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CLASS OF 1922

Department of Chemistry

Undergraduate Theses of

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A PROCESS
for the
UTILIZATION OF PYRITE ASH

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Thesis
by
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for the degree of Bachelor of Science
in Chemical Engineering.

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A PROCESS FOR THE UTILIZATION OF PYRITE ASH

Introduction.

The purpose of this investigation was to find a commercial process by which the iron could be recovered, as ferrous sulfate, from burnt pyrite.

Pyrite, Fe S_2 , is very widely distributed in nature. The largest deposit is at Rio Tinto, Spain, where it occurs associated with both gold and silver. The chief mines in the United States are in New Jersey, Pennsylvania, New York, Massachusetts, Virginia, Georgia, Colorado, and California (1).^{*} Practically the entire output is used in the manufacture of sulfuric acid. The total consumption in the United States, for 1915, was 1,358,758 long tons. By 1920 it had fallen to 607,606 long tons, because of the increased use of sulfur (2).

The burnt residue of ferric oxide, known as "blue-billy", has various uses. At the Stauffer Chemical Company's plant in Los Angeles, it was used solely as a road-bed material. Although the roads are at first firm and dry, they are soon pulverized by the traffic and in wet weather become very muddy.

^{*} Numbers refer to Bibliography at end of paper.

The material is used as a catalyst to promote the combination of sulfur dioxide and oxygen (3). It is also used to catalyze the ferrite process for the manufacture of sodium hydroxide (4).

A process has recently been developed in Italy, for the preparation of ferric sulfate from pyrite ash and niter cake (5). The moistened cinders may also be used to absorb hydrochloric acid from salt-cake furnace gases, etc. (6). Paint pigments may be made from the ash either directly or by first forming ferrous sulfate (7). Numerous methods are proposed to cut down the sulfur content of the ash so that it may be used in the manufacture of pig iron (8).

There are two main processes for the manufacture of ferrous sulfate from pyrite ash. In the first, known as the A. and P. Buisine process (9), the material is heated with 60° Be'. sulfuric acid (boiling point 190°C.) to somewhat less than 300° C. Although the resulting mass of ferric sulfate is not immediately soluble in water, it becomes soluble by hydration at somewhat higher temperatures. The solution, after being reduced to ferrous sulfate by digestion with iron, is evaporated to 27-28° Be'. (measured at 90°C.) and crystallized with pieces of scrap-iron suspended in the vat.

In the other method devised by Pezzolato (10), the pyrite ash is heated to a red heat in a closed vessel with enough powdered charcoal to reduce it to magnetic iron oxide. After concentrating with a magnetic separator, it is treated with sulfuric acid until dissolved. From there the process is similar to the one described above. In both cases any copper present is separated out on the excess scrap-iron.

Plan of Experimental Work.

The logical method of utilizing burnt pyrite from a sulfuric acid plant would be to produce ferrous or ferric sulfate. The two methods, at present used for this purpose have been described above.

Preliminary experiments with the ash showed it to be but slightly soluble in cold sulfuric acid of moderate concentrations. This partially explains why, in the Buisine process, a concentrated acid at a very high temperature is used. This method, besides requiring a considerable initial outlay for equipment would also have a large upkeep cost due to the high pressures used.

The Pezzolato process appears to be unnecessarily complicated besides being difficult to carry out in practice. The magnetic separation removes the non-mag-

netic impurities from the iron. However those impurities, which are soluble in sulfuric acid, may probably be separated by fractional crystallization. A preliminary experiment with a horse-shoe magnet showed that considerable finely divided carbon, from the reduction, was carried mechanically with the large iron particles and a clean separation was not obtained. The material would need to be ground extremely fine to separate each iron particle from the adjacent gangue and this would greatly increase the cost of operation.

The first step of this investigation was to determine the efficiency of the solution of the ash with various temperatures, times of treatment, concentrations and amounts of acid. It was hoped that with this data an inexpensive procedure for the solution of the ash could be worked out. It was desired to determine from an economic standpoint the relative efficiencies of the several processes and also to test out the method finally selected on a large scale.

Analysis of the Pyrite Ash.

The sample for this work was obtained from the Stauffer Chemical Company of Los Angeles. It contained material ranging from about 50-mesh up to lumps nearly

half an inch in diameter. The finer portion of the sample appeared to be well burnt to a reddish purple color but the larger lumps when broken up showed a core of unburnt pyrite. In some of these a yellow substance, apparently free sulfur, could also be seen. The thoroughly burnt pyrite could be pulverized readily but the larger lumps, containing the unburnt portion, were hard.

Lunge states (11) that the pyrite cinders when properly burnt have the red color of ferric oxide, but if much copper is present they are black. They are light and porous, have no unburnt core in the larger pieces, and contain no fused slag, (the latter showing that the temperature of the combustion was correct). The sample used in this work fulfilled these requirements, except that it contained some unburnt material.

The sample was ground down to approximately 80-mesh in a Braun Pulverizer, type UA4, driven at about 570 r.p.m.

Moisture Content

When a sample was dried in an electric oven at 108°C. , it gave a distinct odor of sulfur dioxide. It reached a constant weight, after heating for two hours, showing a loss corresponding to a moisture content of

2.40%. Another sample, dried to a constant weight in a sulfuric acid dessicator for 50 hours showed a loss of 2.15%. The higher value is undoubtedly due to the loss of sulfur. This action has been noted by Jones (12) who states that hydrogen sulfide and thio-sulfide acid are formed. (Lunge, however, (13) recommends determining the moisture in sulfur by heating a sample for several hours at 100°).

The latter of the two results, giving a moisture content of 2.15% of the original sample, is taken as the correct value and all analyses reported in this paper are determined from the dessicator-dried sample and corrected by this value.

Free Sulfur.

The free sulfur will be assumed to be entirely crystalline. It was determined by extraction, for $11\frac{1}{2}$ hours, with c.p. carbon disulfide in a Soxhlet apparatus. The result computed from the loss in weight of the sample gave 0.88% free sulfur. When computed from the weight of the residue, after volatilizing the carbon disulfide, 1.02% was obtained. The mean of these two, giving 0.95% free sulfur in the original sample, is taken as correct.

Total Sulfur.

At first it was attempted to determine total sulfur by the Fresenius method (14). In this procedure the sample is fused with sodium carbonate and potassium nitrate in a nickel crucible. The analysis was attempted three times but each time the crucible was eaten through before the charge could be completely fused. The difficulty appeared to be due to the high temperature required to flux the mixture.

The sodium peroxide fusion method (15) was tried as it was known that this would give a readily fusible mixture. Here the sample is fused with sodium peroxide and sodium carbonate. The sulfate is extracted with dilute acid and determined as the barium salt. Two determinations gave 3.04 and 2.81% of total sulfur in the original material. A blank test showed no barium sulfate precipitate.

Mellor's fusion method (16) was used as a check. Here the sample is fused with a sodium carbonate and sodium nitrite mixture. The result obtained by this method was 2.96%, giving an average for all three of 2.94% which is taken as the correct value.

Determination of Iron.

