RECOVERY OF FERROUS SULFATE CRYSTALS
FROM
PICKLING LIQUOR

Thesis

by

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I. INTRODUCTION

Pickling liquor is nothing more than dilute sulfuric acid used in the iron and steel industry for removing scales on the surface of iron work which is to be further treated. The reaction for pickling may be represented by the equation

$$FeO + H_2SO_4 = FeSO_4 + H_2O.$$

Thus we see from this equation that H_2SO_4 is gradually used up and $FeSO_4$ formed during the process. It is evident,then, after a certain length of time, H_2SO_4 will be too weak for further pickling, and the amount of $FeSO_4$ will be too valuable to cast away. This $FeSO_4$ may be converted into an oxide which is a pigment, or taken out in the form of $FeSO_4.7H_2O$ crystals. The latter is the purpose of this work. $FeSO_4.7H_2O$ has the following uses:

photography; writing ink; Prussian blue;
preparation of iron oxide for illuminating gas purification;
water purification; madiciene; disinfectant;
textile and leather industries;
analytical reagent;
making other iron salts.

II. PROPERTIES OF $FeSO_4$

Aqueous solutions of $FeSO_4$ are easily oxidized. In a neutral solution the reaction may be represented by (1), and in acid solution by (2):

$$(1)\quad 4FeSO_4 + O_2 + 2H_2O = 4Fe(OH)SO_4$$

$$(2)\quad 4FeSO_4 + O_2 + 2H_2SO_4 = 2Fe_2(SO_4)_3 + 2H_2O\ .$$

Metallic iron, if present in a neutral solution, will be oxidized into oxides; but if present in an acid solution it has a reducing tendency. Thus we have

$$Fe_2(SO_4)_3 + Fe = 3FeSO_4.$$

Crude $FeSO_4.7H_2O$ crystals contain $Fe_2(SO_4)_3$ which gives the crystals a decidedly green color. They are also frequently coated with a layer of yellowish basic salt. By washing with absolute alcohol this salt, being soluble, is removed and the crystals are thus rendered permanent. Hydrates of $FeSO_4$ having $1H_2O$, $2H_2O$, $3H_2O$, $4H_2O$ and $6H_2O$ are known, but the one having $7H_2O$ is the only one stable at room temperature. It will, however, effloresce at 33°C.

The solubilities of $FeSO_4$ are shown in the following table:

(According to Handbook of Solubility by Arther M. Comey)

t = temperature in degrees Centigrade,

C = parts of $FeSO_4$ in 100 parts of water.

t	0	5	10	15	20	25	30	35
C	7.9	12.0	16.2	20.4	24.7	29.0	33.5	38.0

t	40	45	50	55	60	65	70	75
C	42.6	47.1	51.9	56.7	61.7	65.7	64.8	64.0

t	80	85	90	95	100
C	62.3	59.8	56.2	51.0	42.6

III. EXPERIMENTAL WORK

The experimental work on pickling liquor consists of 1. evaporation, 2. filtration, 3. crystalization, 4. drying crystals and 5.

analysis.

Evaporation was carried out in open beakers in laboratory scale, in steam jacketed enamal kettles in engineering scale. Steam was admitted at 20 pounds pressure, the temperature of the liquor was 100.5°C. Metallic iron in the form of iron filing was used to react with the free acid in the liquor. Evaporation was stopped when the solution was saturated and anhydrous $FeSO_4$ began to appear.

Ordinary suction filter was used for filtration in laboratory scale, filter leaf with the add of diatomaceous earth in engineering scale. Centrifugal machine was used for separating the crystals in the latter case.

Both slow cooling and rapid cooling with running water have been tried. The significance of them will be seen in the table.

All crystals were dried at atmospheric temperature, and no mechanical devise was attempted.

For determining free H_2SO_4 in the pickling liquor, the liquor was titrated with standard KOH using methyl orange as indicator. Its $FeSO_4$ content was ascertained by determining Fe^{++} with $KMnO_4$ of known strength. The Fe^{+++} content in $FeSO_4.7H_2O$ is determined as follows: 40 grams $FeSO_4.7H_2O$ made up 105cc. solution. 100 cc. of it was heated to 60°C, 5cc. HCl was added. 5cc. of $SnCl_2$ whose strength was determined with $KMnO_4$ was then added. Back titrate the excess $SnCl_2$ with I_2 whose ratio to $SnCl_2$ was determined in each experiment; starch used for indicator. The other 5cc. of $FeSO_4.7H_2O$ solution was diluted to 50cc. Its Fe^{++} was determined with $KMnO_4$. Knowing the amount of Fe^{+++} and Fe^{++} their relative percentage can be figured out.

