Using Iron Ores of Kalabagh. II. Production of Limonite-Acid Method

By M. I. ALI*

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Earlier work[1] done in this laboratory on limonite production from local iron oxide ore by alkali method was technically disadvantageous. In view of those results, some other suitable process was looked for. Next attempt was made to utilize acid method. Several acid methods covered under patents acclaimed satisfactory results. A brief review is given below:

A mixture of ferrous and ferric sulfate and chloride on heating produced iron oxide[2] and liberated chlorine which was recycled for production of further chloride.

The oxidation of ferrous sulfate was carried out by passing oxygen or air through the hot solution in presence of zinc or magnesium oxide[3]. Sometimes iron shaving were added and oxidation was carried out under pressure (5 atm.) at 120°C[4].

Another cyclic process[5] utilized iodine as attacking agent to produce iodide which on oxidation liberated free iodine for reuse.

Thermal decomposition of nitrate, oxalate and carbonyls of iron, etc. constituted another method of limonite production[6].

One patent[7] has been claimed the production of limonite and free chlorine by decomposing iron chloride at 1000°C. Chloride was produced by using hydrogen chloride and chorine.

Recently, U. C. B.[7] tried to produce limonite from oxide ores of iron. The ore was first reduced to ferrous oxide (FeO) by using process gas $(CO+H_2=56.0\%)$ at 700°C. Ferrous oxide was treated with chlorine or hydrochloric acid to obtain ferric oxide and chloride. This on treating with ammonia yielded hydrated ferric oxide (and ferric hydroxide) i. e. limonite.

Another method[9] described the production of iron sulfate by heating soluble iron salt with ammonium sulfate. This iron sulfate was treated with ammonia in oxidizing medium to obtain hydrated ferric oxide. Ammonium sulfate was being recovered as alum by treating it with bauxite.

None of the above methods was found to suit the purpose. Finally, the use of locally produced dilute sulfuric acid was tried to produce iron sulfate from limonite ore. This proved satisfactory (presenteted in A). Iron sulfate was then treated with ammonia to obtain ferric hydroxide (and hydrated oxide) and ammonium sulfate (in solution). Ferric hydroxide was dried and blended to proper consistency while ammonium sulfate solution was suggested to be sent to sulfatation plant.

Disposal of spent limonite was another problem. Sulfuric acid manufacturing facilities in the country either use elementary sulfur or hydrogen sufide gas. So, the spent material cannot be disposed there. On the other hand, the standard methods of washing out sulfur from spent limonite leaving revivified material ready for further use, could not be practised due to non-availability of cheap solvent. The production of limonite by sulfuric acid method opened up the idea of recovering both limonite and sulfur simultaneously from spent material by following the same procedure. This is presented in B.

A) Production of Limonite from Iron Oxide Ore

(Using Sulfuric Acid)

Considering the scopes and limitations of the above-mentioned methods, none of them was found suitable for the purpose. The use of corrosive chemicals like chlorine, nitric acid and hydrochloric acid, etc. were not desired. The non-availability of the required chemicals in the country was another vital consideration. Finally, it was thought that locally produced sulfuric acid (60° Bé) could be tried for the production of ferric sulfate. This could easily be converted into ferric hydroxide by the action of ammonia. Recovery of by-product ammonium sulfate was also thought to be

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* Present address: Natural Gas Fertilizer Factory, Fenchuganj, Sylhet, East Pakistan.

1) M. I. Ali, This Bulletin, **35**, 878 (1962).
2) C. Podberg., German Pat. 568239 (1931).
3) J. W. Ayers and G. Plews, U. S. Pat. 2255607 (1941).
4) I. Riskin and G. Pugacheva, *J. Appl. Chem.* (*U. S. S. R.*), **11**, 25 (1934).
5) L. G. Grindin and M. V. Pavlova, *Zhur. Priklad Khim.*, **24**, 1151 (1951).
6) Vereinigte Stahlwerke A. G., German Pat. 581657 (1933).
7) U. E. Bowes, U. S. Pat. 2291206 (1946).
8) Union Chimique Belge (Belgium), private communication (1957).
9) V. Parishat, *Indian.*, **42**, 281 (1951).

feasible. The reactions involved were likely to be as follows:

$$Fe_2O_3+3H_2SO_4 \rightarrow Fe_2(SO_4)_3+3H_2O \quad (1)$$

$$Fe_2(SO_4)_3+6NH_4OH \rightarrow 2Fe(OH)_3+3(NH_4)_2SO_4 \quad (2)$$

$$2Fe(OH)_3 \rightarrow Fe_2O_3(H_2O)_x \quad \text{(Partly)} \quad (3)$$

Experimental

A suitable variety of limonite ore was procured from Kalabagh iron mines. The sample was crushed and grinded to 100 mesh (French series) and analyzed[1]. Some exploratory experiments were carried out to ascertain the possibility of the reaction 1 under varied conditions of acid concentration, temperature and reaction time.