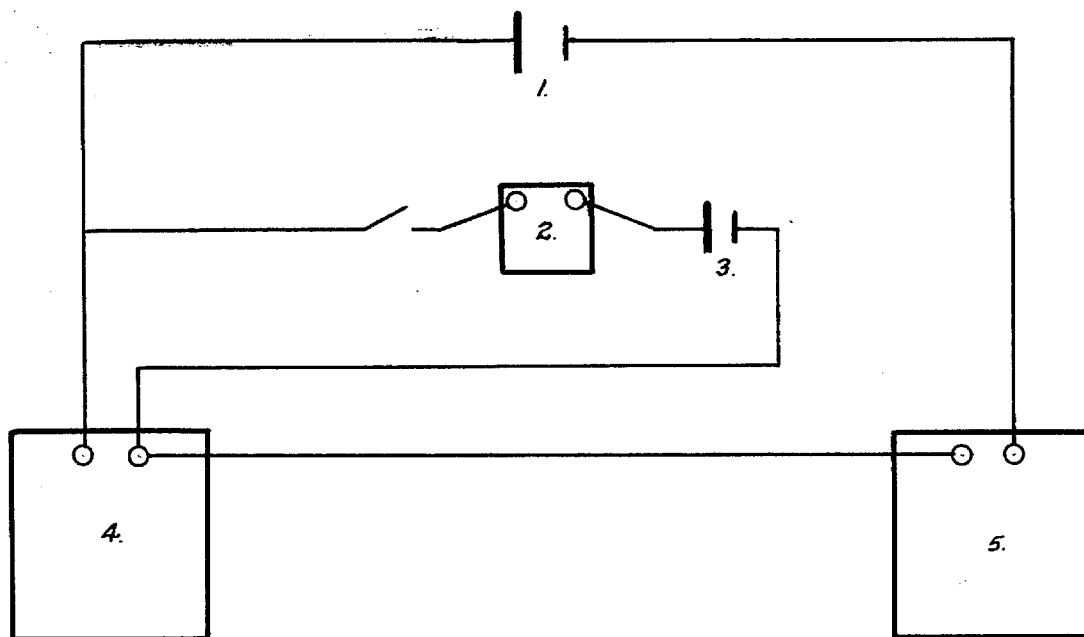
During the first part of the work the iron was determined by the permanganate method after reduction by stannous chloride (17), but later the electrometric dichromate method was used (see below).

Two analyses of the pyrite ash by the permanganate method gave 48.42 and 47.65% of iron in the original material. (Average value 48.03% iron). A definite end-point and consistent results were difficult to obtain by this method. The chief trouble seemed to be due to the lack of permanence in the end-point when titrating an actual iron solution. Experience in this analysis would probably remedy the difficulty but since the time was limited it was thought advisable to try another method.

The electrometric titration of iron by potassium dichromate has been studied by Hostetter and Roberts and found to be very satisfactory (18). While the procedure used here is essentially the same as described by them a few minor changes were made. A diagram of the apparatus is shown in Fig. 1. The titration half-cell consisted of a 250 cc. beaker, surrounded by cotton and asbestos paper to provide heat insulation. The temperature of the solution during the titration dropped from about 100° C. at the start to from 20° to 50° at the end,

Fig. 1.

WIRING DIAGRAM FOR ELECTROMETRIC TITRATION



1. Electra storage battery, 2.03 volts.
2. Galvanometer. P C L #4. Rated sensibility 1.05
3. Titration cell.
4. Decade resistance box, 10,000 ohms. PCL #3
5. " " " " " PCL #4

depending on the time taken for the analysis. This became shorter as experience was gained and varied from two and a half hours for the first few titrations to about half an hour for the last ones made. The capillary at the end of the bridge from the calomel cell was flushed out at intervals from an elevated reservoir containing 1-normal potassium chloride solution saturated with calomel. The sum of the two resistances in the decade boxes was kept always at 10,000 ohms. By this arrangement the voltage of the titration cell is directly proportional to the resistance of one of the boxes. The voltage of the storage battery, during the two months it was used, did not drop more than 0.004 volt.

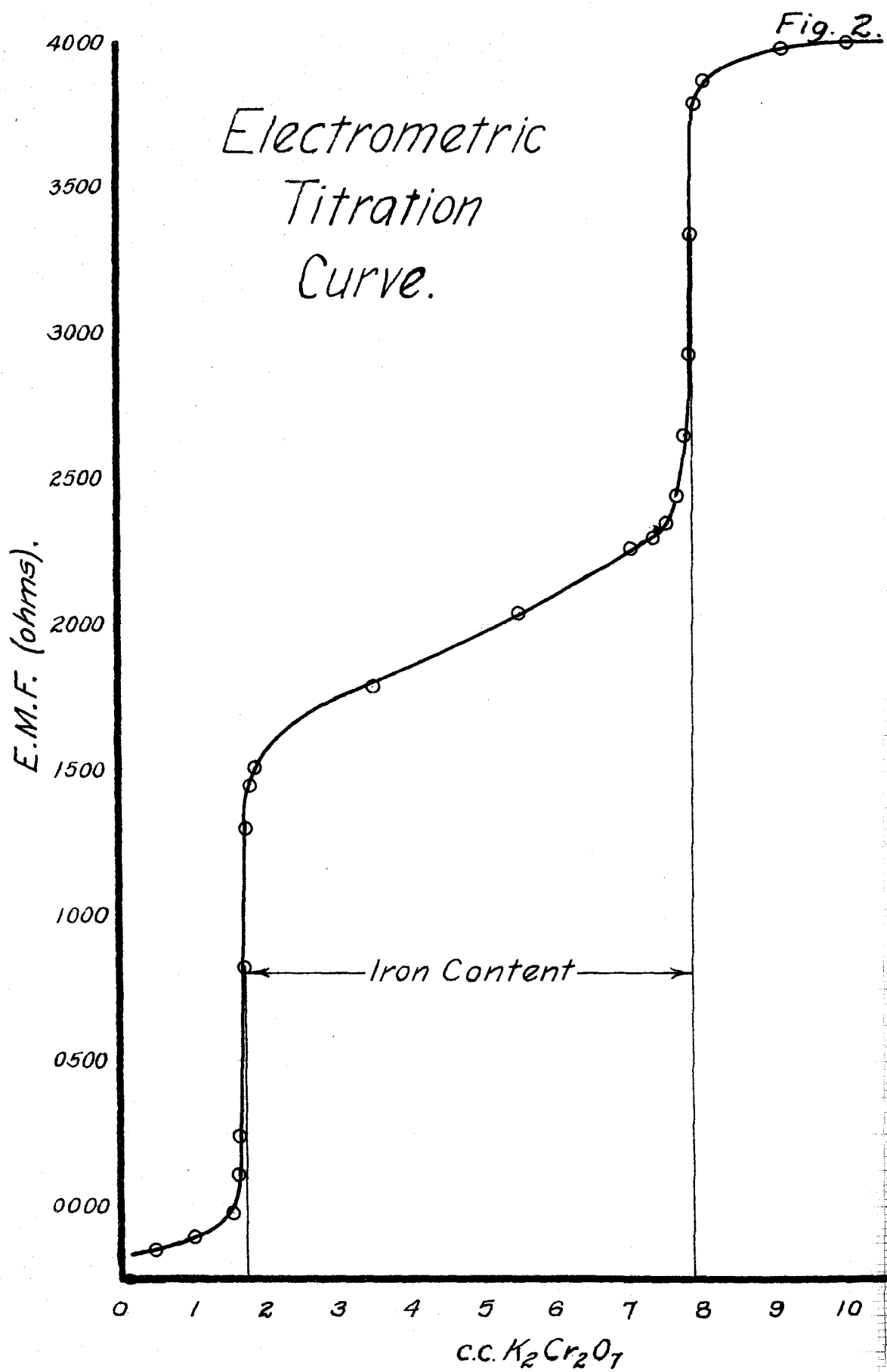
The procedure used in the analysis is as follows:

The solution to be analyzed is made up to 500 cc. in a standard volumetric flask. A 50 cc. portion is placed in the 250 cc. beaker and 100 cc. of 35.0 normal sulfuric acid added. The solution is allowed to stand for about ten minutes in the air or from three to five minutes in running tap water until the temperature has dropped to about 100° C. While this is being done, the electrode is ignited and the tip of the capillary bridge rinsed out. The solution is then put in place and stan-

nous chloride run in until the voltage is lowered to about ± 0.03 volt. The dichromate solution is then added in about 0.05 cc. portions and the e.m.f. read to the nearest 0.002 volt. Hand stirring was used throughout, being stopped for about two seconds before each reading was taken. It was found that the e.m.f. at the stannous chloride end-point rises from ten to twenty minutes before reaching a constant value. The average increase at this end-point is about 0.28 volt. The second or ferrous end-point comes to a constant value in less than one minute with a rise of about 0.16 volt.

