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SUBJECT: Darex Flowsheet (Batch Operations)

Classification cancelled (or changed to UNCLASSIFIED)
by authority of ltr. Fl. Dec. Rl. 11-28-58
by J. C. Ridenour TIE, date 12-11-58

TO: F. L. Culler

FROM: W. E. Clark

AEC RESEARCH AND DEVELOPMENT REPORT

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NOTICE

This document contains information of a preliminary nature and was prepared primarily for internal use at the Oak Ridge National Laboratory. It is subject to revision or correction and therefore does not represent a final report.

1 3921

DISCLAIMER

The completed Darex flowsheet is transmitted herewith. Major contributors to its preparation include J. R. Flanary, J. H. Goode, and A. H. Kibbey of Chemical Development Section B and F. G. Kitts of Unit Operations.

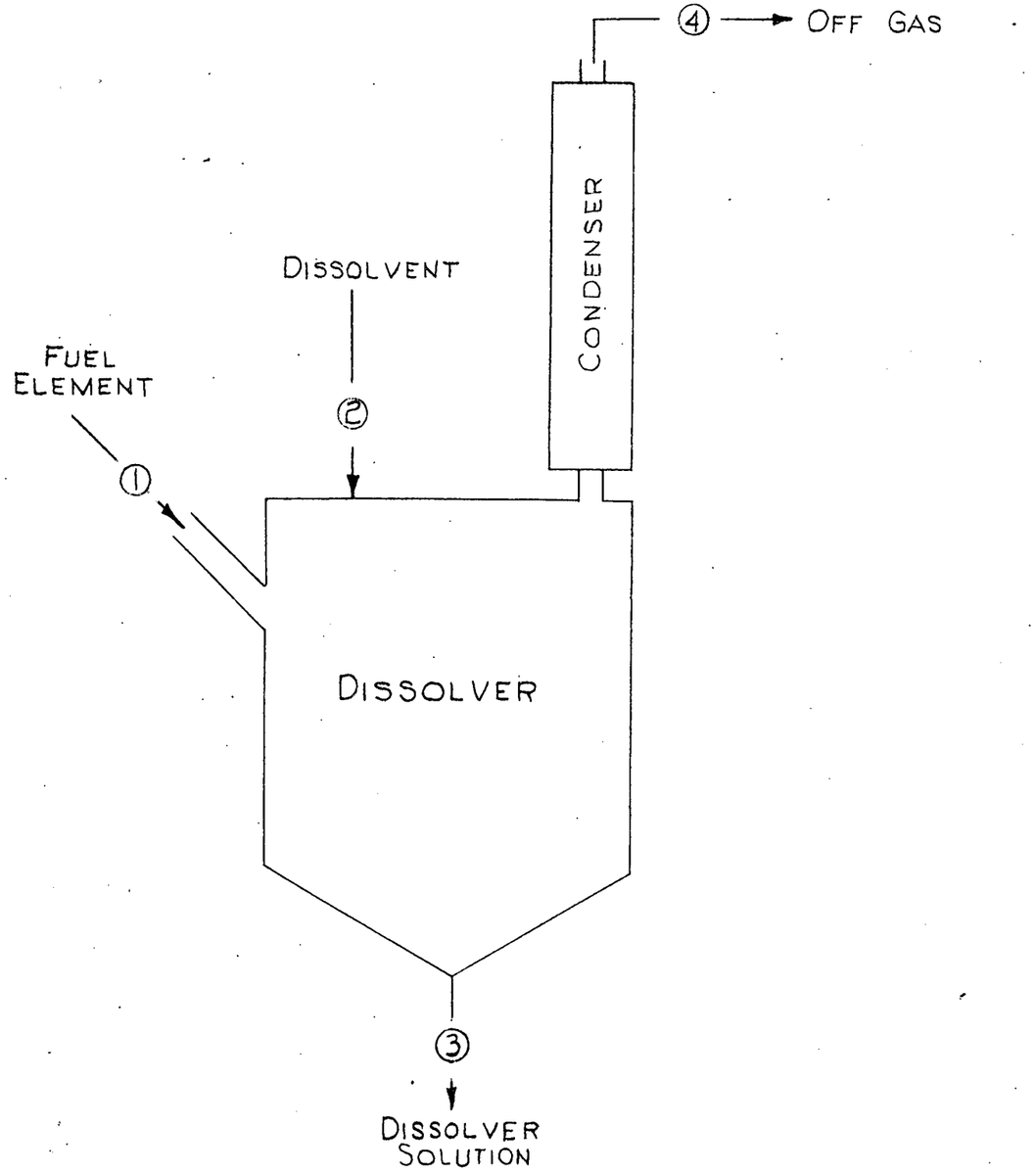
It is recognized that this represents an interim flowsheet since continuous operation will doubtless prove to be advantageous. Continuous operation of the dissolver appears to be particularly desirable because of the relative ease with which the dissolution rate can be controlled as compared with a batch dissolver.

