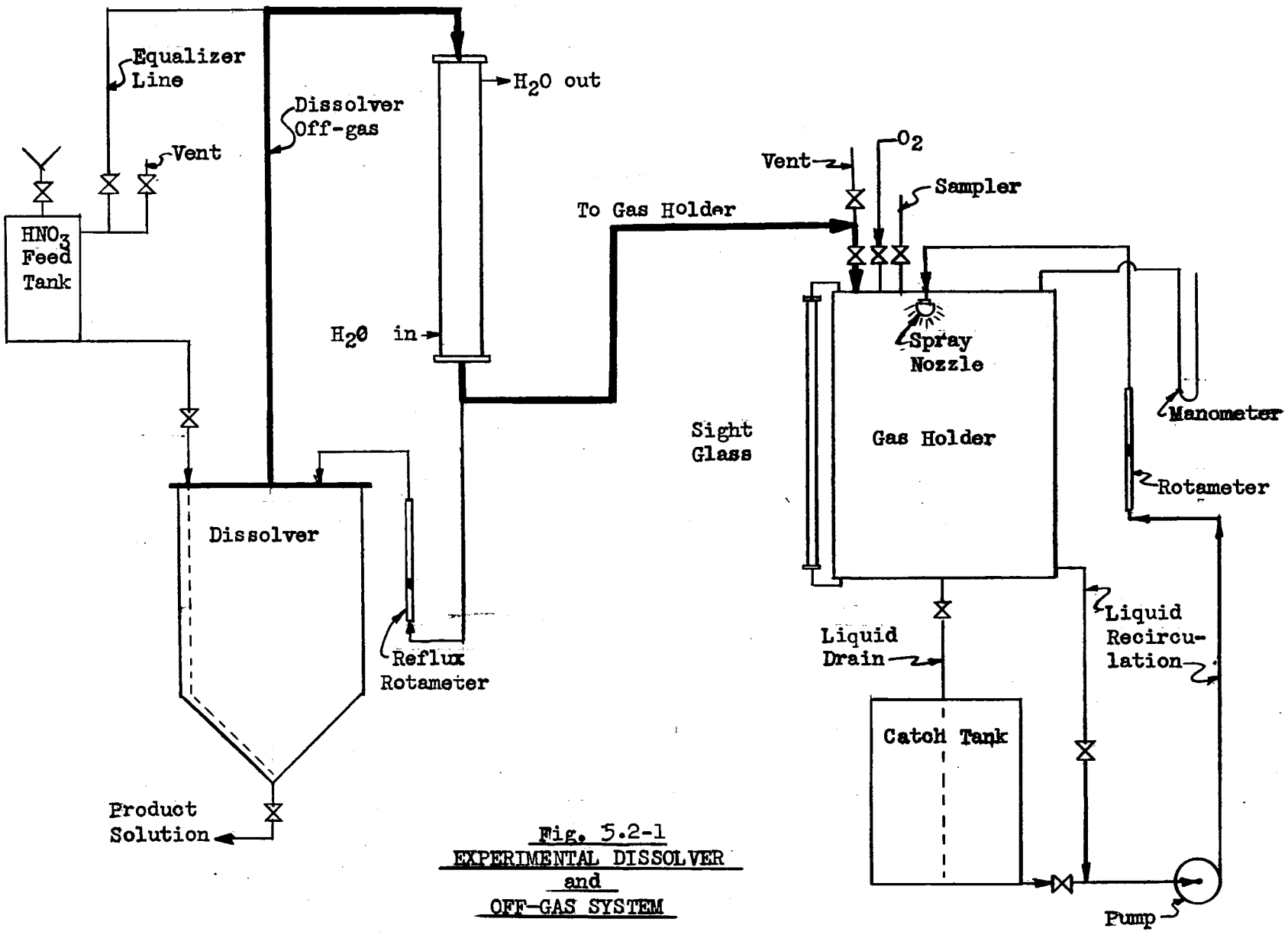

Fig. 5.2-1
EXPERIMENTAL DISSOLVER
and
OFF-GAS SYSTEM

Drawing 16591

Drawing 416592

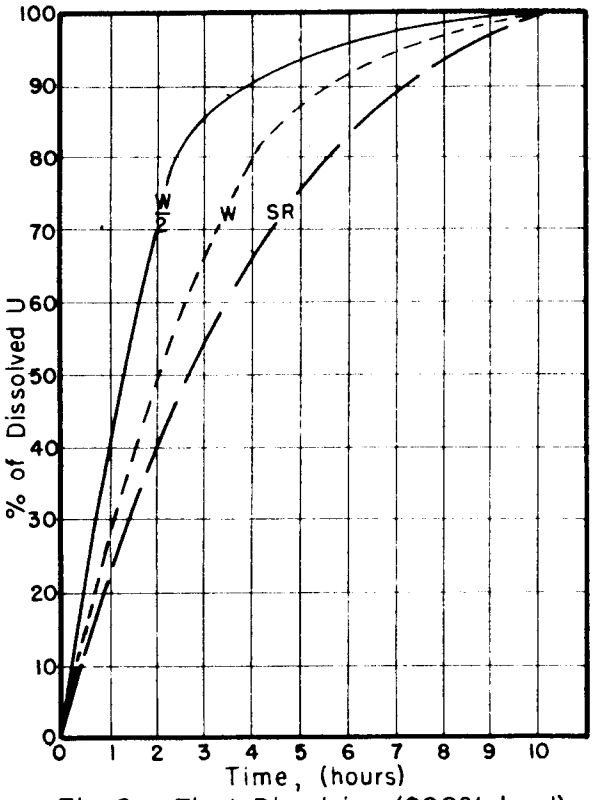