It was noticed that when hydrochloric acid was used instead of sulfuric acid in making up the solution the stannous chloride end-point passes through zero, while with sulfuric acid the curve is entirely positive.

In all, over fifty analyses were made by this method and, while at no time could an analysis be made as rapidly as with the permanganate method, the results obtained check with one another and are regarded as much more reliable. In every case in which an indistinct end-point was obtained, it was found that the platinum electrode in the titrating solution was at fault. If the glass near the tip is cracked the results are extremely variable.



A representative set of curves is shown in Figure 2.

An idea of the accuracy of this method of analysis may be obtained from the standardization data of the dichromate solution. The normality of the solution when computed from the amount of c.p. potassium dichromate used in its preparation was 0.12598. The normality found by an electrometric titration with standardization iron wire was 0.12592, the difference being .05%. The latter value is taken as the correct one because it includes all errors inherent in the method. It is probable that some of the analyses, to be given below, are not this accurate, for in a few the solution was added in 0.10 cc. portions at the end-points. The maximum error due to this cause depends on the total iron content and in no case is greater than about 1%.

The amount of iron in the pyrite ash, determined electrometrically and calculated on the basis of the original sample was 48.22%. This agrees fairly well with the mean permanganate value (48.03%) and will be used (as the correct value) rather than a mean. The sample for the electrometric titration was dissolved in hydrofluoric acid while the one for the permanganate was dissolved in hydrochloric. The agreement shows that

all of the iron in the pyrite ash is soluble in hydrochloric acid.

Silica.

The residue from the hydrochloric acid treatment was a sandy white and probably pure silica; of the other impurities found in the qualitative analysis: S, Cu, Al, Zu (?), and Ca, all but the first have soluble chlorides. While the free sulfur is insoluble, it may be destroyed by ignition. The residue from each of the two analyses was filtered, washed, ignited, and weighed. The weights give as the per cent of silica in the original sample the values 23.679% and 23.682% with a mean of 23.68%.

The state in which the combined sulfur is present in the sample is unknown. From the large amount of unburnt pyrite in the center of the lumps, it is reasonable to assume that most of it is present in that form, although some may be in the form of sulfate, either of iron or the other metals. Assuming that all of the combined sulfur is present as pyrite and that the remainder of the iron occurs as ferric oxide, the following computed results are obtained (based on the original sample):

Moisture	2.15%
Free S	0.95%
Fe S ₂	3.72%
Fe ₂ O ₃	66.53%
Si O ₂	23.68%

Undetermined:

Cu, Al Zu (?)

and Ca oxides

or sulfates 2.97%

100.00%

Theoretical Behavior with Sulfuric Acid.

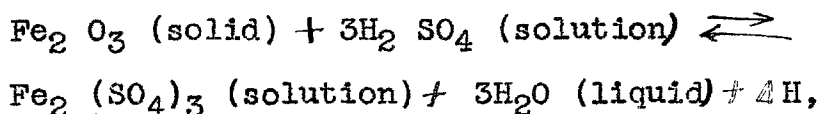
Ferric oxide is "attacked by acids with difficulty, the more so the higher it has been heated. Hydrochloric acid is the best solvent, in which it is more quickly soluble by long digestion at a gentle heat than by boiling. * * * It is most easily soluble in sixteen parts of a mixture of eight parts sulfuric acid and three parts water." (19) This latter is equivalent to 6.3 times the theoretical quantity of 25.4 normal acid. Friend states that nitric acid does not attack the ignited oxide (20).

No direct theremo-chemical data for the solution of ferric oxide in sulfuric acid could be found.

The following values are given by Landolt-Bornstein (21) for the heats of formation of the compounds involved:

$\text{Fe}_2 \text{O}_3$, solid	+195,600. cal.	
$\text{H}_2 \text{SO}_4$ 16.6 H_2O	+208,600	(6-normal)
$\text{Fe}_2 (\text{SO}_4)_3$, solution	+650,500.	
H_2O , liquid	+68,150.	

Therefore in the equation



$\Delta H = -33,550$ cal., and the reaction is exothermic. It would be expected, therefore, that a small increase in temperature although increasing the rate would decrease the solubility. If the temperature is raised above the boiling point of the solution, both the speed of the reaction would increase and the equilibrium would be shifted forward, because water, a product of the reaction, will then be partially removed. If the temperature is increased beyond 317°C ., the pressure remaining at atmospheric, the sulfuric acid completely boils and the reaction stops. Further increase beyond 530°C . reverses the reaction by decomposing the ferric sulfate to ferric oxide (22).

The amount of pyrite ash dissolved by a given solution of acid depends on both the concentration and

the total amount of hydrogen ion available. Since the ionization decreases with increasing acid concentration and since for low concentrations the hydrogen ion is also low, it would seem that there should be a concentration most efficient for dissolving the ash. The greater the amount of acid present the larger should be the percent of the total iron soluble in a given time. The magnitude of these effects cannot be determined theoretically for the concentrated solutions which are to be used but must be ascertained by experiment.

Since the rate of the reaction depends on both the hydrogen and the sulfate ion concentration, it might be expected that it would fall off rapidly as the amount of ferric sulfate increases. Since, moreover, the ionization constant for a concentrated solution is much smaller than for a dilute, a given amount of ferric sulfate in solution in each would cause a greater decrease in the rate in the first case than in the latter.

Solubility Experiments on the Original Material.

All of the experiments reported below were made in one of two ways:

A 2.50 gram sample was weighed out to the nearest 0.01 gram and placed in a thin 6-inch test-tube to which the proper quantity and normality of acid was then added. The test-tube was placed in a 50-cc. boiling flask, nearly filled with concentrated sulfuric acid, and heated over a small flame. The temperature was regulated to the nearest degree using a thermometer, whose bulb was completely immersed in the acid, and so placed that it just touched the outer surface of the test tube. In nearly all cases the solution was stirred by hand, with a glass rod, for about fifteen seconds per minute. (In the two exceptions noted below, the stirring was not possible because, due to either the high temperature or the small quantity of acid added, the mixture caked-up before the end of the run). After the sample had been treated in this manner for times ranging from 15 to 180 minutes, the test-tube was removed, the solution immediately filtered, and the residue thoroughly washed with boiling water. The filtrate was made up to 500-cc. in a volumetric flask and a 50-cc. sample taken for analysis. The permanganate method was used and, for the reasons given above, these

results, which are all underlined when quoted, are to be regarded as somewhat less accurate than those obtained by the other method. The results are, if anything, too high so that the errors, which are perhaps as high as 2% in some cases, do not affect any of the conclusions to be drawn below.

The second procedure used the electrometric dichromate method of analysis described above. The maximum error is perhaps about 1% with the average error much lower. Samples of 1.250 grams were weighed out to the nearest 0.005 gram and placed with the acid in small 50-cc. flat-bottomed flasks. All of the samples were kept at from 15° to 20° C. (normal room temperature), and the stirring effected by shaking the solution about once every three hours in the daytime. The solutions were filtered, washed and the sample taken as described above.

The same amount of acid was added to both the reduced and the unreduced samples where the theoretical quantity specified was the same. (The error in this, based on an analysis of the reduced material, was about 0.1%. The decrease in weight due to the oxygen lost was almost exactly balanced by the weight of the carbon remaining).

All of the results given below are expressed

on the basis of the per cent of the total iron, present at the start, dissolved by the acid treatment.