These results are shown in the following table:

No. of exp.	No. of crops	Condition for evapor.	Appear. of cry.	% yield	% Fe^{+++}
1	1st.	excess iron filing	large, dirty	53.5	0.10
	2nd	neutral solution	" "	23.5	
	3rd	" "	" "	10.5	
				87.5	
2	1st	theoretical amt of Fe	" clean	41.0	0.06
	2nd	neutral solution	" dirty	34.5	
	3rd	" "	" "	20.0	
				95.5	
3	1st	less than theor. Fe	" clean	62.5	0.00
	2nd	acidic solution	" "	22.5	
	3rd	" "	" "	13.5	
				98.5	
4	1st	less than theor. Fe	" "	58.5	0.00
	2nd	acidic solution	" "	31.5	0.05
	3rd	" "	" "	5.0	0.08
				95.0	
5	1st	2/3 theoretical Fe	" "	48.6	0.00
	2nd	1/4 " "	" "	34.7	0.02
	3rd	1/8 " "	" "	11.5	0.08
				94.8	
6	1st	2/3 theoretical Fe	small "	49.0	0.0
	2nd	1/4 " "	" "	31.4	0.0
	3rd	1/8 " "	" "	12.1	0.0
				92.5	
7		C.P. $FeSO_4 \cdot 7H_2O$ from stock room			0.0
8		commercial " " "			0.02
9	1st	19/20 theoretical Fe	small clean	50.8	0.0
	2nd	(evap. in enamal kettle)			
	2nd	acidic solution in ket.	" "	15.0	0.0
	3rd	" " "	" "	6.2	0.0
	4th	" " beaker	" "	4.6	0.0
	5th	" " "	" "	2.4	0.0
				78.0	

Reaction rate of Fe in the form of 10 iron nails and H_2SO_4.

At room temperature		At 90°C	
Time in days	Normality of H_2SO_4	Time in min.	Norm. of H_2SO_4
0	0.59	0	0.62
1	0.20	15	0.42
2	0.00	30	0.22
		45	0.13
		80	0.02
		100	0.00

Corrosion test of H_2SO_4 upon cast iron:

Wt of C I plate before	After	Dif. in wt gm	Surface of plate in^2	Norm. of acid	Time hrs.	Rate of cor. gm/in^2/hr.
12.795	12.563	0.232	2.193	0.36	16.4	0.00648
13.517	13.262	0.255	2.393	0.36	16.4	0.00658

IV. A PLAN FOR PRODUCING 2 TONS $FeSO_4.7H_2O$ DAILY.

This plan is based upon the experimental results as far as they are serviciable. When experimental data is lacking, theoretical consideration is relied upon.

Experiments show that a solution containing the reaction product of iron filings and saturated with $FeSO_4$, is very difficult to filter. This is probably due to the carbon content of the iron filings and the formationof massive anhydrous iron salts, both of which tend to block the openings of the filtering medium. Fortunately the foregoing table shows that as long as the evaporating liquor is slightly acidic and crystals quickly collected, the crystals are clear and not excessive in Fe^{+++} content. It has also shwon that that the reaction between Fe and H_2SO_4 can be complete in two days at room temperature. According to Alexander Smith, the carbide and graphite content of steel and cast iron will not react with cold dilute H_2SO_4. Take these facts into consideration, it seems best to let the iron react with the free acid of the liquor at room temperature for two days in wooden tank; and then after a process of sedimentation and decantation, the liquor is submitted for filtration

Evaporation can be conducted in cast iron vessel, for the liquor will be practically neutral when it comes to this stage. Steam coil is to be used for supplying heat. Air stream will be directed against this coil in order to prevent the formation of anhydrous salts due to local and excessive heat in the first place, and secondly to increase the rate of evaporation. It will increase the oxidation but this disadvantage may be more than offset by its advantages.

In order to produce two tons of crystals daily, the percentage yield at each stage of evaporation must be definitely known. From this percentage the volume of the pickling liquor has to be handled each day can be ascertained. Since the experimental data concerning this percentage do not agree with each other, the theoretical solubility of $FeSO_4$ will be taken as a starting point for the following calculations.

By analysis of pickling liquor

$FeSO_4$ resulting from free acid		41 grams per litre
" " "	Fe^{++} content	178 grams per litre
	Total $FeSO_4$	219 grams per litre.

