

THE PREPARATION OF FINELY
DIVIDED FERRIC OXIDE


Thesis for the Degree of M. S.
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William Francis Taffee, Jr.
1949

THESIS

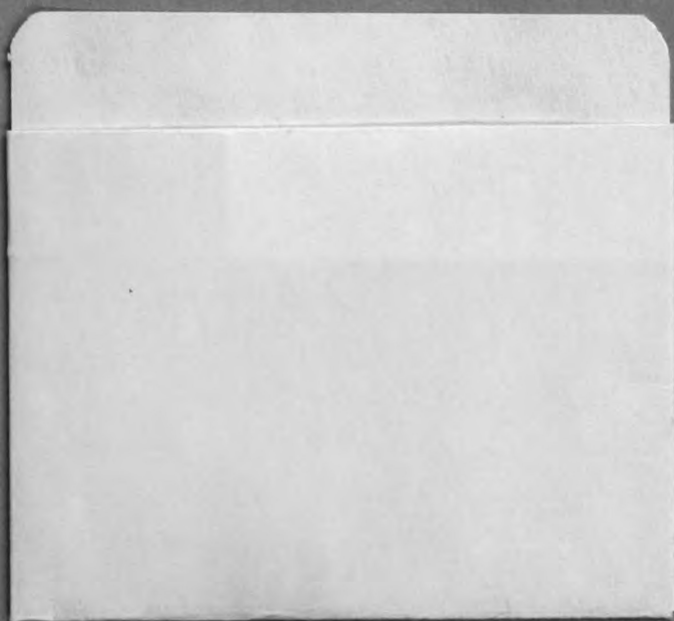
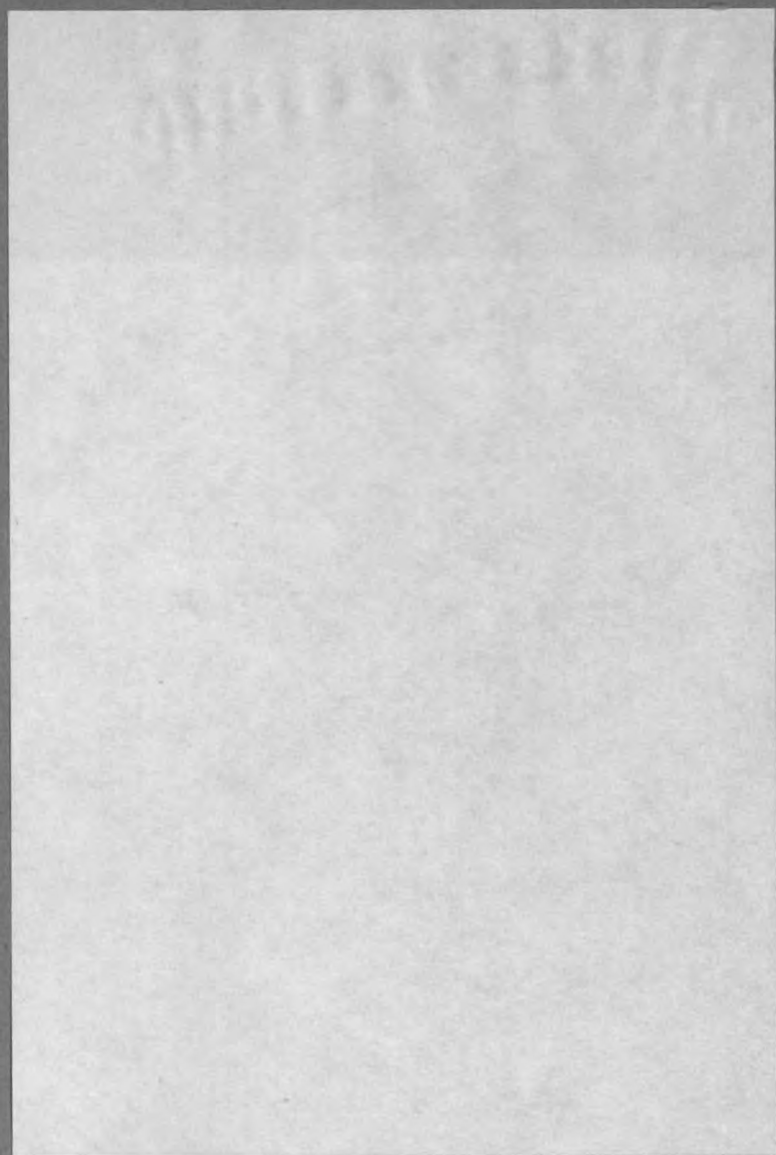


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Major professor

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THE PREPARATION OF FINELY
DIVIDED FERRIC OXIDE

By

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INTRODUCTION

The problem of waste recovery has long held the attention of many people. Business men are interested because it means more saleable goods. State and Federal government conservation authorities are interested because of the stream pollution abatement brought about by proper waste treatment. Lastly, the public may be interested if the by-product thus recovered means a new, better or less expensive consumer good.

A particular problem of interest to all three groups is exemplified by the spent pickle liquor from steel fabricating mills. This is composed of ferric and ferrous sulfates and a small amount of sulfuric acid. Because of the acidity and dissolved solids the liquor cannot be dumped directly into streams or sewer systems. Here then, the problem is of concern to both pollution control and the businessman.

The steel men have, at the insistence of conservation authorities, set about to find satisfactory methods for the disposal of this waste, which in 1945 amounted to nearly 1.3 billion gallons. As yet no entirely satisfactory method for disposal or recovery has been found.

To be satisfactory the process should provide for the following:

1. Neutralization of the excess acid.
2. Removal of the dissolved solids.
3. Conversion of these recovered solids to a saleable form by an economically feasible process.
4. Provide an effluent of nearly neutral character which may flow directly into streams or sewer systems.

At present the processes used for the treatment of waste liquor fail to meet all of the above requirements. The method of treating with lime and recovering a building material from the sludge is not economically feasible except in areas when building materials are scarce or particularly expensive.

Other methods for the recovery of ferrous sulfate and its eventual conversion to ferric oxide, are available. The ferrous sulfate may be sold as such, to a limited market, or it may be converted to ferric oxide by the calcination method of Fireman.

A third method which meets all the conditions set forth is the precipitation of the ferric hydrogel and the conversion of this hydrogel to ferric oxide by means of heat and pressure.