Fig. 2a. First Dissolving (200% heel)

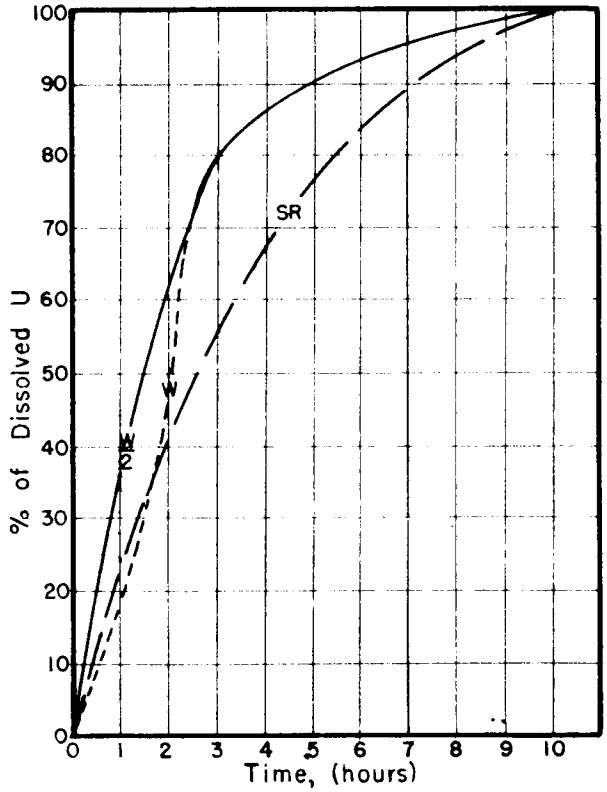

Fig. 2b. Second Dissolving (100% heel)

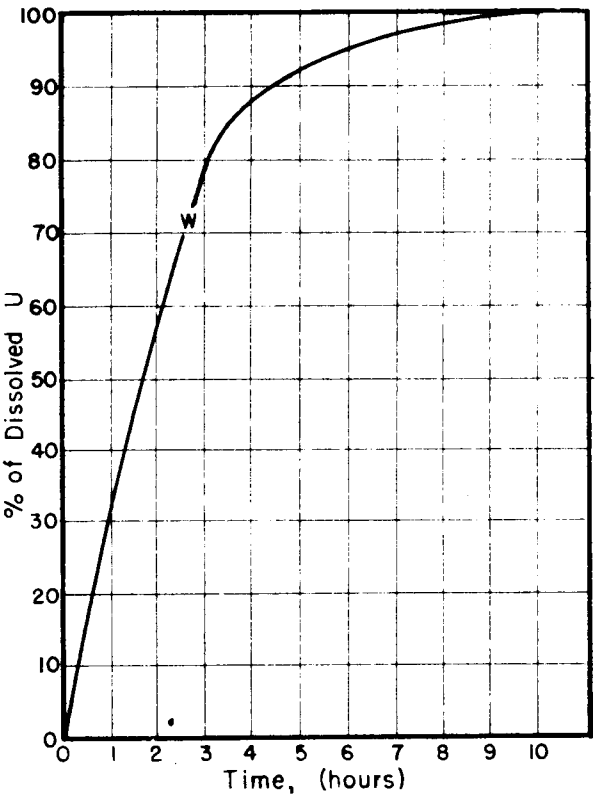

Fig. 2c. Third Dissolving (200% heel)