Assuming the evaporation is to be at 100°C:

Solubility of $FeSO_4$ at 100°C is 42.6 parts per 100 parts of water,
" " at 20°C is 24.7 parts " " " " "

According to experiment, when 45.2 grams of $FeSO_4.7H_2O$ which is equivalent to 24.7 grams of $FeSO_4$ was added to 100 cc. of water the final volume was 121 cc. Water added to the final volume from water of Crystallization is 45.2 (126/276) = 20.6 cc., 126 being the molecular weight of $7H_2O$, and 276 being the molecular weight of $FeSO_4.7H_2O$. To simplify the calculation, we can assume that the increase in volume due to the addition of $FeSO_4$ is negligible. That is to say when 24.7 grams of $FeSO_4$ is added to 100 cc. of H_2O the final volume is still 100 cc.

Starting with 1000cc. of this liquor the saturated volume at 100°C is 21.9/42.6 = 515 cc. Water to be evaporated is 1000 - 515 = 485 cc. Let X be the $FeSO_4$ in grams which we should get when the saturated liquor cools down to 20°C. Each gram of $FeSO_4$ separating out from the liquor will take up 126/152 = 0.83 cc. of water as water of crstallization, 152 being the molecular weight of $FeSO_4$. We have then the following relation: $(219 - X)/0.247 = 515 - 0.83X$ = saturated volume at 20°C. $X = 116$ grams. The percentage crystallization is 116/219 = 0.528 or 52.8%. $FeSO_4$ left in the solution is 219 - 116 = 103 grams. Volume to start for the second evaporation is 515 - 0.83 (116) = 419 cc. Saturated volume after the second evaporation is 419 (24.7/42.6) = 243 cc. Again

$(103 - X)/0.247 = 243 - 0.83X$ $X = 54$ grams of $FeSO_4$.

$FeSO_4$ left in the liquor is 103 - 54 = 49 grams. In the same way the calculations go on for the third, fourth, and the fifth evaporation. These results are tabulated as follows:

Theoretical Volumes and Yields Based on Solubility.

Basis; 1000 cc. of liquor contains 178 gm $FeSO_4$ and 0.537N free acid giving a total of 219 gm $FeSO_4$ per litre. (The first evaporation including the reaction of Fe with free acid. Solubility of $FeSO_4$ at 100°C is 42.6 and at 20°C is 24.7 parts per 100 parts of H_2O.

Symbols used:

(a) = volume to start evaporation in cc.
b = saturated volume at 100°C.
c = H_2O in cc. evaporated.
d = volume after separating crystals and saturated at 20°C.
e = $FeSO_4$ in grams
f = % crystallization (crystals obtained/total $FeSO_4$ in 1000 cc.)
g = % crystallization (crystals obtained/total $FeSO_4$ in the solution at that stage)

Evap.No.	1st	2nd	3rd	4th	5th
a	1000	419	198	94	44.4
c	485	176	83	39.5	18.6
b	515	243	115	54.5	25.8
d	419	198	94	44.4	21
b/a	0.515	0.58	0.58	0.58	0.58
c/a	0.485	0.42	0.42	0.42	0.42
d/b	0.815	0.815	0.815	0.815	0.815
e	116	54	25.8	12.2	5.8
f	52.8	24.6	11.8	5.6	2.64
g	52.7	52.7	52.7	52.7	52.7
d/a	0.419	0.473	0.473	0.473	0.473

Solution left 21cc. $FeSO_4$ in the solution = 5 gm or 2.3%.

From the foregoing table a schedule for a month's run can be figured out as follows:

Two tons of $FeSO_4.7H_2O$ is equivalent to 1.092 tons of $FeSO_4$. To produce 1.092 tons of $FeSO_4$ the theoretical amount of pickling liquor needed is (1.092)(2000)(454)/116 = 8560 litres. =(8560)(0.264) = 2260 gallons. If we take 2660 gals. for the first day, according to the foregoing table, we shall have to evaporate 2660(0.485) = 1285 gals.

Volume left after the first evaporation is 2550 (0.419) = 1115 gals. The amount of crystals we should have from the first evaporation is theoretically 2 (26660/2260) = 2.350 tons. Assuming 90% of this amount is obtainable practically, we have 2.350(0.9) = 2.10 tons $FeSO_4.7H_2O$ for the first day's run. For the second day we take in another 2660 gals. of liquor and have another 2.120 tons of product. For th third day we combine the two portions of liquor left over during the last two days which is 2230 gals. Water to be evaported is 2230 (0.42) = 936. Volume left for the next evaporation is 2230(0.473) = 1,055 gallons. The amount of crystals we should have is

2230(1/0.264) (54/0.419) (1/454x2000) (278/152) (0.9) = 1.970 tons.