HISTORY

This approach to the problem is not altogether new. Rather it is a combination of several ideas proposed many years ago but apparently neglected after their conception.

It was recognized by Williams⁽⁴⁾ early in 1802 that heat and pressure would bring about the dehydration of ferric hydroxide. By far the largest amount of work appears to have been done on ferrous iron salts.

These processes are based on the precipitation of ferrous hydroxide and its oxidation to ferric hydrogel. The ferric hydrogel is then converted to ferric oxide. There is no attempt on the part of this author to discuss in detail the exact mechanism of the conversion of the hydrogel to hematite (anhydrous Fe_2O_3) or goethite, $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, (ferric oxide monohydrate) but rather to illustrate some of the factors controlling the rate of conversion and the physical properties of the product.

Little work appears to have been done before the year 1800 on the precipitation methods of preparing ferric oxide pigments. Scheele⁽⁴⁾ writing in 1777 mentions the preparation by precipitation. In 1802 J. L. Williams,⁽¹⁶⁾ in England, secured satisfactory precipitates by dissolving ochres and pyrites in nitric acid and adding an excess of ammonia. Lord Rosse,⁽⁴⁾ at about the same time, prepared polishing rouge by a combination of precipitation and calcination.

The pattern set by Rosse has been faithfully followed throughout the years. Calcination has been the mainstay of the preparation of ferric oxides. The raw materials varied from pyrites through mill scale and pickle liquor but in all cases the last process was calcination. The calcination

processes devised by Fireman and Penniman - Zoph are still used by the Magnetic Pigment Company. As late as 1919 Marks⁽¹¹⁾ recommended the use of calcination, as an alternative in a process which would appear to be the forerunner of the work done regarding the effect of pressure on the oxidation of ferrous iron salt solutions.

The idea of using increased pressures to hasten the oxidation of ferrous salt solutions was first patented by Marks.⁽¹¹⁾ After Marks came DuFair⁽⁵⁾ who treated ferrous sulfate solutions with calcium chloride and removed the resulting calcium sulfate. After the removal of the sulfate ion, he was left with a solution of ferrous chloride rather than the ferrous sulfate with which he began. This ferrous chloride solution was then precipitated with calcium carbonate and the mass agitated with air, under pressure to precipitate the iron in its ferric state. DuFair does not mention the fact, but it would appear possible to recover the calcium chloride formed in the precipitation step and recycle it to the first treatment step.

Muller⁽¹²⁾ in 1938 patented a method for preparing ferric oxide by heating ferric hydroxide to "above 100 deg. C. at raised pressure, in the presence of dissolved ferrous salt". Uebler and Muller⁽²⁰⁾ also patented a process for making red pigments by heating ferric oxide in a closed vessel to "130 deg. C. or more in the presence of an excess of water". In this case the pressure would approach 40 psia.

In the same vein J. W. Ayers⁽¹⁾, in 1939, patented a process for producing red oxide pigments by treating a ferrous salt solution with sodium carbonate and heating the resulting slurry to a temperature in the range of

50 to 175 deg. C. at pressures above atmospheric. The same Mr. Ayers,⁽²⁾ in 1939, successfully prepared black oxide pigments by adding an excess of sodium hydroxide to a hot ferrous sulfate solution and heating the resulting slurry to between 220 deg. and 290 deg. F. under a pressure of 40 to 100 psia., at the same time supplying air to the mixture. The black pigment resulting is undoubtedly a mixture of ferric and ferrous oxides, and if the air blow and heating were continued for a sufficiently long time, a red pigment would result, the shade of which would depend upon the amount of sodium hydroxide added in excess of the stoichiometric quantity.

This same reasoning, of the effect of pH on pigment color, may have occurred to Ayers or his co-workers, for in 1940 the C. K. Williams Co.⁽²¹⁾ patented in Germany a process specifying the specific gravity of both the iron salt solution and the alkali to be used and the temperature at which they are to be mixed. The resulting slurry is then heated to 105 to 150 deg. C. at a pressure of 2.8 to 7 atmospheres while passing an oxidizing gas through the solution. However, the black pigment was not as finely divided as it should have been, for a grinding step was necessary. This patent may be considered as an extension of Ayers Canadian patent number 379,225.⁽²⁾ In these two patents by Ayers is the first indication of any recognition of the effect of pH on the precipitation and subsequent conversion of the hydroxide gel to ferric oxide, or as specified by the patents, ferroso-ferric oxide mixtures.

Another path pursued by many individuals was the use of a catalyst of some kind to hasten the conversion of the ferrous iron to ferric iron or to speed up the conversion of the hydroxide gel to the oxide. One of the

earliest pieces of work recorded in this field was that of Obladen⁽¹³⁾ who prepared pigments "ranging from yellow to red" by heating an aqueous suspension or a paste of ferric hydroxide gel. The gel was heated, under pressure to "a temperature above 100 deg. C.", using boric acid or the salts thereof as a catalyst.

Bruno Uebler⁽¹⁹⁾ suggested that anhydrous ferric hydroxide be added to an aqueous suspension of ferric hydroxide gel and the mixture heated to above 100 deg. C. under pressure. He states that red pigments may thus be obtained.

An I. G. Farbenindustrie A. G. patent⁽¹⁰⁾ in 1928 claims the manufacture of a finely divided ferric oxide from the hydrate, by heating an alkaline solution at a temperature above 100 deg. C. Here again no thought is given to pH.

In 1931 Stahl Chemie G.M.B.H.⁽¹⁸⁾ procured the following patent:

"A red material of a remarkable coloring power is prepared by heating, under pressure, iron rust or the hydroxides of iron poor in water. The material used must be moistened with a small quantity of solution of ferric salts or hydrochloric or sulfuric acid".

Obviously the reference is to the preparation of finely divided ferric oxide. However no control is exercised over the amount of acid or acid salt added. It is presumed, on the basis of the work reported in this investigation, that no effective color control of the product was possible.

A Swiss patent, issued to I. Hunyady in 1938⁽⁹⁾, discloses a method for the recovery of both iron and aluminum oxides from bauxite. This is accomplished according to the patent, simply by adding ammonium sulfate to the mixture and heating in a closed vessel.

Renkowitz,⁽¹⁴⁾ in 1938, patented another method for catalyzing the oxidation and conversion. His idea involves the use of an iron-oxygen compound of the structure of iron rust, heated under pressure. This work would seem to follow, very closely, the pattern set by Uebler⁽¹⁹⁾.