No provision has been made in this flowsheet for the absorption and/or rectification of the off gases from the dissolver and the stripper. The chemistry of this process is presently under investigation. It appears that this step also will lend itself to continuous operation and recycle in a system similar to that outlined by Guthrie (ORNL-CF-56-8-167).

Walter E. Clark
W. E. Clark

WEC/jr

FLOWSHEET:



*REACTIONS:

1. $HNO_3 + 3HCL \longrightarrow NOCl + Cl_2 + 2H_2O$; $\Delta H = 42.2$ K-cal/mole Cl_2 FORMED
2. $M + nNOCL \longrightarrow MCL_n + nNO$; ΔH (K-cal/mole REACTED): Fe = 95.7, Cr = 133.5, Ni = 35.8, Mn = 73.5, UO_2 = 47.5
3. $UO_2 + 4HNO_3 \longrightarrow UO_2(NO_3)_2 + 2NO_2 + 2H_2O$; $\Delta H = 17.9$ K-cal/mole UO_2 DISSOLVED
4. $xM + (2x+2)HNO_3 \longrightarrow xM(NO_3)_n + (\frac{2x+2}{4})NO + (x+1)H_2O$; ΔH (K-cal/mole DISSOLVED): Fe = 217.3; Cr = 154.5; Ni = 199.5; Mn = 100.0; UO_2 = 29.3
5. $M + 2n\,HNO_3 \longrightarrow M(NO_3)_n + nNO_2 + nH_2O$; ΔH (K-cal/mole DISSOLVED): Fe = 87.0; Cr = 137.4; Ni = 55.1; Mn = 88.6; UO_2 = 17.9
6. $Fe(NO_3)_2 + 2HNO_3 \longrightarrow Fe(NO_3)_3 + NO_2 + H_2O$; $\Delta H = 14.8$ K-cal/mole $Fe^{+2} \longrightarrow Fe^{+3}$

(NOTE: M = Fe; Ni; Cr; n = 2, 3; x = 1 OR 3)

PROCEDURE:

1. CHARGE FUEL ELEMENTS TO DISSOLVER.
2. ADD THE MIXED ACIDS SLOWLY WHILE STILL WARM (~50°C) FROM PREPARATION, UNTIL TEMPERATURE RISES TO BOILING (~110°C). FINAL ADDITIONS OF ACID MUST BE MADE CAUTIOUSLY TO AVOID UNCONTROLLABLE GAS EVOLUTION.
3. RETURN VOLATILIZED HCl, HNO_3 AND EXCESS WATER TO THE DISSOLVER BY USING CONDENSER ON OFF-GAS STREAM

*(1) HEAT OF REACTION PER BATCH DISSOLUTION OF ONE FUEL ELEMENT ≅ 88.6 MOLES OF S.S. + UO_2 = 19,684.8 K-cal. (ASSUME 20,000 K-cal./APPR ELEMENT A GOOD APPROXIMATION FOR MAXIMUM ΔH VALUE.) THIS VALUE IS BASED ON USE OF EQUATIONS 1, 2, 3, 4, AND 6, ABOVE, SINCE EQUATION 5 IS BELIVED TO BE A MINOR REACTION TAKING PLACE ONLY AT THE BEGINNING OF THE DISSOLUTION