The effect of the temperature of the acid on the amount dissolved. Samples, treated with 5.6 times the theoretical amount of 35.0 normal sulfuric acid for 15 minutes, showed the following results:

<u>Temperature in ° C.</u>	<u>% Dissolved</u>	<u>Ratio of % to abs. temp.</u>
100°	<u>34.8%</u>	.09
175	<u>67.8</u>	.15
250	<u>71.2</u>	.14

These results show that the amount of the ash dissolved by sulfuric acid is greatly increased by increasing the temperature. For high temperatures it seems to be roughly proportional to the absolute temperature but for lower ones the rate falls off.

The second conclusion is shown more clearly by another experiment. A sample treated with 5.6 times the theoretical amount of 6-normal acid for 15 minutes at 90° C. showed 8.91% dissolved while one treated with 8.4 times the theoretical amount of 6-normal acid for ten days showed only 9.24% dissolved. It will be shown below that the amount of acid used has but little effect on the percentage dissolved so that it may be seen that increasing the temperature from 20° to 90° C. is nearly

equivalent to decreasing the time of treatment from ten days to fifteen minutes.

Two samples were treated with 5.6 times the theoretical amount of 20-normal acid for 15 minutes:

Temperature	% Dissolved
130° C.	<u>72.4%</u>
120° C.	<u>65.4%</u>

In the first case all of the acid boiled away and left a pink colored residue of ferric sulfate and ferric oxide. In the second case the acid did not boil. These results show that the amount of soluble material formed is somewhat increased by allowing the water contained in the acid, or formed during the reaction, to evaporate.

The effect of the concentration of the acid.

Samples were treated with various concentrations of acid at temperatures ranging from 8° to 25° below the boiling point of the acid. The time of treatment was 15 minutes, using 5.6 times the theoretical amount of acid.

Concentration	Temperature of Treatment.	B.P. of Acid.	% Dissolved	Ratio of % to Conc. ²
6 n	95°	106°	<u>8.91%</u>	0.247
10 n	105°	113°	<u>20.4%</u>	0.204
15 n	115°	127°	<u>52.9%</u>	0.235
20 n	120°	150°	<u>65.4%</u>	0.164
35 n	250°	281°	<u>71.2%</u>	0.058

These results represent about the highest temperatures and therefore the maximum solubilities which can be attained without boiling the acid. If the last result be neglected the solubility can be approximately determined by the empirical formula:

$$\% \text{ dissolved} = 0.2 \times (\text{conc. of acid})^2$$

It would have been very interesting to compare the per cent dissolved with the concentration of the acid, the temperature remaining constant, but because of the lack of time this was not possible.

The effect of the amount of acid. The solubility of the ash in 35.0 normal acid at 250° C. for 15 minutes was determined:

Amount of acid.	% Dissolved.
2.8x theoretical	<u>58.2%</u>
5.6x "	<u>71.2%</u>
8.4x "	<u>72.8%</u>

The amount of the acid used is seen to have comparatively little effect on the per cent dissolved. These results are not complete enough to form the basis for any empirical relation but they indicate that the increased yield from large amounts of acid is not large enough to compensate for the increased manufacturing cost.

Effect of changing both the concentration and

the amount of acid, keeping the volume constant. It has been found by previous experiments that the higher the concentration of acid the larger the amount of soluble iron formed per unit weight of pyrite ash. However, the higher the concentration of the sulfate ion the smaller the amount of ferric sulfate which can go into solution. A coating of ferric sulfate may form on the surface of the particles in the more concentrated solutions and protect them against further action by the acid. But increasing the sulfate ion concentration automatically decreases the hydrogen ion concentration. If this decrease is appreciable, as it probably would be in a concentrated solution, it would diminish the rate of the reaction as explained above.

It might be expected, therefore, that the solubility in a concentrated solution at first would be much greater than for a dilute solution. As the reaction proceeds, however, and ferric sulfate is formed and ionized, the reaction in the concentrated solution should slow down, for the two reasons given above. The reaction in a dilute solution, due to the greater ionization constant, (and hence the greater hydrogen ion concentration), would continue at a more uniform rate.

To test this experimentally a series of runs were made at room temperature, extending over a period

of three weeks.

Time in days:	1	3	7	10	14	21
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Acid used:

8.4x theor.of 6-n	4.56%	7.30%	7.41%	9.24%	9.46%	10.70%
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4.2x theor.of 3-n	3.65	3.76	5.69	6.73	8.32	10.60
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1.4x theor.of 1-n	3.99	4.22	4.79	5.59	6.38	7.41
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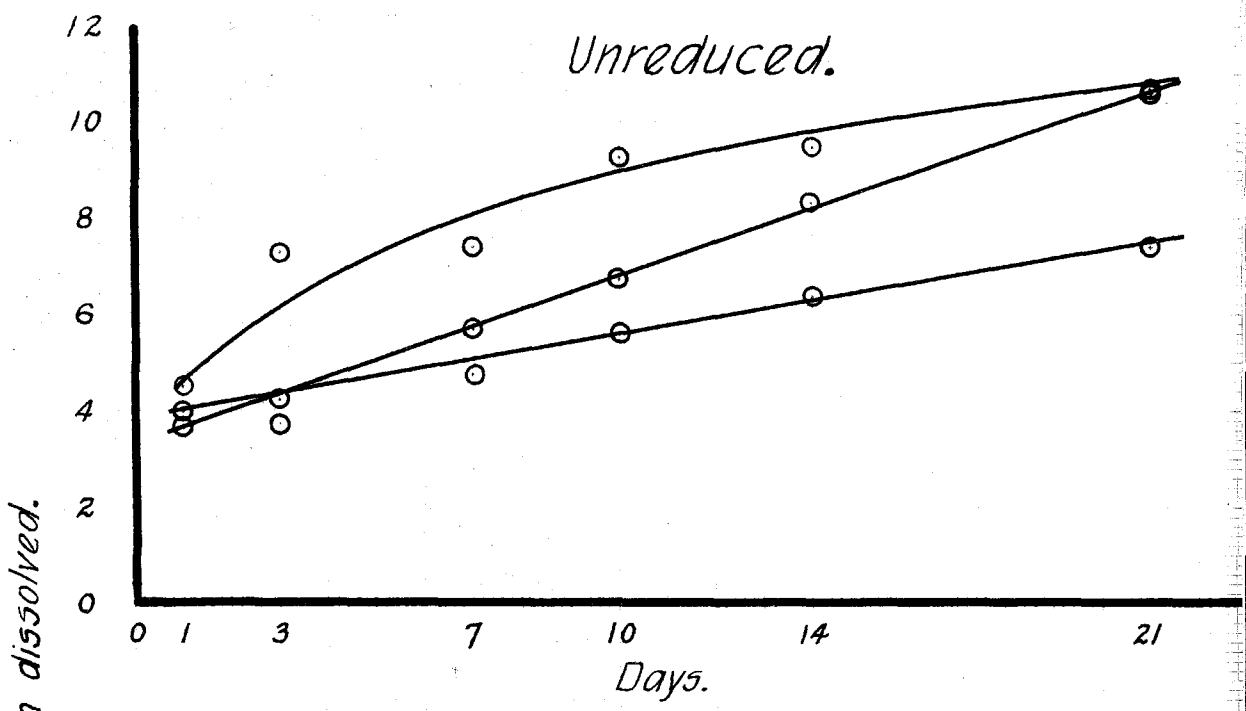
These results which are plotted in Fig. 3, are in accordance with this view. The initial reaction rate in each case (or the slopes when $t = 0$) should be somewhat proportional to the concentration of the acid. This may be seen to be roughly true by an examination of the curves. Afterward, the slope for the 6-normal solution steadily decreases, while the other slopes remain approximately constant, showing that only the ionization constant for the former is sufficiently small to retard the solution.