Riskin, Neroslovskaya and Pugacheva,⁽¹⁵⁾ also in 1938, suggested the use of iron shavings in ferrous sulfate or ferrous chloride solutions to catalyze the oxidation which was done under a pressure of 5 atmospheres and at a temperature of 120 deg. C.

Muller⁽¹²⁾, in December 1932, patented a process for preparing red ferric oxide in which a ferrous chloride solution was treated with calcium hydroxide to precipitate ferrous hydroxide. The ferrous hydroxide was subsequently converted to ferric hydroxide by blowing in air. The slurry, still moist with ferrous chloride solution, was heated to 132 deg. C. for one hour in an autoclave. Muller may have had a specific dosage of calcium hydroxide in mind, however, he failed to mention any specific dosage, thus had no pH control.

Wurzschnitt and Beuther⁽²²⁾ in 1928 patented a process very similar to that of Muller except that they utilized ferrous sulfate solutions precipitated with sodium hydroxide.

Sierp⁽¹⁷⁾ in 1938 suggested the treatment of spent pickle liquor, which has been neutralized and clarified, with either sodium carbonate or ammonia. The resulting precipitate is oxidized and the ferric hydrogel placed in an autoclave at a pressure of seven atmospheres.

If a yellow pigment is desired, Crepaz⁽³⁾ suggests the oxidation of ferrous hydroxide hydrogel, with an atmosphere of oxygen. The oxidation is

to be conducted first at "ordinary" temperatures then at the temperature of boiling under 2 to 3 atmospheres. The ferrous hydroxide hydrogel may be prepared by precipitating a ferrous salt solution with sodium carbonate, sodium hydroxide or calcium hydroxide. However, again there is no mention of pH control.

Upon careful consideration of the work cited a generalized pattern, which all follow, begins to take form. The pattern is this:

1. Precipitation of a ferrous hydroxide hydrogel.
2. Oxidation of this hydrogel to its ferric state.
3. Conversion, with or without a catalyst, of the ferric hydrogel by heat and pressure, to the desired form of ferric hydroxide.

This pattern is followed by all the investigators cited. These men showed little interest in reproducing their colors from ~~batch~~ to batch. Perhaps this is one reason why none of these methods, though they are basically sound, are in use today and why there is no record of any pilot plant or full-scale plant work having been done on them.

From previous work in this Laboratory there was evidence that pH of the ferrous salt solutions had a profound effect on the velocity of the oxidation reaction. However, in all of the available literature but one vague reference is made to the pH of the solutions.

If pH is important in the oxidation step, why should it not be important too in the conversion of the iron hydrogel to the finely divided iron oxide? Since pH exerts an influence on the conversion product of a gel⁽⁶⁾ in addition to controlling the rate and character of precipitation and agglomeration, it seemed worthwhile to investigate the production of finely divided iron oxide under adequate control conditions.

This objective suggested the outline for the work to be accomplished in the present investigation. Since pH had previously been neglected, a study of the effect of pH of the slurry was made with special reference to:

1. Time required to convert the hydrogel to the oxide.
2. Temperature requirements.
3. Effect on color, everything else being constant.
4. Effect on other physical properties (e.g. particle size, ability to mix with oil, drying characteristics, etc.).

PROCEDURE

The procedure followed in these tests has been standardized in order that the results might be compared. The method is as follows:

1. Dissolve an amount of iron salt equivalent to 3.75 pounds of FeCl_3 in a 30 gallon crock.
2. Prepare a solution containing approximately 5% more than the calculated stoichiometric amount of NaOH .
3. Add the NaOH and iron salt alternately to the mixing tank. After the solutions are in the tank, turn on the mixer and add sufficient water to make 40 gallons. Mix for five minutes and test pH. Adjust pH if necessary by use of base or acid.
4. Pump out mixing tank into system and close system.
5. With pump running turn steam into heat exchanger.
6. Take samples every 15 minutes after start of run, using the bottom sampling tap. Centrifuge the sample to remove oxide from water suspension.
7. Smear a thin film of oxide on glass plate and place in oven to dry.
8. After drying, rub the oxide with oil using a spatula and glass plate, to demonstrate color and mixing characteristics.
9. If no color difference is apparent between two samples taken 15 minutes apart, the run may be considered complete at the time of the earliest sample.

The pH determinations were made with a Beckmann pH meter and with Hydrion paper and are accurate to .25 pH units.

*Slaked lime was substituted in Runs 3 and 9 otherwise the procedure remained identical.

EQUIPMENT

The equipment used in this work is the result of several years of experimentation in this Laboratory. When pumping the ferric hydroxide slurry through a heat exchanger was first attempted, pump failures were common and frequent. Heat exchangers of sufficient area and at the same time possessing a tube size small enough to maintain turbulent flow were unavailable.

Previous work of this Laboratory had pointed to the necessity of having available some means of cooling the bearings and stuffing box of the pump used; all previously used pumps had failed due to bearing seizure and scoring of the shafts in the packing section. After more than a year of correspondence, two manufacturers agreed to furnish a pump which they felt would handle an alkaline or slightly acid ferric hydroxide slurry at temperatures up to 350 deg. F. and under a total pressure of 125 psig. Of these two, the pump manufactured by Dean Bros. Co. of Indianapolis, Indiana was offered at less than half the price of its competitor.

This pump is a 1" by $1\frac{1}{2}$ " single stage centrifugal, having both water cooled stuffing box and ball bearing case, capable of delivering 25 g.p.m. under a total head of 50 feet. It has performed very satisfactorily for the period of this work, and shows no sign of wear or other deterioration.

The heat exchanger provided a second problem. A commercially available exchanger of large area at low cost was desired. Again the problem was finally solved by an exchanger made by Bell and Gossett Co. of Morton Grove, Illinois. This exchanger, originally designed for hot water supply work, is of the shell and tube type with four tube passes and U tube con-

struction, steam on the shell side. The tube bundles are approximately six feet long and the inlet and outlet connections $1\frac{1}{4}$ " diameter. Steam inlet is $\frac{1}{2}$ " diameter, however in this work steam was supplied through a $\frac{1}{2}$ " line. The exchanger has served admirably in its present condition and would appear to be the best exchanger yet tried in this service.