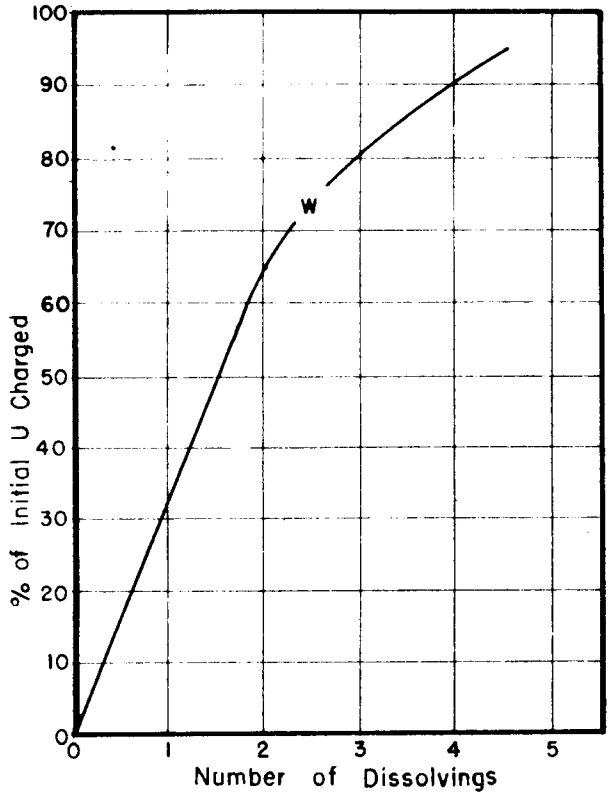

Fig. 2d.

Fig. 5.2-2

U DISSOLUTION RATES

Initial Soln. 55% (11.7 N) HNO_3
Final Soln. 1.5-2.0 M U
< 1.5% (0.3 N) HNO_3

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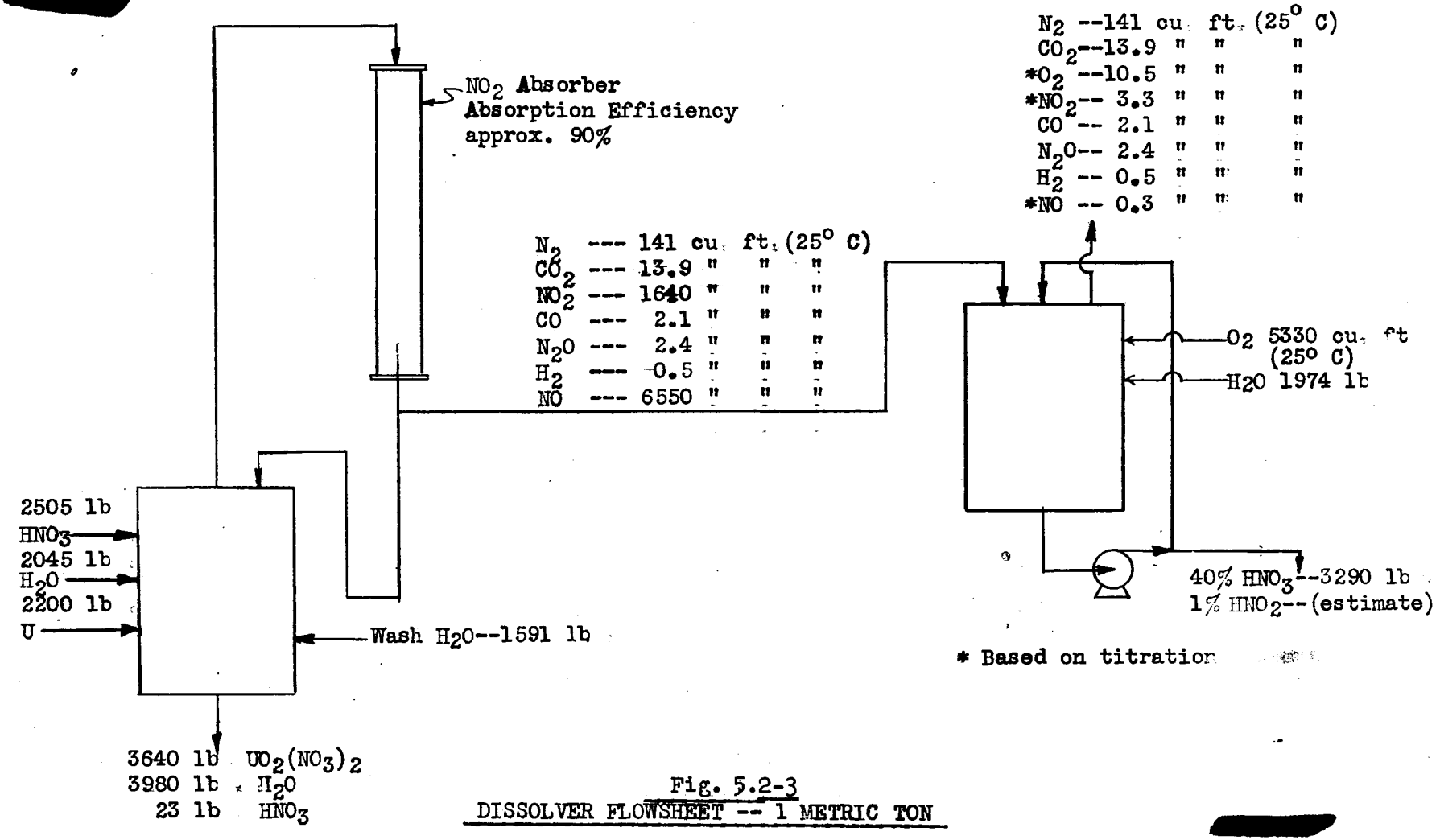