In general, for a short time of treatment, (up to about one week) a better yield is obtained, at room temperature, by using a large amount of concentrated acid. For times of treatment between one and three weeks, it seems that 3-normal acid is the best to use. In all cases, judging from the curves, it is undesirable to use dilute acid at room temperature.

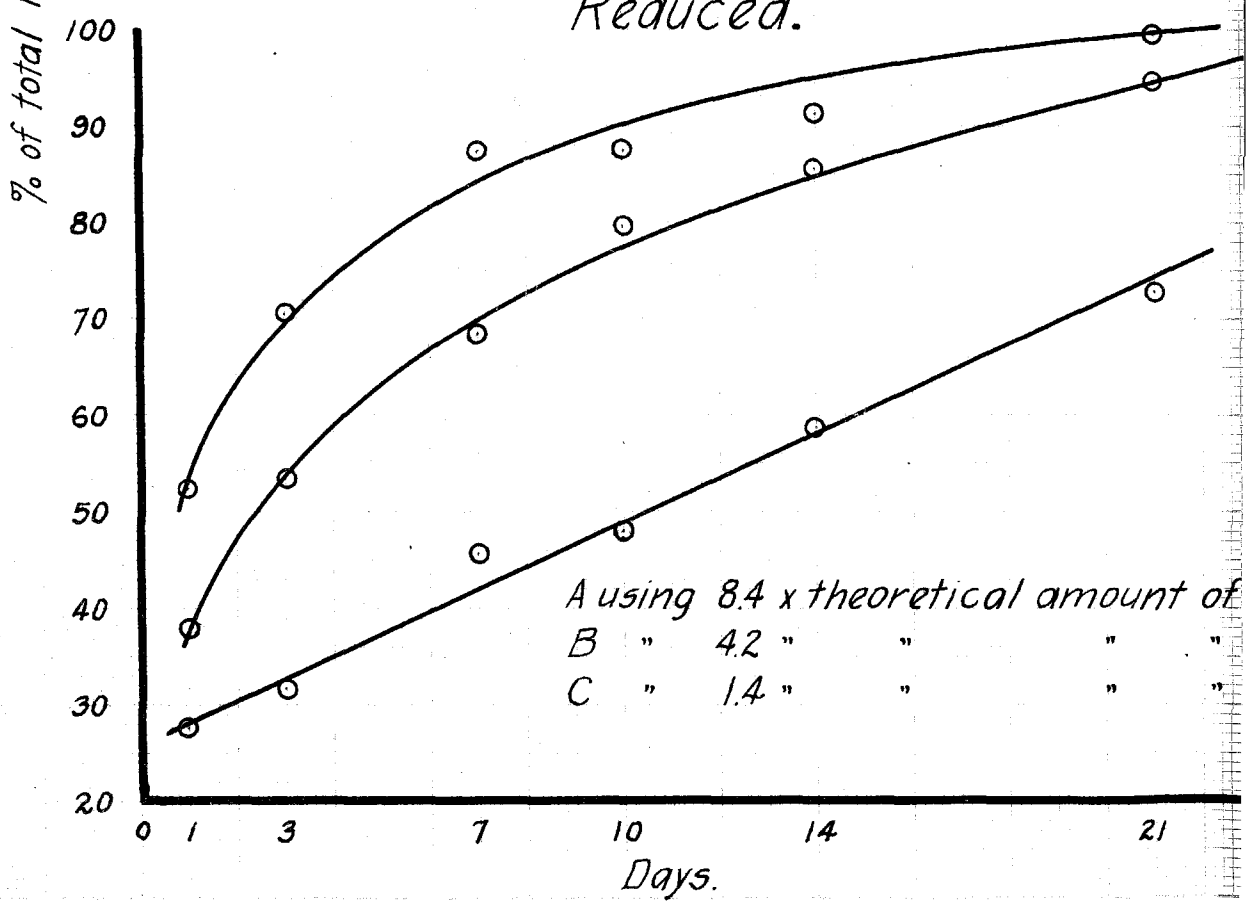
Fig. 3.

Solubility of Pyrite Ash in Sulfuric Acid at 20°C.

Unreduced.



Reduced.



The effect of the time of acid treatment.

For conditions at room temperature this may be shown by the curves from the preceding section. From them it may be seen that if the more concentrated acid is to be used it would perhaps be more economical to treat the ash for two short time intervals than for one long one (assuming that it is not due to a surface effect). For the other conditions of acidity there would be, apparently, no difference.

The results for the 1-normal solution may be expressed by the empirical equation,

$$\% \text{ dissolved} = 3.82 + 0.17 \times \text{time in days.}$$

Although this can only yield approximate results when extrapolated beyond the experimental data, it is probable that the time for complete solution, so calculated, will be the minimum value. This is found to be 566 days.

The similar equation for the 3-normal solution is

$\% \text{ dissolved} = 3.25 + 0.35 \times \text{time in days,}$
which gives 276 days as the time for complete solution.

The results for the 6-normal solution are not sufficient to form the basis for either an empirical equation or an estimate of the time for total solution.

A set of experiments carried out with 5.6 times

the theoretical quantity of 35.0 normal acid at 250° C. gave the following results:

Time of treatment.	% Dissolved.
5 minutes	<u>68.9%</u>
15 "	<u>71.2%</u>
30 "	<u>71.8%</u>

These results also show that the reaction rate decreases markedly with the time, just as noticed above. It is probably due to the small ionization constant of the acid and the high sulfate ion concentration.

Summary. The above experiments on the solubility of the original material in sulfuric acid show, that in order to obtain any appreciable solution it is necessary to use fairly concentrated acid, (20-normal or above), at a temperature close to its boiling point. There is no benefit to be derived from treating the acid for a long time at this temperature, in fact it would seem better to treat it for two shorter time intervals with fresh portions of acid. The total quantity of acid need not be high, probably not over the theoretical amount.

Solubility of the Reduced Material.

The effect of the reduction. Since the solution of the original material in sulfuric acid was found so difficult, a few preliminary experiments were made to determine whether the solubility could be increased by first reducing the material to either magnetic oxide, ferrous oxide, or iron, by heating with finely powdered wood charcoal as suggested by the Pezzolato process.

The results quoted below are grouped in sets, in each of which, usually, all of the experimental conditions, except one, are kept uniform. Any change in the solubility of the ash will, therefore, be due to the effect of this variable. To avoid unnecessary repetition, these experimental conditions and results are collected in Table II, to which frequent reference will be made.

By comparing runs 14 and 15, it is seen that, where the subsequent acid treatment is for 17 hours at room temperature, reducing the ash increases the amount dissolved from 5.95% to 36.3%. By comparing 11 with 17 it is seen that, where the acid treatment is at 105° C. for one hour, reduction increases the solubility from 44.4% to 95.8%. These results show that the solubility is markedly increased by first reducing the material.

The effect of the method of reduction was next studied. Both porcelain and iron crucibles heated to a bright red heat by a bunsen burner and a fireclay crucible heated to about 1050° C. in a crucible furnace were used. All of the crucibles had covers of the same material. After the reduction the mixtures were treated with 5.6 times the theoretical amount of 6-normal acid for the time given.

Method.	Time of Reduction.	Time of Acid treatment.	% Dissolved.
18. Iron Crucible	1 hour	1 hour	<u>80.6%</u>
19. Porcelain "	1 hour	1/2 hour	<u>73.8</u>
20. " "	1 hour	2 hours	<u>73.9</u>
23. Fireclay "	1/2 hour	Sample entirely reduced and fused in Crucible.	

It was noticed that the iron crucible had a tendency to scale off during the heating. This was probably the cause of the high result in comparison with the mean of the two values for the porcelain crucible. For this reason those values quoted below which were obtained by reduction in iron crucibles may be regarded as somewhat unreliable. It was seen that although the mixture was heated for only one-half the time in the crucible furnace the reduction was much more complete.