Referring to the drawing of the equipment one can easily see that it is essentially a device for heating, batch-wise, a quantity of liquid by pumping it through a shell and tube heat exchanger with 90 pound steam on the shell side. It becomes immediately evident that the pressure of this system, with all vents closed, will approach that of the steam plus the head developed by the pump. In the case of a concentrated slurry this combination may well reach 130 psig. at the pump discharge and 105 psig. in the tank as indicated in the data for Run number 2. Obviously then the requirements of heat and pressure are easily met in this apparatus since temperatures of 320 deg. F. were recorded. When full 90 psig. steam is available, the maximum is somewhat greater.

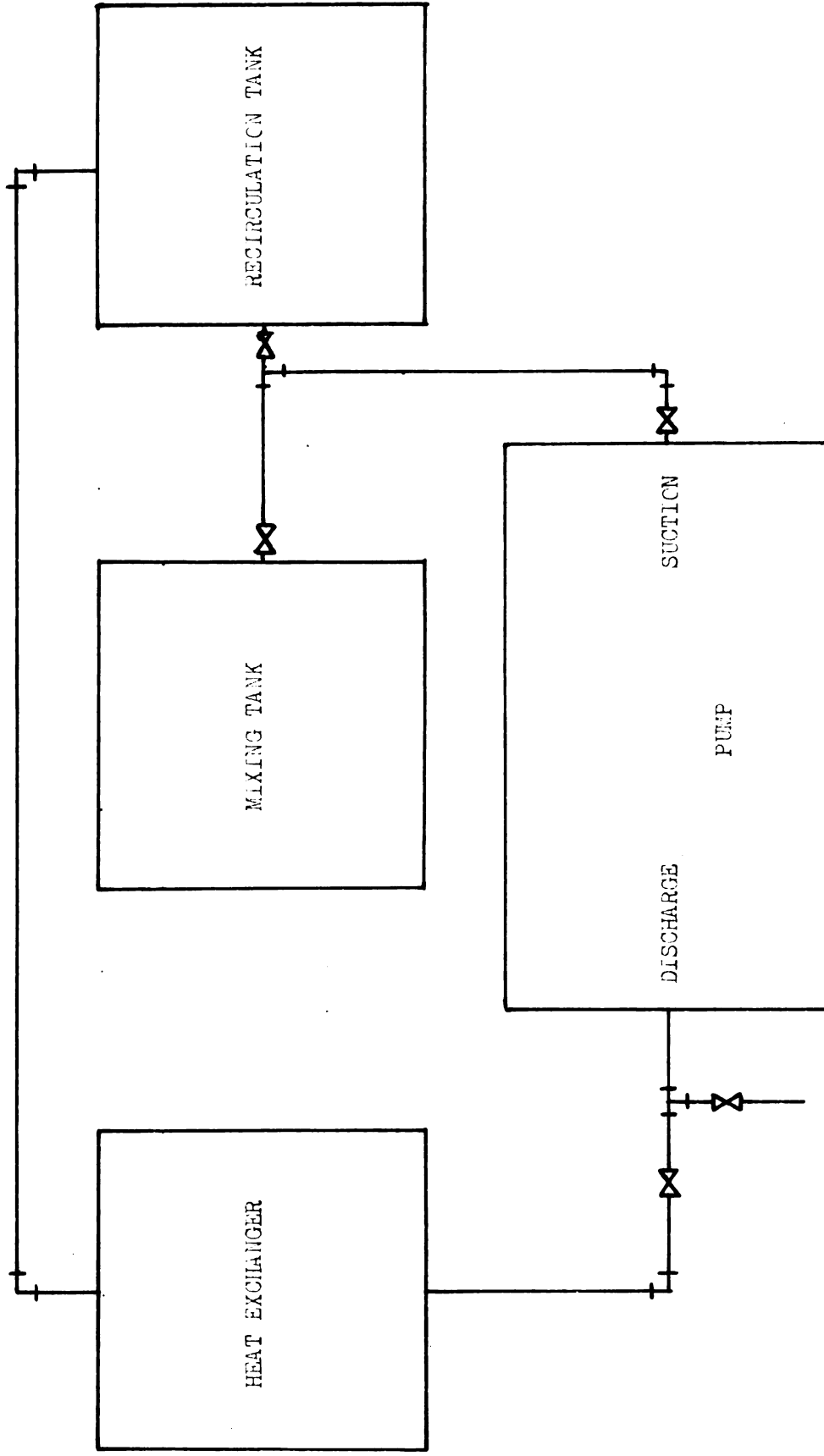
Temperature control was attained by the use of an air operated valve in the steam line, the air supply to the valve being regulated by a proportioning, recorder-controller, supplied by the Foxboro Instrument Company, Foxboro, Massachusetts. This combination gave excellent service, holding the temperature exactly at the predetermined level by throttling the steam supply.

The tank in the recirculation system was constructed of $1/4$ inch boiler plate. The ends were dished and all joints were welded. This tank has a capacity of 100 gallons with $1\frac{1}{2}$ inch screwed inlet and outlet connections at the top and bottom. In addition 1 inch sampling taps were installed.

These taps were welded into the side of the tank, on vertical centers, at distances of 6, 12, 24 and 36 inches from the bottom.

A mixing tank, made from a 52 gallon steel drum with the head removed, was used. A $1\frac{1}{2}$ inch pipe coupling was welded in the bottom of this drum to allow its connection with the recirculating system through suitable piping.

On this mixing tank was mounted an electric driven propellor type mixer, Model C 4, manufactured by the Mixing Equipment Company, Rochester, New York. This mixer performed very satisfactorily, and its stainless steel shaft was not attacked by either the alkaline or the acid solutions in which it was used.



LINE DIAGRAM OF EQUIPMENT

SUMMARY OF RESULTS

pH	Iron Source		pH Adjuster		Time to Convert in Minutes	Color
	Compound	Amount	Compound	Amount		
6	FeCl ₃	8.75 lbs	NaOH	4.2 lbs	105	dark red brown
7	FeCl ₃	8.75 lbs	NaOH	4.5 lbs	90	good red
8	FeCl ₃	8.75 lbs	NaOH	4.8 lbs	80	good red
10	FeCl ₃	8.75 lbs	NaOH	5.3 lbs	25	good red
12	FeCl	8.75 lbs	NaOH	5.5 lbs	15	good red
10	Fe ₂ (SO ₄) ₃	13.3 lbs	NaOH	9.1 lbs	35	good red
10	FeSO ₄	2.73 lbs	NaOH	5.4 lbs	65	"VanDyke" Brown
	Fe ₂ (SO ₄) ₃	14.4 lbs				
11	FeCl ₃	8.75 lbs	Slaked Lime	8.1 lbs	60	light, bright, red
10	Fe ₂ (SO ₄) ₃	13.3 lbs	Slaked Lime	8.1 lbs	footnote A	unsatisfactory

(A) Conversion was only partially complete at the end of 105 minutes. The run was then stopped since such times would be unfeasible for commercial operation.