DAREX PROCESS FLOWSHEET

I. BATCH DISSOLUTION OF APPR. FUEL

CLASSIFICATION	ORNL-LR-DWG
AS: CONDIFIDENTIAL PER W.E. Clark	24310

DRAWN	DATE	CHECKED	DATE
J.W. DAY	18-29-57		
DESIGNED	DATE	APPROVED	DATE
C.H. Kline	1-14-57	W.E. Clark	9/11/57

CHEMICAL TECHNOLOGY DIVISION

				U		Fe		Ni		Cr		Mn		Si	P	B	H^+		NO_3^-		Cl^-		H_2O		NO		NO_2		Cl_2	
STREAM NO	VOL. L	MASS Kg.	SPG g/cc	M	Kg.	M	Kg.	M	Kg.	M	Kg.	M	Kg.	Kg.	Kg.	Kg.	M	Kg.	M	Kg.	M	Kg.	gMOLES	Kg.	gMOLES	Kg.	gMOLES	Kg.	gMOLES	Kg.
STREAMS IN 1		5.34			.377		3.42		.397		.893		.099	.099	.050	.003														
2	76	90.4	1.19														7.0	.536	5.0	23.6	2.0	5.40	3380	60.9						
TOTALS 2	76	95.74			.377		3.42		.397		.893		.099	.099	.050	.003		.536		23.6		5.40	3380	60.9						
STREAMS OUT 3	61	84.9	1.39	0.026	.377	1.0	3.42	0.11	.397	0.28	.893	0.03	.099	.099	.050	.002	1.50	.0922	3.95	14.9	1.74	3.77	3370	60.8						
4	(2) (STP) 10,900	10.8														.001							230	4.11	81.2	2.44	57.8	2.66	22.9	1.63
TOTALS 2	10,961	95.7			.377		3.42		.397		.893		.099	.099	.050	.003		.0922		14.9		3.77	3600	64.91	81.2	2.44	57.8	2.66	22.9	1.63

NOTES: (1) APPR FUEL IS 304L-S.S. CLAD SINTERED S.S.-UO_2; FOR SPECIFICATIONS SEE CONFIDENTIAL LETTER FROM L. D. SCHAFFER TO J. W. ULLMANN DATED 4-11-57
(2) GAS VOLUME INCLUDES H_2O PRESENT AS VAPOR

DAREX PROCESS FLOWSHEET
I. BATCH DISSOLUTION OF (1) APPR FUEL.