The effect of various reduction mixtures on

the solubility was shown by the following set of experiments:

	Ratio of pyrite ash to carbon.	% Dissolved.
24.	2:1	65.3%
28.	13.5:1	73.4
25.	20:1	62.9
27.	40:1	57.3

The ratio 13.5:1 is the theoretical mixture required to give ferrous oxide and carbon monoxide as the products (regarding the samples as 100% Fe_2O_3). The results show that this is approximately the composition giving the best results under the conditions stated. It could be seen that this reduced material contained some unconsumed charcoal but not in a large amount. The product was a dull black and the reduction to ferrous oxide appeared to be fairly complete.

The low yield for the mixtures with a larger proportion of carbon was undoubtedly due to the incomplete reduction of the material. These samples were very crisp and contained, apparently, but little unconsumed carbon. Each contained a considerable quantity, (estimated at about 5% of the total weight), of a very hard metallic material, either iron or magnetic oxide, present in small particles about $1/32$ " in diameter.

The run made up in the ratio of 2 to 1 yielded a product in which a large amount of unreduced carbon could be seen. The material when cold and pulverized was a dark brownish black showing that the reduction was not entirely complete.

The effect of the time of the reduction was studied with the results given below. For a porcelain crucible at bright red heat:

	Time of reduction.	Color of Product.	% Dissolved
20.	1 hour	black	<u>73.9%</u>
22.	2 hours	reddish-black	<u>13.3%</u>
x.	3 hours	reddish-purple	<u>x x</u>

Since the 1 hour sample was black, the reddish-black color of the two hour sample showed that it had evidently been reduced and later partially reoxidized. The 3 hour sample was not analyzed as it was apparently completely reoxidized to ferric oxide.

Reduction in a fireclay crucible at about 1050° C.:

	Time of Reduction.	% Dissolved.
23 & 29.	1/2 hour	55.4%
26.	1/4 hour	78.9%

The sample for the 1/2 hour treatment was completely fused in the bottom of the crucible. On the

assumption that it was principally metallic iron, an analysis was made on an equivalent weight of cleaned and polished iron wire. It had a diameter of about $1/32$ inch and was cut in pieces about $3/4$ inch long. It is probable that the lower result obtained with it is due to the larger particles used and not wholly to the change in the time of the reduction. Since the iron was quite pure the decreased solubility might also be due to its "passivity."

While the above experiment gives inconclusive results for the relative solubilities it does at least show that the time of the reduction should be less than $1/2$ hour. Additional experiments should have been made at shorter time intervals. However, even if this had been done it would throw no light on the best conditions for large scale operation, for the efficiency of the reduction is so dependent upon the character and the temperature of the furnace that what might be best for a small scale laboratory process would probably not be at all suitable for commercial practice.

The effect of the amount of acid on the solubility of the reduced material is shown by a set of experiments with the following results:

	Amount of acid.	% Dissolved
28.	1.4 times theoretical	73.4%
26.	4.2 " "	78.9%
30.	8.4 " "	52.3%

On this basis, the maximum solubility is obtained with about 4 times the theoretical amount of acid. However, since the amount dissolved by about the theoretical quantity is so little lower, it should be preferred for economy and to prevent the evolution of hydrogen when the ferric sulfate is reduced.

A study of the effect of the concentration of the acid yielded the following results:

	Concentration.	% Dissolved.	%/Concentration.
31.	3-normal	37.9%	12.6
26.	6-normal	78.9%	13.1

It is seen that the per-cent dissolved is greatly increased by increasing the concentration of the acid and that for treatment at room temperatures it is roughly proportional to the concentration. The normality of the acid which may be efficiently used is limited by the volume of the solid material which is to be dissolved. The smallest convenient amount of acid for 1.25 grams of the reduced material is about 5 cc. If only the theoretical amount of acid is to be used, this limits the

concentration to about 6-normal.

The effect of the temperature of the acid treatment is shown rather poorly by the two results following:

	Temperature.	Time of treatment.	% Dissolved.
21.	20° C.	2 hours	72.0%
17.	105° C.	1 hour	95.8%

It is seen that, for 10-normal acid, despite the doubled time of treatment at room temperature, the other at 105° C. dissolves about one-third more.

An increase of the temperature of the treatment with 6-normal acid from 20° to 90° C. is approximately equivalent to increasing the time of the treatment from 1/2 hour to 24 hours as shown by the following data:

	Time of reduction	Temp. of reduction	Time of acid treatment	Temp. of acid	Amt. of acid	% Dissolved
19.	1 hour	red heat	1/2 hour	90°C.	5.6x theoretical	<u>73.8%</u>
24.	1/4 hour	at 1050°C.	24 hours	20°C.	4.2x theoretical	65.3%

It is seen that raising the temperature of the acid greatly accelerates the solution of the pyrite ash, but it should be noted that varying the concentration of the acid changes both the temperature and the time required for a given quantity to dissolve.

The effect of the time of the acid treatment
on the amount dissolved is shown by the following results at 90° C.:

	Time in hours.	% Dissolved.
19.	1/2 hour	<u>73.8%</u>
20.	2 hours	<u>73.9%</u>

This shows that the curve is very flat which is the same effect noticed above in the case of the unreduced material.

For room temperatures the effect of the time of the acid treatment on the amount dissolved is shown by the following table. The reduction mixture ratio was 13.35 to 1 and the time of the reduction 1/4 hour in the crucible furnace.

Time in days:		1	3	7	10	14	21
Acid used:							
8.4 times	theoretical of 6-normal	52.3%	70.3%	87.3%	87.4%	91.2%	99.6%
4.2	" theoretical of 3-normal	37.9	53.3	68.5	79.8	85.4	94.7
1.4	" theoretical of 1-normal	27.7	31.7	45.6	48.0	58.8	72.9

These results which are plotted in Fig. 3, are rather peculiar in that the curves for both the 6- and 3- normal solutions show a decreasing rate with respect to time while that for the 1-normal is constant. This

verifies the assumption used in the previous discussion, that the reaction in a concentrated acid solution slows down as the concentration of the sulfate ion increases because the ionization of the acid is depressed. Apparently the ionization constant of the 3-normal solution is sufficiently small to cause the rate to decrease where the solution is fairly concentrated in ferric sulfate, as in this case, but where the sulfate ion concentration is small, as was the case with the unreduced material, the rate remains uniform. Although these results cannot be directly compared with those quoted immediately above, which were obtained at 90° , yet, a possible reason for the flat portion of the curve occurring at a lower per-cent in the latter case may be due to the fact that, since the reaction is exothermic, the equilibrium is displaced as the temperature rises.

By extrapolation, which may be subject to considerable error, the minimum time necessary for complete solution may be determined in each case:

6-normal	21 days
3-normal	29 days
1-normal	33 days

The effect of changing both the concentration and the amount of the acid is also shown in the above

table. While specific conclusions cannot be drawn it may be seen that in general a large amount of concentrated acid is considerably more efficient for short time intervals than a small quantity of dilute acid. This shows that during the first period, even though the solution of the material may be somewhat retarded by the large sulfate ion concentration the amount the hydrogen ion is increased more than compensates for this.

Since the cause of the retarding of the solution does not seem to be wholly a surface phenomenon, it would apparently be also better in this case to treat the material for two short time intervals rather than for one long one.

Summary. These experiments on the solubility of the reduced material lead to the following conclusions:

1. To secure rapid and complete solution the material must be reduced to the ferrous state.

2. The best reduction mixture for treatment at 1050° C. is one part of carbon to approximately 13 parts by weight of pyrite ash.