In the following presentation of Results, the terms "slight", "complete" and "fair" are used to describe the degree of conversion of the ferric hydrogel to the oxide. These terms are based on the color change with reference to the color of the original hydrogel. "Slight" means very little color change; "complete" means no color change between two samples taken 15 minutes apart; and "fair" refers to a color change intermediate between the two.

RUN 1

pH 6

Maximum Temperature 320 deg. F.

Reagents: Ferric Chloride, 8.75 lbs.

NaOH

Solutions mixed 5 minutes at room temperature

Elapsed Time (Minutes) (Steam on =0)	Pressure (psig)		Tank Temperature	Conversion
	Pump Discharge	Tank		
30	90	70	300°	
45	100	85	310°	
60	100	85	310°	Slight
75	95	76	308°	
90	95	76	308°	Fair
105	95	76	308°	Complete

Color of Final Product

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RUN 2

pH 7

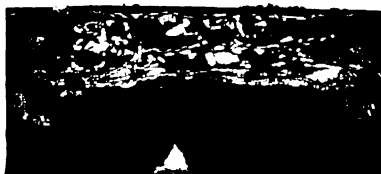
Maximum Temperature 300 deg. F.

Reagents: Ferric Chloride, 8.75 lbs.

NaOH

Solutions mixed 5 minutes at room temperature

Elapsed Time (Minutes) (Steam on =0)	Pressure (psig)		Tank Temperature	Conversion
	Pump Discharge	Tank		
15	100	90	300°	None
45	100	90	300°	None
60	100	90	300°	Slight
75	100	90	300°	Fair
90	100	90	300°	Complete

Color of Final Product

RUN 3

pH 8

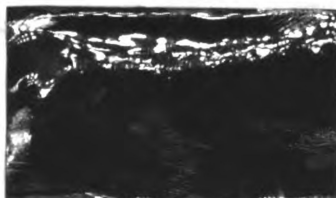
Maximum Temperature 320 deg. F.

Reagents: Ferric Chloride, 8.75 lbs.

NaOH

Solutions mixed 10 minutes at room temperature

Elapsed Time (Minutes) (Steam on =0)	Pressure (psig)		Tank Temperature	Conversion
	Pump Discharge	Tank		
25	120	100	320°	
40	120	100	320°	Slight
60	120	100	320°	Fair
75	120	100	320°	Complete

Color of Final Product

RUN 4

pH 10

Maximum Temperature 320 deg. F.

Reagents: Ferric Chloride, 8.75 lbs.

Sodium Hydroxide, 5.3 lbs.

Solutions mixed 5 minutes at room temperature.

Elapsed Time (Minutes) (Steam on =0)	Pressure (psig) Pump Discharge	Tank	Tank Temperature	Conversion
15	98	30	310 ^c	Fair
30	100	35	320 ^o	Complete

Color of Final Product



RUN 5

pH 12

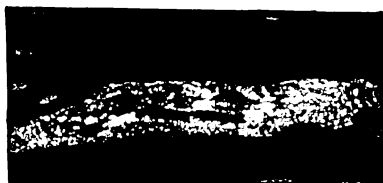
Maximum Temperature 315 Deg. F.

Reagents: Ferric Chloride, 8.75 lbs.

Sodium Hydroxide, 5.5 lbs.

Solutions mixed 5 minutes at room temperature.

Elapsed Time (Minutes) (Steam on =0)	Pressure (psig) Pump Discharge	Tank	Tank Temperature	Conversion
8	80	65	270°	Complete

Color of Final Product

RUN 6

pH 10

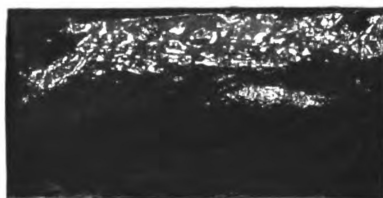
Maximum Temperature 310°

Reagents: Ferric Sulfate, 13.3 lbs.

Sodium Hydroxide, 9.1 lbs.

Solutions mixed 30 minutes at room temperature

Elapsed Time (Minutes) (Steam on =0)	Pressure (psig) Pump Discharge	Tank	Tank Temperature	Conversion
15	100	82	308°	
25	108	82	310°	Complete

Color of Final Product

RUN 7

pH 10

Maximum Temperature 315 deg. F.

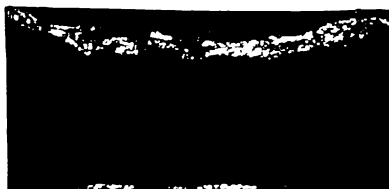
Reagents: Ferrous Sulfate 2.73 lbs.

Ferric Sulfate 14.4 lbs.

Sodium Hydroxide 5.4 lbs.

Solutions mixed 10 minutes at room temperature

Elapsed Time (Minutes) (Steam on =0)	Pressure (psig)		Tank Temperature	Conversion
Pump Discharge	Tank			
15	90	70	300°	
45	100	85	310°	Slight
65	100	85	310°	Fair
80	100	85	312°	Complete

Color of Final Product

RUN 8

pH H

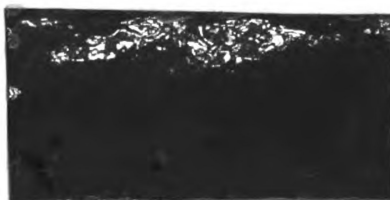
Maximum Temperature 320 deg. F.

Reagents: Ferric Chloride, 8.75 lbs.

Slaked Lime, 8.1 lbs.

Solutions mixed for one-half hour at room temperature.

Elapsed Time (Minutes) (Steam on =0)	Pressure (psig)		Tank Temperature	Conversion
	Pump Discharge	Tank		
15	90	70	300°	
30	100	85	315°	
45	100	86	317°	
60	110	94	320°	Slight
75	110	94	320°	Complete

Color of Final Product

RUN 9

pH 10

Maximum Temperature 305 deg. F.

Reagents: Ferric Sulfate 13.3 lbs.