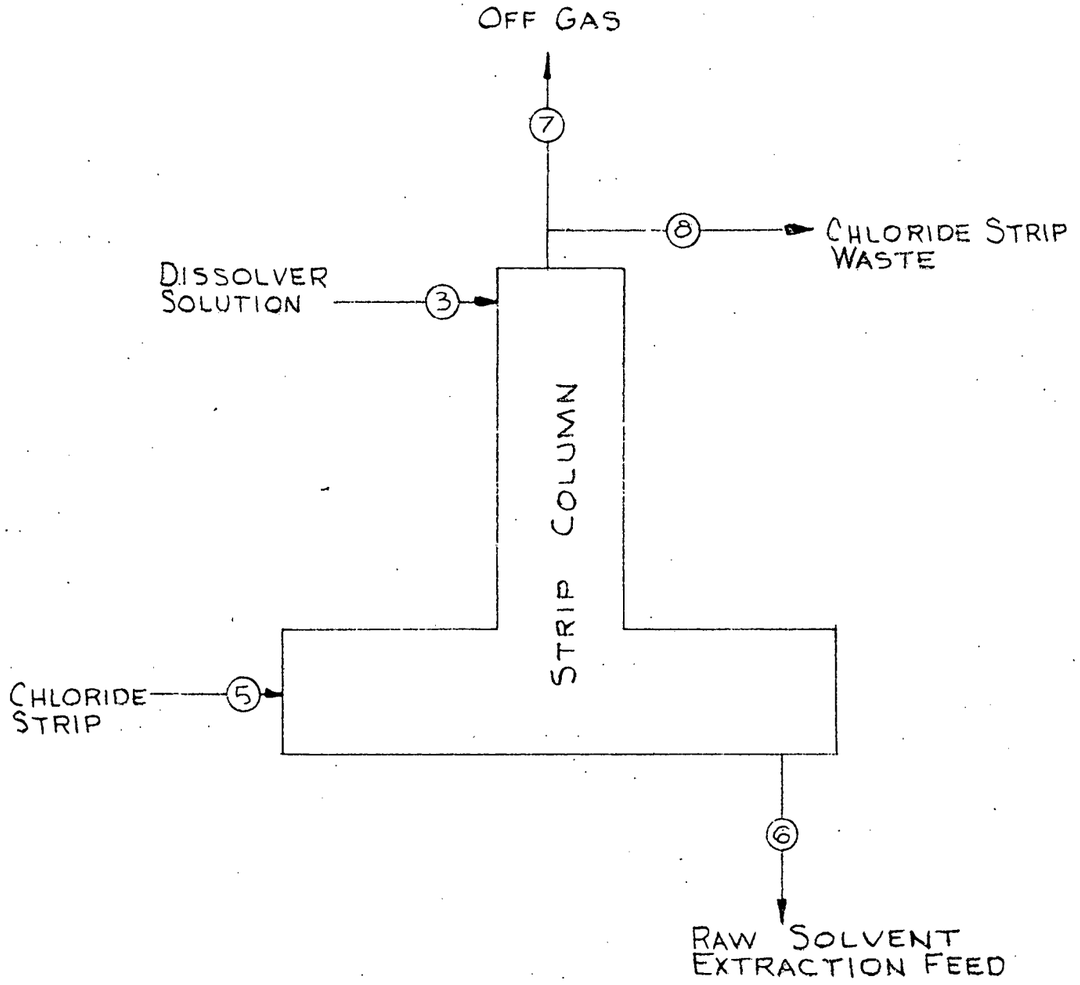
DRAWN	DATE	CHECKED	DATE
J.W.DAY	8-29-57		
DESIGNED	DATE	APPROVED	DATE

CLASSIFICATION AS: CONFIDENTIAL PER: K. E. Clark

ORNL-LR-DWG. 2432A

CHEMICAL TECHNOLOGY DIVISION

FLOWSHEET:



REACTION:

1. $2HNO_3 + 2HCl \longrightarrow 2NO_2 + Cl_2 + 2H_2O$

(THIS APPEARS TO BE THE DOMINANT REACTION AT NO_3^-/Cl^- MOLE RATIO OF APPROXIMATELY 17/1)

PROCEDURE:

COLUMN OPERATION CONDITIONS:
(1) V/L MOLE RATIO = 1
(2) NUMBER OF STAGES = 3
(3) TEMPERATURE:
(a) TOP = 110°C
(b) BOTTOM = 123°C

CHLORIDE CONTENT OF STREAM 6 IS SPECIFIED AS $\leq$ 30 ppm

DAREX PROCESS FLOWSHEET
II CHLORIDE REMOVAL FROM DISSOLVER SOLUTION

DRAWN	DATE	CHECKED	DATE
J.W. DAY	18-29-57		
DESIGNED	DATE	APPROVED	DATE
J.W. Kaye	9-11-57	W.E. Clark	9/11/57

CLASSIFICATION AS CONFIDENTIAL PER W.E. Clark

ORNL-LR-DWG 24382

				U		Fe		Ni		Cr		Mn		Si	P	B	H^+		NO_3^-		Cl^-		H_2O		NO		NO_2		Cl_2	
STREAM NO	VOL. L	MASS Kg	S.G. g/cc	M	Kg.	M	Kg.	M	Kg.	M	Kg	M	Kg.	Kg.	Kg.	Kg.	M	Kg.	M	Kg.	M	Kg.	g MOLES	Kg.	g MOLES	Kg.	g MOLES	Kg.	g MOLES	Kg.
STREAMS IN																														
3	61	84.9	1.39	0.026	.377	1.00	3.42	0.11	.397	0.28	.893	0.03	.099	.099	.050	.002	1.50	.092	3.95	14.9	1.74	3.77	3380	60.8						
5	118	167	1.42														15.2	1.81	15.2	111			3000	54.0						
TOTALS																														
2	179	251.9			.377		3.42		.397		.893		.099	.099	.050	.002		1.902		125.9		3.77	6380	114.8						
STREAM OUT																														
6	61	94.2	1.55	0.026	.377	1.00	3.42	0.11	.397	0.28	.893	0.03	.099	.099	.050	.002	10.58	.650	14.8	55.8	30 ppm or less		1800	32.4						
7	STP 3310	7.87																					5	.084			95.5	4.40	47.8	3.39
8	118	150	1.27														8.89	1.06	8.80	64.4	0.09	.377	4670	84.1						
TOTALS																														
3	3489	252.1			.377		3.42		.397		.893		.099	.099	.050	.002		1.71		120.2		.377	6475	116.6			95.5	4.40	47.8	3.39