3. The time of the reduction giving the best results varies with the method used.

4. The theoretical amount of acid should be used.

5. The concentration should be as high as possible but it cannot be greater than about 6-normal for practical reasons.

6. Raising the temperature greatly increases the initial rate of solution.

7. It is better to heat for two short time intervals rather than one long one.

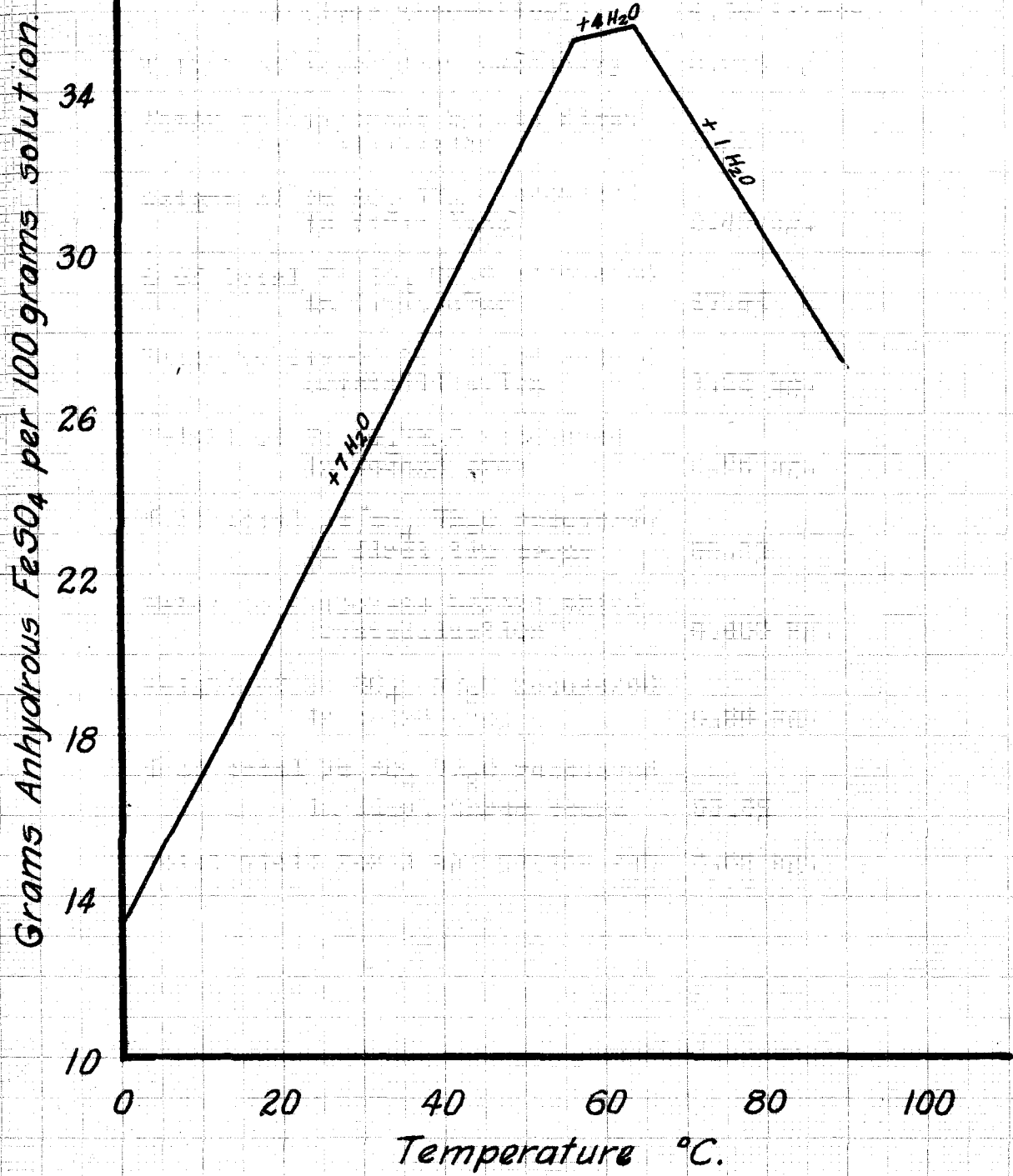
Thermo-Chemistry of the Acid Treatment

The theoretical volume of 6-normal acid required to dissolve 1 kg. of the pyrite ash as ferric sulfate is 4.36 liters. The weight of the resulting solution is 5.635 kg. From above, the heat liberated by the solution of 1 mol. of ferric oxide to ferric sulfate is 33,550 cal. Therefore, assuming the specific heat of the solution as .8, the amount the temperature will raise, if there is no loss by conduction, will be $32^{\circ}5$. The actual heat loss will depend on the physical characteristics of the treating tank and the time of treatment, and cannot be determined until these are known.

Distillation and Crystallization

After all of the iron has been gotten into solution the next step is the reduction of the ferris sulfate to ferrous sulfate by digestion with scrap iron. The solubility of ferrous sulfate in water is shown in Fig. 4. The following results are calculated on the assumption that the solution is evaporated at 55° (the point of maximum solubility) until saturated, and crystallized at 20° C. It is further assumed that all of the dissolved iron is present in the ferric state.

Ferrous Sulfate Solubility Curve.



Initial charge of pyrite ash	1.000 kg.
Volume of 6-normal acid used (1 times theoretical)	4.36 liters
Weight of scrap iron necessary	0.246 kg.
Water to evaporate before first crystallization	<u>None</u>
Weight of $\text{Fe SO}_4 \cdot 7\text{H}_2\text{O}$ recovered in first crop	2.49 kg.
% of total $\text{Fe SO}_4 \cdot 7\text{H}_2\text{O}$ recovered in first crop	67.6%
Water to evaporate before second crystallization	1.25 kg.
Weight of $\text{Fe SO}_4 \cdot 7\text{H}_2\text{O}$ recovered in second crop	0.75 kg.
% of total $\text{Fe SO}_4 \cdot 7\text{H}_2\text{O}$ recovered in first two crops	88.1%
Water to evaporate before third crystallization	0.453 kg.
Weight of $\text{Fe SO}_4 \cdot 7\text{H}_2\text{O}$ recovered in third crop	0.28 kg.
% of total $\text{Fe SO}_4 \cdot 7\text{H}_2\text{O}$ recovered in first three crops	95.6%
Total yield for 1 kg. pyrite ash	3.52 kg.

The heating with an excess of scrap iron, over the theoretical amount recommended above, should occur in an open tank, with the solution at 55° C. The time necessary for the complete conversion must be determined by experiment. As soon as the reduction is complete, the solution should be at once transferred to a crystallizing tank and cooled to 20° C. It may be found necessary to add some excess water to the liquor in the reduction pan to take up the ferrous sulfate which will crystallize out, but this should be avoided if possible.

The subsequent concentrations should occur in a vacuum evaporator.

The crop from the first crystallization should be quite pure but the others, especially the last, may contain small amounts of aluminum and zinc sulfates.

Large Scale Laboratory Crystallization

This portion of the work, while it yielded no important quantitative results, showed that

1. A more efficient vacuum than can be readily obtained commercially is necessary in order to evaporate the solution at 55° C. It was found that toward the end of the concentration the liquor boiled at 75° under a vacuum of 27 inches. However, since the solution con-

tained an unknown amount of free acid during the concentration, not too much reliance should be placed on this result. Landolt-Bornstein (23) quotes results which show that at 46.2° a saturated solution of ferrous sulfate has a vapor pressure only 5.5 mm. lower than pure water at that temperature.

2. It is very advisable to use only the theoretical amount of acid to eliminate the undesirable evolution of hydrogen during the reduction.

3. Experiments should be made on a large scale in order to minimize as far as possible mechanical losses.

4. The recovery of the copper from the excess scrap iron will be difficult because of the small amount present.

5. Further experiments are necessary in order to determine the quality of the product obtained as time was not available to analyze either the crystals or the mother liquor.

Outline of a Suggested Plant Method

A commercial method for the preparation of ferrous sulfate from pyrite ash might be as follows:

The material should be pulverized until approximately 95% passes through a 70 mesh screen. Since none of the pieces are larger than $3/8$ inch in diameter it may be run directly through any of the dry pulverizers of which probably some form of the steel ball mill would be most suitable.