Slaked Lime 8.1 lbs.

Solutions mixed for 45 minutes at room temperature.

Elapsed Time (Minutes) (Steam on =0)	Pressure (psig)		Tank Temperature	Conversion
	Pump	Discharge Tank		
15	90	70	290°	
30	130	105	302°	
45	120	100	300°	
60	100	80	290°	
105	100	80	290°	very slight

Final product could not be used as pigment, and differed
very little from the original hydroxide.

DISCUSSION

Even though the literature records many methods for the preparation of ferric oxide pigments, none of the precipitation methods, and very few calcinations are in use in this country today. There exists no literature explaining why so many ideas have failed of fruition. However on the basis of past experience in this Laboratory one may draw some conclusions.

In the first place the oxidation step, from ferrous to ferric is slow unless catalyzed and conducted under pressure. This problem has been investigated by Forsberg⁽⁷⁾. His work indicates the technique of securing rapid and complete oxidation of ferrous sulfate, using N_2O_4 as a catalyst-oxygen carrier. This eliminates the first possible deterrent. Secondly, in previous work the conversion of the precipitated ferric hydrogel has been somewhat slow, yields have been erratic and color reproduction impossible of achievement. These are factors of interest in this report.

The number of catalysts tried and reported in the literature would indicate an attempt to hasten the conversion of the hydrogel and at the same time perhaps promote color stability. In the present work conversion time and color are shown to be functions of pH. The existence of an optimum pH has also been demonstrated.

The results of this work have shown conclusively that pH has a definite effect on color of the final product and on the time required for conversion as well. There may also be some effect on the grinding characteristics of the resulting oxides, although this variation is not great enough to be significant.

The data, as regards color, show conclusively that pH has a definite effect on shade of color produced. These runs were made using ferric chloride from a single drum obtained from Dow Chemical Company, Midland, Michigan. This procedure was intended to obviate, insofar as possible, any variation in raw material and thus restrict the number of variables. Tap water was used to mix the solutions; however, the daily fluctuation in mineral content of the water was not great enough to exert a significant influence on the color. For most of the precipitations commercially pure sodium hydroxide was used. This was also from the same source to minimize quality variations. In two runs, lime was used. This lime was from a single sack thus precluding any great variation in quality.

In view of the above precautions it would appear that all variables had been eliminated with the exception of pH, temperature of heat transfer and time of transfer.

The temperatures were held at 320 deg. F. and the times set as those necessary to obtain complete conversion. By this means the variables of the process are reduced to one, namely pH, and the shades produced are strikingly different, thus establishing definitely that pH has an effect on the shade produced.

In the ferric chloride run at pH 12, conversion was completed in about 15 minutes after the steam was turned on. At this time the temperature was 270 deg. F. The yield was good and color satisfactory. This would lead to the conclusion that pH is of great importance in controlling conversion time, since the runs at lower pHs were all of longer duration. It should be pointed out however that the run at pH 10 showed a distinct

acceleration, in the conversion of the hydrogel, as compared to the run at pH 8.

The oxide recovered by this process has another advantage in that the particles are of a sufficiently small size that the resulting product may be used directly as a pigment with a minimum of regrinding and screening. If a proper recovery system were set up (probably a drum dryer) it is the opinion of the author that an oxide could be prepared of a size and moisture content which could be used directly in the paint industry as pigment without undergoing further unit processes.

On this basis it would appear that at a pH of 10 or above, conversion can take place at a lower energy level than in the cases of lower pHs. This is advantageous as previously pointed out, because it permits a greater temperature difference to be maintained. This allows a greater quantity of heat to be transferred in a shorter period of time. In addition the design of an economically feasible heat exchanger to convert the hydroxide, in one pass through the exchanger, becomes possible. This of course provides a continuous process for conversion. If the continuous conversion process is coupled with a continuous oxidation process, a ferrous or ferric salt may be handled with ease. Here then are the principles for a more practicable recovery system than has yet been reported for ferric oxide production.

Ferric sulfate was also used as an iron source. Of the two runs made only one was successful. Since anhydrous ferric sulfate is not particularly water soluble, it was necessary to add the NaOH solution directly to the ferric sulfate suspension. This resulted in precipitation of the ferric hydrogel plus ferric sulfate. Mixing had to be continued for approximately one-half hour in order to precipitate all the iron as ferric hydroxide.

This batch was then run at pH 10 which is apparently not the optimum pH for the ferric sulfate, since conversion required slightly more than thirty minutes.

The second run attempted with ferric sulfate failed, apparently because of the pH adjusting agent used. Lime was added slightly in excess of the stoichiometric amount, pH adjusted to 10, and the mixture stirred for 30 minutes. Apparently, however, the presence of the calcium sulfate and undissolved calcium hydroxide and perhaps a small amount of ferric sulfate remaining, retarded the conversion of the hydrogel.

The run with ferric chloride and lime, on the other hand, proved very satisfactory. The conversion was completed in slightly under one hour. The time may quite possibly be reduced by changing the pH, since the original work indicates the existence of an optimum pH. The difference between the results obtained, using ferric sulfate in place of ferric chloride, probably lies in the salt formed; calcium sulfate being insoluble, while calcium chloride is extremely soluble in water. Another point worthy of mention is the fact that not all of the calcium hydroxide was dissolved before entering the system, however upon recovery all of the calcium hydroxide particles were coated with a ferric oxide film. This of course provides a lighter color and gives a much greater yield of colored solid material. Based on the iron content alone, the yield is of the order of 175%.

The fact that ferroso-ferric oxides produce colors other than red has been established by mixing ferrous and ferric sulfates in the proportion of one-third mol percent of ferrous ion and two-thirds mol percent of ferric ion and converting the precipitated hydroxide mixture. A brown ferroso-

ferric oxide was achieved. It is probable that other ratios would give different colors.

The conclusions based on this investigation may be summarized as follows:

1. pH controls the shade of color attained in the oxide produced by converting a ferric hydroxide hydrogel.
2. pH is an important factor in controlling the length of time required for this conversion.
3. Lime is satisfactory for adjusting the pH of ferric chloride solutions but not for ferric sulfate solutions at pH 10.
4. Oxides in colors other than red may be produced by means of ferrous-ferric oxide mixtures.

USES

Ferric oxide has been used as paint pigment since the earliest times. This use constitutes the largest single outlet for the oxides produced. The oxide produced by the precipitation and conversion method reported in this work are particularly well suited to use as pigments, because of their small particle size and because good color control may be achieved through control of pH.