Fig. 5.2-3
DISSOLVER FLOWSHEET -- 1 METRIC TON

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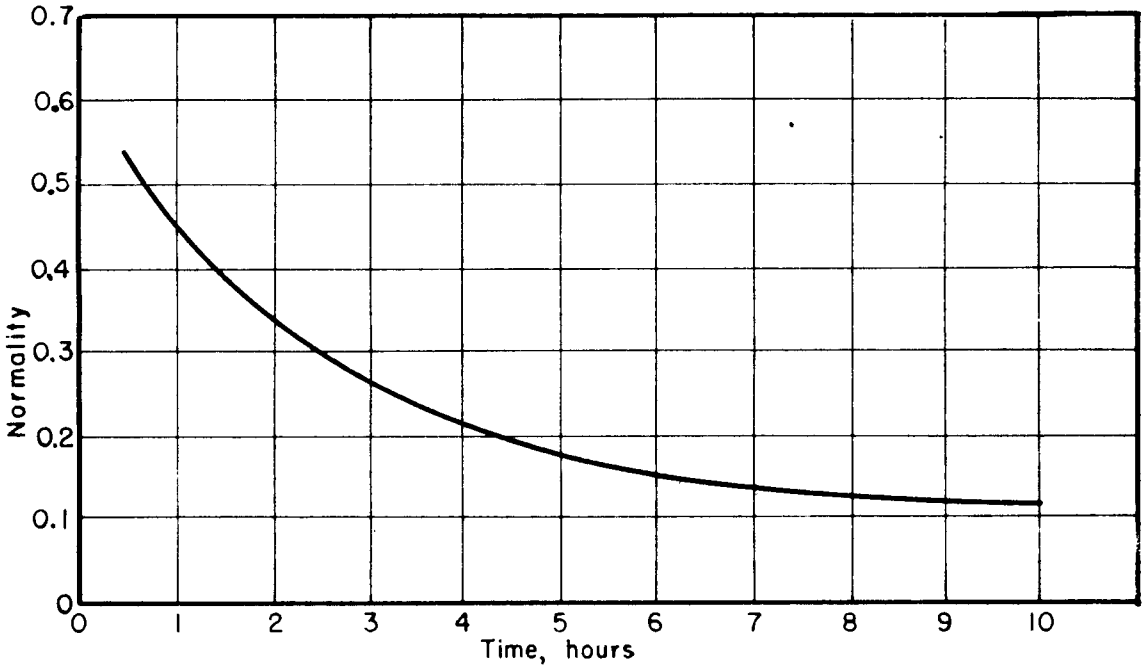
Drawing #16593



HNO_2

Total Acid ($HNO_3 + HNO_2$)

Fig. 5.2-4

REFLUX ACID CONCENTRATION vs TIME

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