A smaller and intermittently operated mill could be used to pulverize the charcoal. It should be carried to about the same degree of fineness recommended above for the ash.

The charge of the pulverized material and crushed charcoal can be mixed in small bins with a shovel as needed. It should be made up in the proportion of about 7-8 pounds charcoal per 100 pounds of pyrite ash.

Some form of a muffle furnace must be used for the reduction, as the material is so finely ground that if it were exposed to the gases as would be necessary in a reverberatory or kiln furnace, part would be blown away. It would be best to use two furnaces heated by the same fire-box so that while the charge in one is being reduced the other may be emptied and recharged. It would prob-

ably be best to spread the charge only six or eight inches thick but this, as well as the time and temperature of the reduction, must be empirically determined by actual runs with the furnace.

The material should be dissolved in the theoretical amount of 6-normal sulfuric acid at 100° C. The reaction should be complete in about a hour and a half. It would probably not be necessary to stir the mixture more than a few times, although this would depend entirely on the uniformity of the grinding. If there is a large amount of both large and small material it may pack.

A large, hemispherical bottomed, enameled-steel kettle would probably be the best to use. It should be steam jacketed and have no cover. The solution and the undissolved material should be drained off, through a large outlet in the bottom, to a tank on the floor below. The thermal effect attending the reaction has been discussed above.

The settling tank, to which the mixture is transferred from the reaction pan, should be made of wood and lined with sheet lead. After settling the solution is decanted through a Duriron pump and pipeline to a steam-jacketed kettle, similar to the one used

in the preceding step. The residue may be washed once or twice by decantation and then pumped out as waste.

In the second treatment in the open kettle the solution is digested at about 55° C. with an excess of scrap iron. When the reduction is complete the solution is dropped into the crystallizing tanks.

These may be made either of wood lined with lead, monel metal, or enameled steel. Pieces of scrap-iron should be suspended in some manner in the solution. When the crystallization is complete the mother liquor is drained off through a hole in the lower end and sent to the evaporators.

These should be single effect high-vacuum pans. The solution should be completely reduced at this stage but to provide against any possible solution due to reoxidation it would be best to use enameled steel. The solution is evaporated at as near 55° C. as possible. If the boiling point is considerably higher it should be concentrated until the water is just sufficient to form a saturated solution at 55° C. When this is complete, the vacuum is shut off and the solution digested with stirring at that temperature until all of the ferrous sulfate has re-dissolved. It is then crystallized as described above.

The crystals are removed from the crystallizing pan and dried first with a centrifuge and then by stacking in a warm room.

Suggested Future Work.

This work which had for its purpose the determination of a commercial method for the preparation of ferrous sulfate from pyrite ash has been almost entirely confined to a laboratory study of the conditions influencing the solution of the material in sulfuric acid. Because of the lack of time very little work was done on the crystallization of $\text{Fe SO}_4 \cdot 7\text{H}_2\text{O}$ from a given dilute solution of ferric sulfate.

Further experiments should be made to determine the following:

1. The solubility of various materials such as Duriron, monel metal, etc. in solutions of ferric sulfate.
2. The conditions of temperature, pressure, and time for carrying out the concentration.
3. The most efficient method for the conversion of ferric to ferrous sulfate with regard to the amount and kind of scrap-iron, its position in the crystallizing tank, whether or not it is necessary to have

the iron present during the evaporation, etc.

4. The amount crystallized as a function of the time of crystallization.

5. The number of crops of crystals which can be obtained.

6. The purity of the crystals in each crop.

7. The regulation necessary in order to obtain the correct size of crystals.

8. The best method of drying the crystals.

Finally, in order to put the process on a commercial basis it would be necessary to

9. Work out completely on the best data obtainable the approximate manufacturing cost per pound of finished product.

10. Determine the state of the market for ferrous sulfate and compare the selling price with the approximate manufacturing cost.

11. Locate and design a plant specifying the type, material, size and cost of the equipment required.

12. Determine the approximate income on the basis of the invested capital.

Summary

A method has been devised for the preparation of ferrous sulfate from pyrite ash. The material is first reduced by carbon and then treated with the theoretical quantity of 6-normal sulfuric acid at 100° C. The evaporation and crystallization of the resulting solution are discussed theoretically.

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TABLE I.

Summary of Results for
UNREDUCED SAMPLE

Number	1	2	3	4	5	6	7	8	9	10	11	12	13
Time (min.)	15	15	15	15	15	15	15	30	5	15	60	15	15
Temp. ° C.	250	250	250	95	130	175	100	250	250	105	105	115	120
Conc. Acid	35.0n	35.0	6.0	20.0	35.0	35.0	35.0	35.0	35.0	10.0	10.0	15.0	20.0
Amount Acid	2.8xt	5.6	8.4	5.6	5.6	5.6	5.6	5.6	5.6	5.6	5.6	5.6	5.6
Ferrous Fe	<u>10.1%</u>	<u>6.16</u>	<u>4.84</u>	<u>1.37</u>	<u>6.16</u>	<u>9.14</u>	<u>1.55</u>	<u>4.07</u>	<u>4.84</u>	X	X	X	X
Total Fe	<u>58.2%</u>	<u>71.2</u>	<u>72.8</u>	<u>8.91</u>	<u>72.4</u>	<u>67.8</u>	<u>34.8</u>	<u>71.8</u>	<u>68.9</u>	<u>20.4</u>	<u>44.4</u>	<u>52.9</u>	<u>65.4</u>

Days	8.4x6n	4.2x3n	1.4x1n
1	4.56%	3.65%	3.99%
3	7.30	3.76	4.22
7	7.41	5.69	4.79
10	9.24	6.73	5.59
14	9.46	8.32	6.38
21	10.70	10.60	7.41
21 (Ferrous)	<0.34	X	1.03

TABLE II.
Summary of Results for
REDUCED SAMPLE.

Number	14	15	16	17	18	* 19	* 20	21	* 22	** 23	** 24	** 25	** 26	** 27	** 28	** 29
Pyr. Ash	2	2	0.5	2	2	2	2	2	2	13.35	2	20	13.35	40	13.35	Metal- lic Fe
Carbon	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	X
Time Red.	1 hr.	0	1	1	1	1	1	1	2	0.5	0.25	0.25	0.25	0.25	0.25	X
Time Acid Treat.	17 hrs.	17	1	1	1	0.5	2	2	2	Reduced to Metallic Iron		24	24	24	24	24
Temp.	20°C.	20	105	105	90	90	90	20	90			20	20	20	20	20
Conc. Acid	6 n	3	10	10	6	6	6	10	6			6	6	6	6	6
Amt. Acid	2.8xt	2.8	5.6	5.6	5.6	5.6	5.6	5.6	5.6			4.2	4.2	4.2	4.2	1.4 4.2
Ferrous Fe	X	X	<u>77.8</u>	X	X	X	X	X	<u>11.7</u>			X	X	X	X	X
Total Fe	<u>36.3%</u>	<u>5.95</u>	<u>86.9</u>	<u>95.8</u>	<u>80.6</u>	<u>73.8</u>	<u>73.9</u>	<u>72.0</u>	<u>13.3</u>			65.3	62.9	78.9	57.3	73.4 55.4

* Porcelain crucible used in the reduction.

** Fire-clay " " " " "

TABLE II. (Cont.)

Reduction Ratio of 13.35 to 1:

Days	8.4x6n	4.2x3n	1.4x1n
1	52.3%	37.9%	27.7%
3	70.3	53.3	31.7
7	87.3	68.5	45.6
10	87.4	79.8	48.0
14	91.2	85.4	58.8
21	99.6	94.7	72.9
21 (Ferrous)	59.1	44.4	36.8

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