A second important use of ferric oxide lies in the petroleum field. Ferric oxide is used as a "builder" or weighting agent for drilling muds used in oil well drilling. An abundant supply of ferric oxide of controlled particle size and size distribution should be a boon to those concerned with the preparation of these muds.

A third important use of ferric oxide is in the foundry. Iron oxide is used in the preparation of molding and core sands. Molding and core sands compounded with iron oxides exhibit high hot strengths, a very desirable property not shown by most natural sands.

Powder metallurgy is a field in which ferric oxide of carefully controlled quality and particle size is now being utilized. Particle size and size distribution as well as particle shape are of particular interest to powder metallurgists and it would appear that these factors could be satisfactorily controlled in the precipitation-conversion method outlined. The only additional step necessary is the reduction of the oxide to iron at elevated temperatures in an atmosphere of hydrogen.

The above mentioned iron might also be used to advantage as a catalyst

in applications where pure iron catalyst of controlled size is desirable. Iron oxide of proper size distribution is an important catalyst in the preparation of synthetic ammonia and sulfuric acid.

Not to be overlooked, is the use of ferric oxide as polishing rouge in the jewelry industry and as an abrasive in lens grinding. These markets, while small, demand and pay for a fine product of carefully controlled size and purity.

SUGGESTIONS FOR FURTHER WORK

1. In order that a clearer picture of the entire mechanism may be had, the author would suggest that a recording pH instrument be obtained and used to record the pH of the slurry during the course of the run.

2. In addition a pressure recording instrument would be desirable in order that the relationship between temperature, pressure and pH in their combined effect on time required for conversion and the resulting color could be demonstrated.

3. The design and pilot operation of a continuous conversion unit to operate from a ferric salt is also suggested. This could be accomplished by using a heat exchanger of the proper design and pumping the slurry through it directly into a closed tank vented through a condenser, thus allowing some of the water to flash off.

Since the ferric oxide settles rapidly, a cone bottom tank might be used and the ferric oxide withdrawn from the vertex of the cone. An overflow for excess water should also be provided.

The problem of recovery from a concentrated slurry or paste still remains. This might however be solved by use of a drum dryer. The speed of the drum and the temperature drop across it could be carried to find the combination resulting in the most desirable moisture content and state of the agglomeration of the particles.

4. It is suggested that ferric sulfate be used in an investigation as to the effect of pH on color produced in ferric oxides obtained by conversion from the hydrogel.

5. Further investigation might be pursued regarding the use of lime as the agent for adjusting the pH of both ferric chloride and ferric sulfate solutions. In addition the method of DuFair⁽⁵⁾ might be investigated; attempting to replace the sulfate ions of the ferric sulfate solution with chloride ions, thus obviating the calcium sulfate difficulty encountered in this work.

6. An investigation to study the color obtained from ferroso-ferric oxide mixtures and the optimum pH for the conversion of these mixtures. In addition a study of the effect of pH on color of the ferroso-ferric oxide mixtures seems in order.