The general procedure of the experiments were as follows: 10.0 g. sample was taken in a beaker with requisite quantity of sulfuric acid and it was heated slowly to boiling. This condition was maintained for a desired length of time which was termed "reaction time". On completion of the reaction the whole mass was treated with water, allowed to settle and filtered. After filtration, the filtrate was analyzed for iron content. The results were expressed in percentage (reaction %) on the basis of total iron contents of the sample ore.

The first set of experiments was carried out with varried concentrations of acid. In this case, 40 ml. of sulfuric acid at different concentrations was used. The results are tabulated below in Table I (Fig. 1, curve I)

TABLE I. EFFECT OF SULFURIC ACID CONCENTRATIONS ON THE SAMPLE ORE

Sample, 10.0 g. Sulfuric acid, 40 ml.
Reaction time, 10 min.

Acid. concn. % (by wt.)	Reaction %	Remark (product after reaction)
15.0	9.2	Turbid liquor
30.0	20.0	Turbid liquor
50.0	39.5	Muddy liquor
60.0	51.2	Muddy liquor
70.0	68.0	Thin paste
80.0	68.5	Paste
97.0	70.0	Thick paste

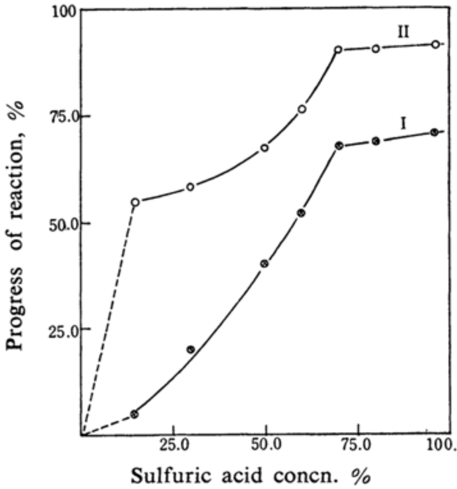

Fig. 1. Progress of reaction with acid concentration.
I, Reaction with ore sample
II, Reaction with spent limonite

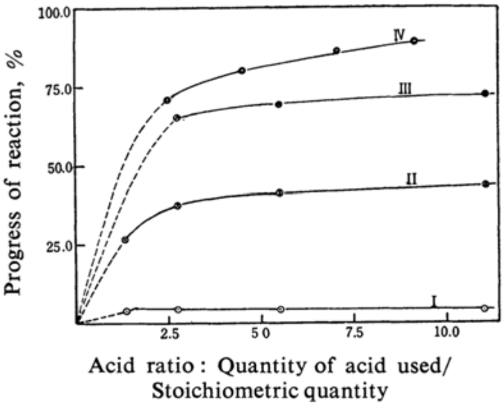

Fig. 2. Progress of reaction with different acid ratio.
I, Reaction with ore sample at 25°C
II, Reaction with ore sample at 98°C
III, Reaction with ore sample at 160~170°C
IV, Reaction with spent limonite at 150~160°C

TABLE II. EFFECT OF TEMPERATURE, REACTION TIME AND ACID/MASS RATIO ON THE PROGRESS OF REACTION 1

Sample taken, 10.0 g. Sulfuric acid concn., 70.0%

Quantity. of acid, ml.	Acid/mass ratio, w/w	Acid ratio (Quantity used / Stoichiometric quantity)	Reaction (%) at room temp. (25°C) for 30 min.	Reaction % at 98°C		Reaction (%) at boiling temp. 160~170°C	
				30 min.	60 min.	10 min.	30 min
13.3	2.12	1.44	4.6	26.0	—	—	—
25.0	4.00	2.70	4.8	38.0	—	65.5	—
50.0	8.07	5.45	5.0	41.0	—	70.0	—
100.0	16.14	10.95	5.0	44.0	66.0	73.5	71.5

Remarks: The reactions at boiling temperature produced a dry pasty mass. So, lengthy reaction time was not possible.

From the above observation 70.0% acid was chosen for further experiments. This time the temperature and reaction time were changed. The results are presented in Table II.

The above results are shown in Fig. 2 (curves I, II and III). It was clear that sulfuric acid needed was much higher than the stoichiometric quantity. The recovery of sulfuric acid as ammonium sulfate was imperative. Some of the experiments were carried out with 1.0 kg. charges each and those were carefully observed to ascertain the prospect of utilizing the method on semi-pilot plant scale. The following observations made thereof are discussed hereunder briefly:

a) **Formation of Ferric Oxide Hydrate.**—On dilution after sulfuric acid digestion, a fluffy brown precipitate found to remain suspended in the liquid while the undigested material settled at the bottom. This was found to be as active as ferric hydroxide towards hydrogen sulfide and was assumed to be ferric oxide hydrate. It was about 5.0% (as Fe) of the total iron. This was, of course, an addition to the overall yield of limonite.