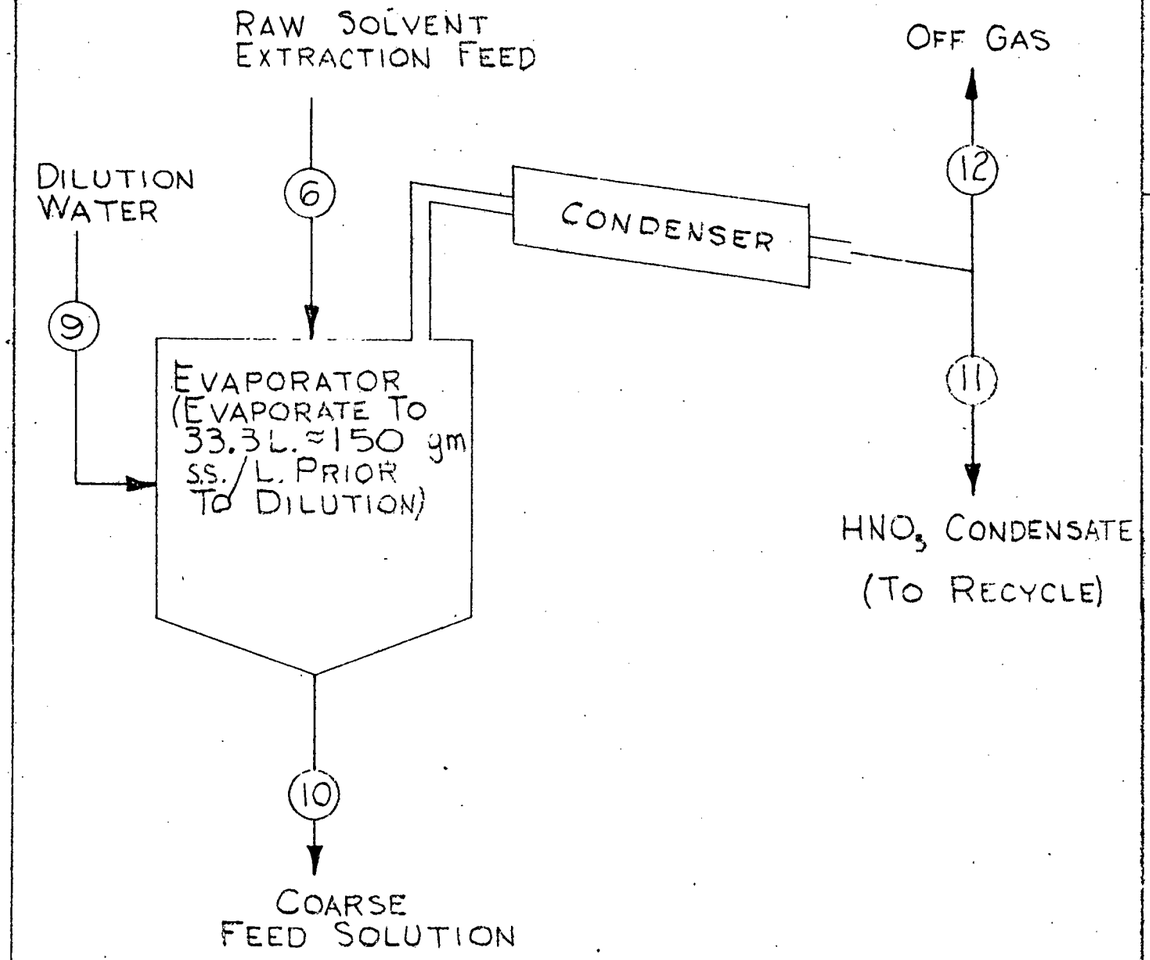
DAREX PROCESS FLOWSHEET
II CHLORIDE REMOVAL FROM DISSOLVER SOLUTION

DRAWN	DATE	CHECKED	DATE
J W DAY	8-29-57		
DESIGNED	DATE	APPROVED	DATE
A N Farley	9-11-57	W. E. Clark	9/11/57

CLASSIFICATION CANCELLED PER: W. E. Clark

ORNL-LR-DWG 24737

FLOWSHEET



DAREX PROCESS FLOWSHEET

III FEED ADJUSTMENT TANK (FAT) - NITRIC ACID REMOVAL

CLASSIFICATION	ORNL-LR-DWG.
AS: CONFIDENTIAL PER: W. E. Clark	24554

REACTION

PROCEDURE:

1. EVAPORATE RAW SOLVENT EXTRACTION FEED TO REMOVE EXCESS HNO_3. AFTER EVAPORATION THE SOLUTION IS ~4m IN FREE ACID. THE AZEOTROPE (15.2M) DISTILLS OFF IMMEDIATELY UNDER THESE CONDITIONS SINCE BOILING POINT OF 118°C - 125°C IS HIGHER THAN THAT OF THE HNO_3 AZEOTROPE (B.P. = 120.5°C)
2. DILUTE BACK TO ORIGINAL 61 L. VOLUME WITH WATER

DRAWN	DATE	CHECKED	DATE
J. W. DAY	9-4-57		
DESIGNED	DATE	APPROVED	DATE
A. H. Rice	9-11-57	W. E. Clark	9/11/57

STREAM NO.	VOL L	MASS Kg	SPG. G/CC	U M	U Kg	Fe M	Fe Kg	Ni M	Ni Kg	Cr M	Cr Kg	Mn M	Mn Kg	Si Kg	P Kg	C Kg	S Kg	B Kg	H^+ M	H^+ Kg	NO_3^- M	NO_3^- Kg	Cl^- M	Cl^- Kg	H_2O gMOLES	H_2O Kg
STREAMS IN																										
6	61	94.2	1.55	.026	.377	1.00	3.42	0.11	.397	0.28	.893	0.03	.099	.099	.050	NEGLIGIBLE		.002	10.6	.651	14.8	55.9	NEGLIGIBLE		1800	32.4
9	27.7	27.6	1.00																						1540	27.7
TOTALS																										
2	88.7	121.8			.377		3.42		.397		.893		.099	.099	.050	NEGLIGIBLE		.002		.651		55.9	NEGLIGIBLE		3340	60.1
10	61	83.2	1.36	.026	.377	1.00	3.42	0.11	.397	0.28	.893	0.03	.099	.099	.050	NEGLIGIBLE		.002	3.69	.227	7.86	29.8	NEGLIGIBLE		2660	47.8
11	27.7	38.7	1.40																15.2	.424	15.2	26.1			668	12.2
12	(NEGLIGIBLE NO_3^- DECOMPOSITION AT S.S. CONCENTRATIONS OF < 200 gm/L)																									
3	88.7	121.9			.377		3.42		.397		.893		.099	.099	.050	NEGLIGIBLE		.002		.651		55.9	NEG LIGIBLE		3328	60.0