The rest of the month can be figured in thesame way, and we shall have three grades of grades of crystals as shown in the following:

Schedule

Date	Evap. No.	Volume Handled (gals)			H_2O Evaporated (gals)			Volume after Crystall. (gals)			$FeSO_4 \cdot 7H_2O$ Crystals (tons)		
		1st Evap.	2nd Evap	3rd Evap	1st Evap	2nd Evap	3rd Evap	1st Evap	2nd Evap	3rd Evap	1st Evap	2nd Evap	3rd Evap
1	1st	2660			1285			1115			2.120		
2	1st	2660			1285			1115			2.120		
3	2nd		2230			936			1055			1.970	
4	1st	2660			1285			1115			2.120		
5	1st	2660			1285			1115			2.120		
6	2nd		2230			936			1055			1.970	
7	3rd			2110			886			1000			1.890
8	1st	2660			1285			1115			2.120		
9	1st	2660			1285			1115			2.120		
10	2nd		2230			936			1055			1.970	
11	1st	2660			1285			1115			2.120		
12	1st	2660			1285			1115			2.120		
13	2nd		2230			936			1055			1.970	
14	3rd			2110			886			1000			1.890
15	3rd			2000			840			946			1.790
16	1st	2660			1285			1115			2.120		
17	1st	2660			1285			1115			2.120		
18	2nd		2230			936			1055			1.970	
19	1st	2660			1285			1115			2.120		
20	1st	2660			1285			1115			2.120		
21	2nd		2230			936			1055			1.970	
22	3rd			2110			886			1000			1.890
23	1st	2660			1285			1115			2.120		
24	1st	2660			1285			1115			2.120		
25	2nd		2230			936			1055			1.970	
26	1st	2660			1285			1115			2.120		
27	1st	2660			1285			1115			2.120		
28	2nd		2230			936			1055			1.970	
29	3rd			2600			1090			1222			2330
30	3rd.			2678			1125			1260			2400

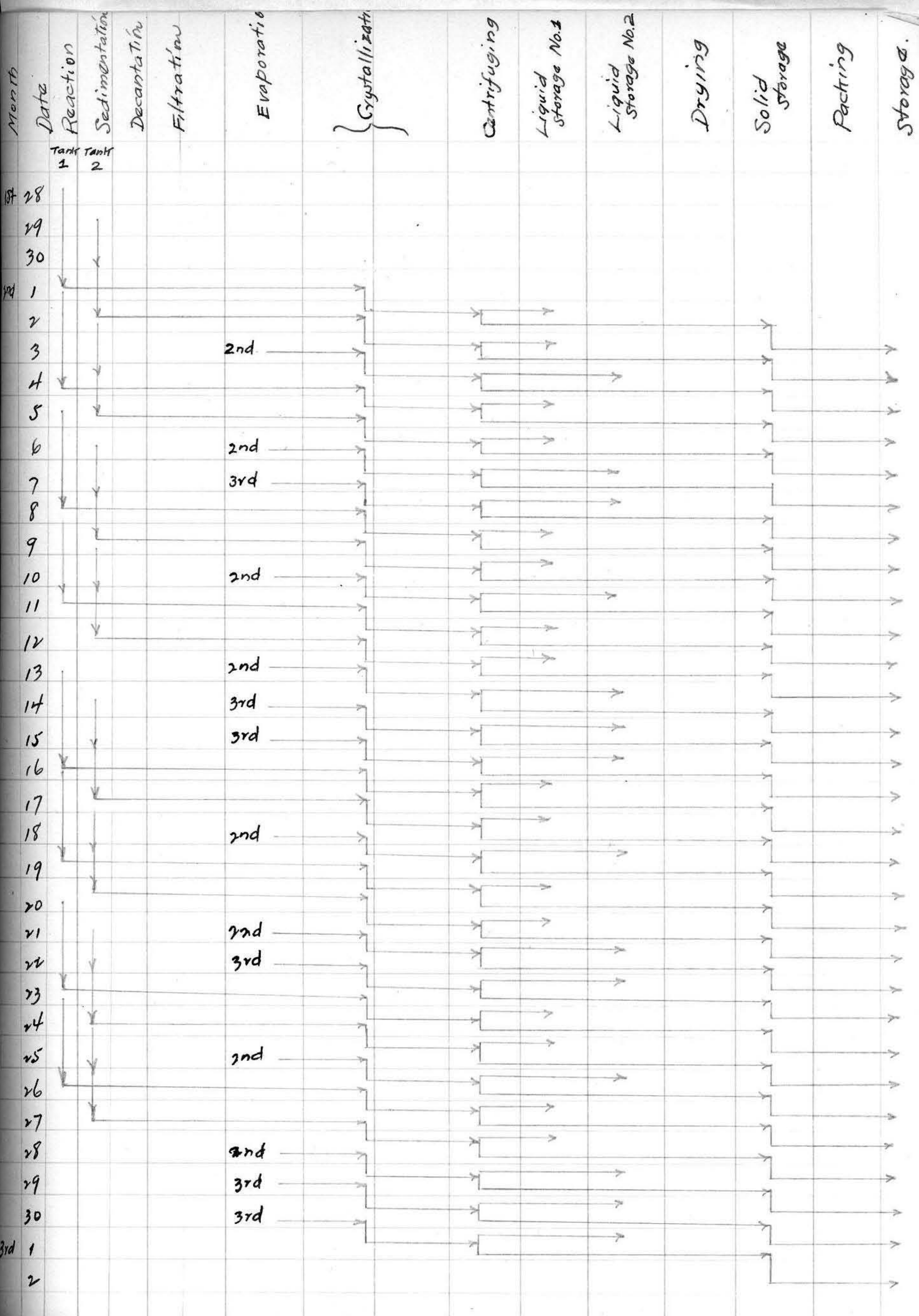
Note 15th 3rd takes up the volume left from 7th 3rd and 14th 3rd.