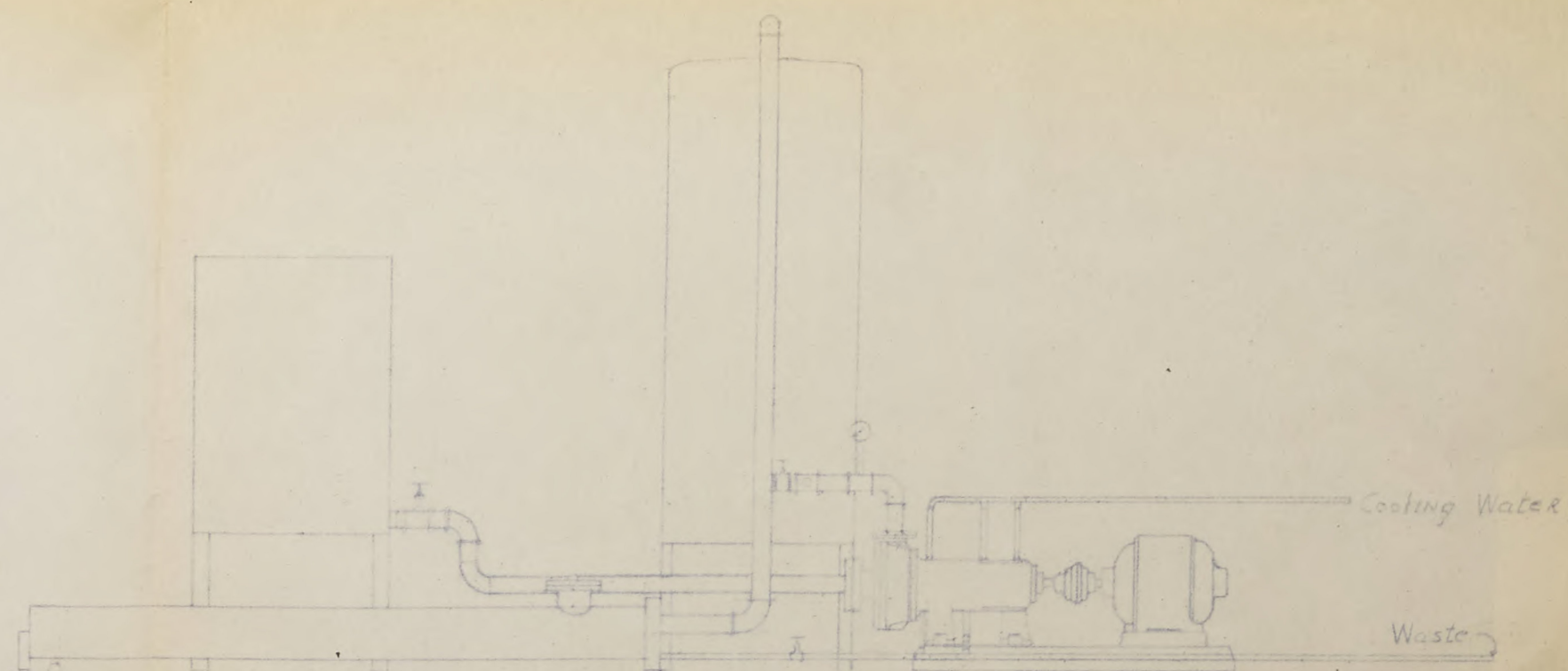
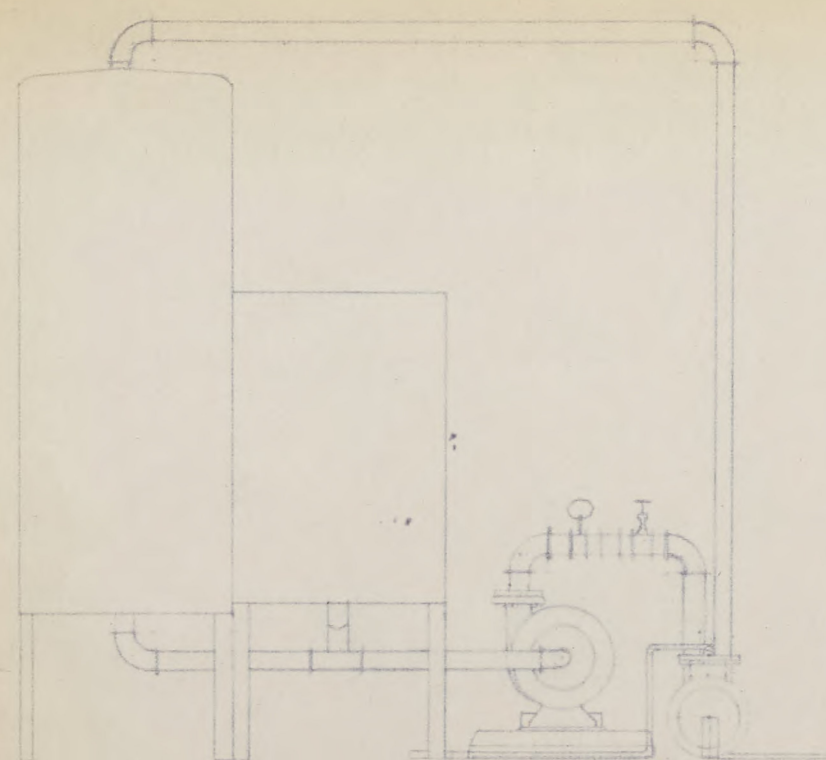
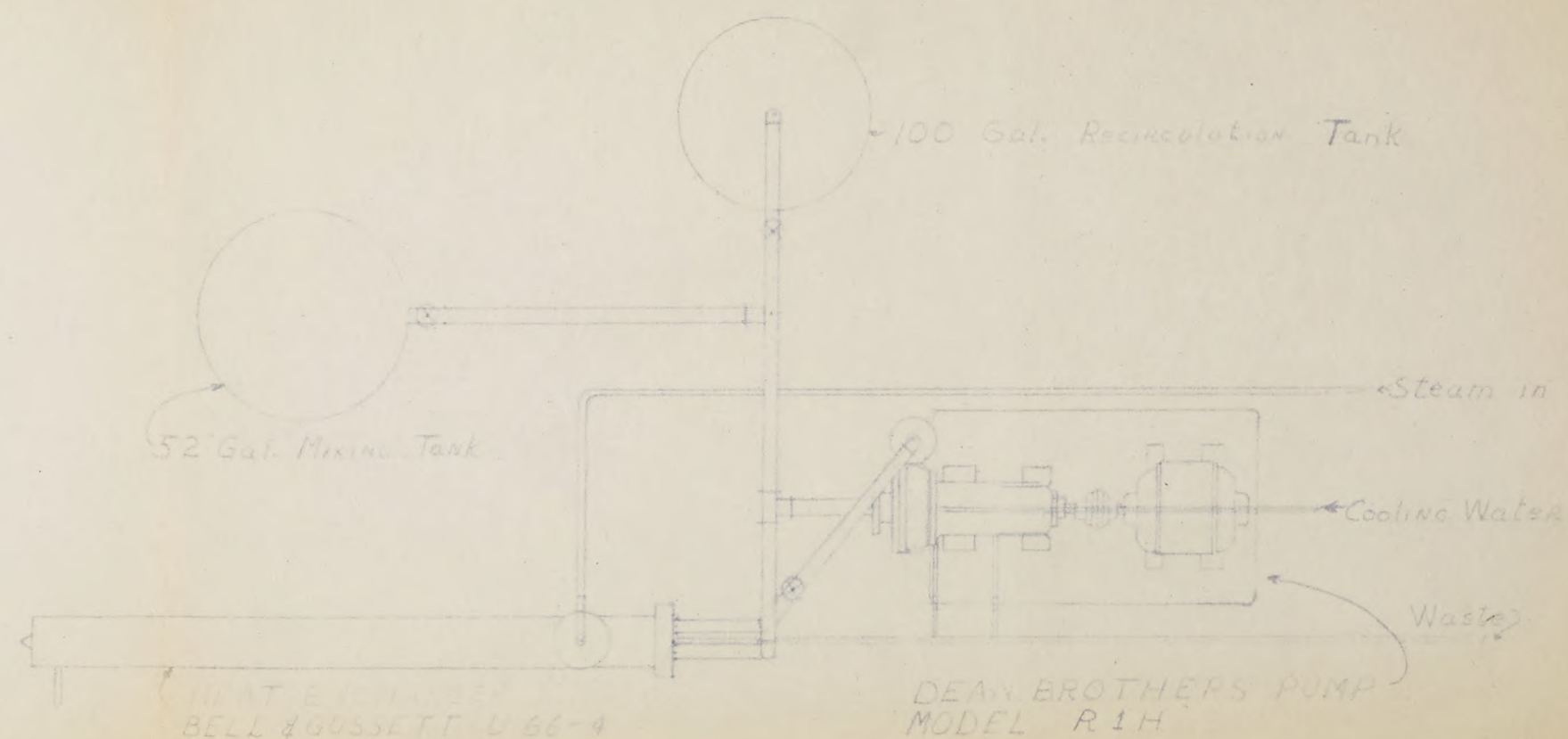
7. In order that the process may be applied to spent pickle liquor treatment, the impurities ordinarily encountered in such liquor should be determined and their effect on color should be ascertained.

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Waste, Steam & cooling water.

Arrangement shown is the one used
in this investigation. Arrangement
not critical, nor are pipe length dimension.



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UNIT FOR THE CONVERSION OF
FERRIC HYDROXIDE TO FERRIC OXIDE

DRAWN - W.F. TAFFEE Jr.
CHECKED - SCALE: 0.1" = 2"
AUGUST 22, 1949

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