DRAWN	DATE	CHECKED	DATE
JW DAY	9-4-57		
DESIGNED	DATE	APPROVED	DATE
A.M. Perry	9-5-57	W.E. Unger	9/5/57

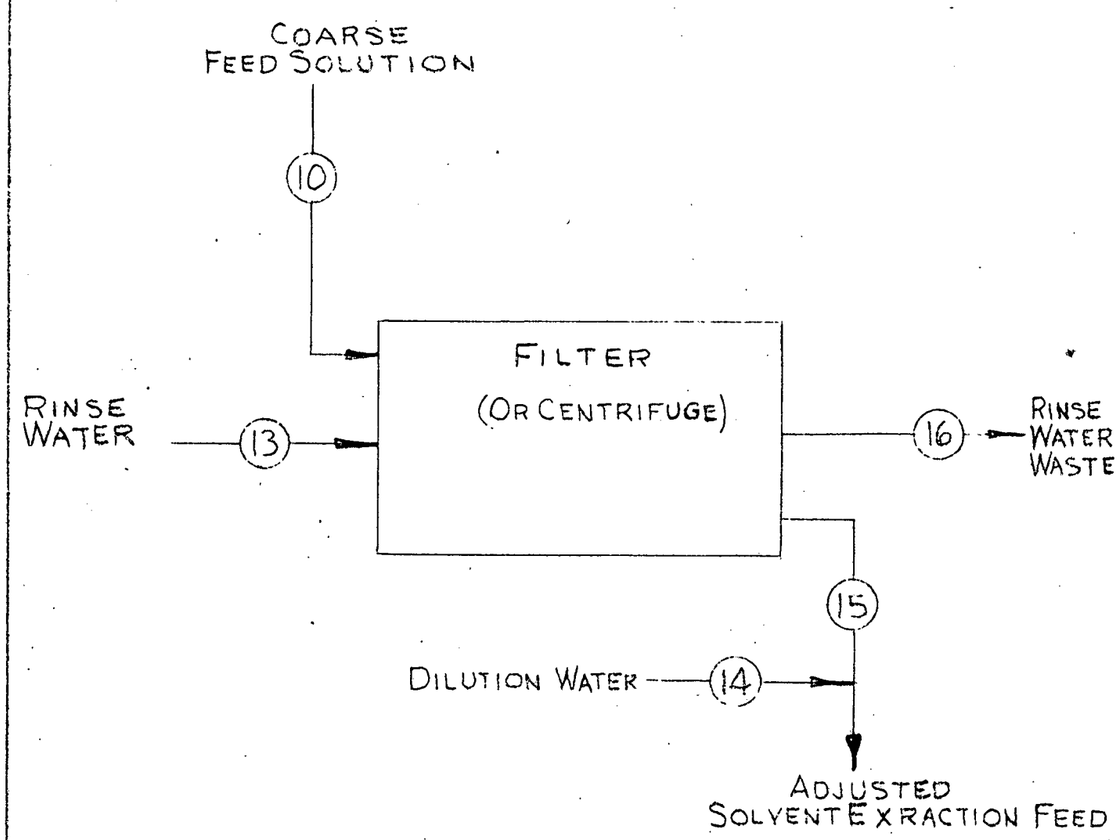
DAREX PROCESS FLOWSHEET

III FEED ADJUSTMENT TANK (FAT)-NITRIC ACID REMOVAL

CLASSIFICATION AS: CONFIDENTIAL

ORNL-LR-DWG

FLOWSHEET



REACTION

PROCEDURE:

1. COARSE FEED SOLUTION IS FILTERED (OR CENTRIFUGED)
2. WATER FOR DILUTION IS ADDED AS 2 WASHES OF 7L EACH FOR THE FILTER CAKE.
3. RINSE WATER IS ADDED AS A BACKWASH TO REMOVE SILICA FROM FILTER (OR CENTRIFUGE), PROBABLY IN 2 ALIQUOTS. SINCE THE VOLUME REQUIRED FOR SILICA REMOVAL IS LARGELY DEPENDENT UPON EQUIPMENT DESIGN, THE RINSE VOLUME WAS ARBITRARILY CHOSEN AS EQUAL TO THE FEED VOLUME.

DAREX PROCESS FLOWSHEET

IV FEED CLARIFICATION – Si REMOVAL

CLASSIFICATION AS: CONFIDENTIAL	ORNL-LR-DWG
PER: W. E. Clark	24386

DRAWN	DATE	CHECKED	DATE
J W DAY	10-5-53		
DESIGN	DATE	APPROVED	DATE
G. H. Jenkins	7-11-57	W. E. Clark	9/11/57

				U		Fe		Ni		Cr		Mn		Si	P	C	S	B	H^+		NO_3^-		Cl^-		H_2O	
STREAM NO.	VOL L	MASS Kg	SPG g/cc	M	Kg	M	Kg	M	Kg	M	Kg	M	Kg	Kg	Kg	Kg	Kg	Kg	M	Kg	M	Kg	M	Kg	g MOLES	Kg
STREAM IN 10	61	83.2	1.36	.026	.377	1.00	3.42	0.11	.397	.28	.893	.03	.099	.099	.050	NEGLIGIBLE		.002	3.69	.227	7.86	29.8	NEGLIGIBLE		2650	47.8
13	61	61.0	1.00																						3390	61.0
14	14	14.0	1.00																						780	14.0
TOTAL 3	136	158.2			.377		3.42		.397		.893		.099	.099	.050	NEGLIGIBLE		.002		.227		29.8	NEGLIGIBLE		6820	122.8
STREAM OUT 15	75	97.2	1.29	.021	.377	.813	3.42	.089	.397	.23	.893	.024	.099		.050	NEGLIGIBLE		.002	3.00	.227	6.39	29.8	NEGLIGIBLE		3430	61.8
16	61	61.0	1.00											.099											3390	61.0
TOTAL 2	136	158.2			.377		3.42		.397		.893		.099	.099	.050	NEGLIGIBLE		.002		.227		29.8	NEGLIGIBLE		6820	122.8

DAREX PROCESS FLOWSHEET

IV FEED CLARIFICATION – Si REMOVAL

DRAWN	DATE	CHECKED	DATE
J.W. DAY	9-5-57		
DESIGNED	DATE	APPROVED	DATE
A.A. Fitch	9-4-57	W.E. Clark	9/11/57

CLASSIFICATION AS: CONFIDENTIAL
PER W.E. Clark 7-17-57

ORNL-LR-DWG