29th 3rd takes up a part of the volume left from 15th 3rd, 22nd 3rd, 25th 2nd and 28th 2nd.

30th 3rd takes the rest of volume left from 15th, 22nd, 25th, 28th, & 29th 3rd.

The next chart shows the operating process and the relative length of time for each operation. The one succeeding list show some of the equipment to be used.

Take in 2660 gallons of liquor on the 28th of the month before, add iron filings, and let it react at room temperature, and then allow it to settle. On the first of the month, the liquor is to be filtered early in the morning. Evaporate on the same day. Crystallization would take place in the night. Early the next morning, the crystals are to be separated with a centrifugal machine; the mother liquor goes to tank No. 1, and the crystals go to the drying process. Evaporation and crystallization are the same on the second day as on the first. On the third day, the crystals formed during the night are to be centrifuged early in the morning; the mother liquor together with that in tank No. 1 goes to the evaporation process during the day time. The rest of the procedure is the same except that the mother liquor left from this coming separation is to go to tank No. 2.


Month
Data
Reaction
Sedimentatio
Decantatin
Filtration
Evaporatio
Crystallizati
Centrifuging
Liquid storage No.1
Liquid storage No.2
Drying
Solid storage
Packing
Storage.
Tank 1
Tank 2
1st 28
29
30
2nd 1
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4
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A list of equipment:

Article	Purpose	Capacity	Material made	Remark
2 Tanks	reaction	3000gal	cypress with asphalt paint	Let the Fe react with free acid at room temperature for 48 hrs. & let solution sediment for 24 hrs.
1 Tank	decantation	3000	"	To hold soln. left from 1st evaporation.
1 Tank	liquid storage No.1	3000	"	
1 Tank	liquid storage No.2	5000	"	Big enough to hold soln. from both 2nd & 3rd evaporation.
1 Evaporator w with steam coil	Evaporation	3000	body - cast iron coil - monel metal	
Filter	filtration		cloth	Leaf filter with diatomaceous earth.
2 Crystal. tanks	crystallization	2000	cypress wood	
2 Centrifu.	separating crystals	180# per run.	cast iron	Talhust Machine Work's self Balancing centrifuge, dia=26" Max. load = 30#, normal RPM=1000, approx floor space 37"x44".
1 drier	dry crystals	2.4tons per 8 hrs.	wooden tray	Tunnel & trucks type described on p.542 Prin. of Chem. Eng. by Walker, Lewis, & McAdams, can be used.
Barrels	shipping			
Auxiliary				
Boiler	steam generation			
Motors	centrifuge, compressed air of agitation and stirrer, fan in drier.			