b) **Decantation and Transfer of Ferric Oxide Hydrate.**—It was possible to separate undigested mass from the rest (Fe in solution and suspended hydrate) by decantation. Ferric oxide hydrate settled only on long standing. Residue was rejected generally.

c) **Ammonia (20∼25%) Treatment and Filtration.**—Ammonia directly from the purge tank of the ammonia section was used for the purpose. Gelatinous iron hydroxide precipitate was formed, the filtration of which was rather difficult. It was improved to some extent by boiling the whole mass with pulp (or saw dust). Though saw-dust was useful, it could not be recommended due to its resin content, which was apprehended to cause trouble in the evaporator. This warrants further investigation.

d) **Drying and Final Removal of Ammonium Sulfate from Residue.**—Hot air at about 100°C was passed over the residue after filtration c) till it was half dried. At this stage, the limonite lost its gelatinous character. It was then washed with water to remove ammonium sulfate. The resultant material was dried under shade at a temperature below 50°C by occasional turning.

e) **Analytical Results.**—Alkaline ammonium sulfate filtrate was analyzed. This was compared with the analysis of ammonium sulfate solution in the neutralization tank of "ammonium sulfate" plant. The results obtained are as follows (Table III):

TABLE III. ANALYSIS OF AMMONIUM SULFATE SOLUTIONS: (1) AFTER FERRIC HYDROXIDE FILTRATION AND (2) SOLUTION FROM NEUTRALIZATION TANK

Ingredient	Ammonium sulfate solution	
	After Fe-hydroxide filtration	From neutralization tank
Acidity (H_2SO_4)	—	0.05 g./l.
NH_3 (free)	1.8 g./l.	—
$(NH_4)_2SO_4$	448.0 g./l.	485.0 g./l.
Fe	0.08 mg./l.	0.3 mg./l.
Ca	20.0 mg./l.	540.0 mg./l.
Cl	nil	17.7 mg./l.

f) **Recovery of Different Materials.**—1) Loss of iron ores …… about 40% (silicous material over 50.0%). 2) Recovery of sulfuric acid …… 90∼95.0% as free acid and Fe-sulfate. 3) Recovery of ammonia as ammonium sulfate and free ammonia, a) 1st stage filtration …… 80∼83.0%; b) 2nd stage washing out …… 10∼12%.

As a matter of fact, these obesrvations stimulated further investigation to find out some more easily digestible material. In this case, high temperature produced better results but it is feared that the corrosion problem will arise in operating at an elevated temperature. Further one sample of "siderite" (available plenty) was found to be more easily digestible. The nature of reaction was more or less similar to that of oxide ore, the yield was high and could be operated at low temperature.

B) Recovery of Spent Limonite and Sulfur (Using Sulfuric Acid)

The spent limonite containing about 50.0% sulfur could not be utilized for the manufacture of sulfuric acid in the country because of the existing plants are based on either elementary sulfur or hydrogen sulfide. The use of carbon disulfide for sulfur extraction in situ was not practicable due to non-availability of cheap solvent. Its economic disposal was a problem. About 100 tons of sulfur could be recovered every year from the spent limonite. The observations made on limonite production by acid method led to the interesting idea of recovering both limonite and sulfur simultaneously. The reactions involve in limonite purifying process may be represented through a cyclic scheme comprising oxide-sulfide-oxide reactions as follow:

$$Fe_2O_3(H_2O)_x + 3H_2S \rightarrow Fe_2S_3(H_2O)_x + 3H_2O \quad \cdots\cdots \text{(Absorption)} \qquad (4)$$

$$2Fe_2S_3(H_2O)_x + 3O_2 \rightarrow 2Fe_2O_3(H_2O)_x + 6S \quad \cdots\cdots \text{(Regeneration)} \qquad (5)$$

Non-regenerative FeS_2 and Fe_8S_9 was also reported to form at elevated temperature.

However, sulfuric acid was considered to be useful for the recovery of sulfur. The experimental procedure adopted was more or less the same as with the iron ores. The first step reaction with regenerated material was:

$$[Fe_2O_3(H_2O)_x + S] + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + H_2O + S \qquad (6)$$

Experimental

The technical analysis of the raw material (spent limonite) was as follows (Table IV):

TABLE IV. ANALYSIS OF SPENT LIMONITE

Constituent	%
Acidity	Neutral
Humidity	26.9
Ash content	37.4
Iron (Fe)	23.8
Sulfur	
a) As sulfate	2.2
b) Elem. sulfur	45.8
Specific weight	
a) Loose packing	680 g./l.
b) Close packing	900 g./l.

The spent limonite was found to be more reactive with sulfuric acid than the oxide ores. One series of experiments was carried out using different concentrations of acid. The results are presented in Table V and in Fig. 1 (curve II). One sample of unregenerated sample was also tried for the purpose.

From the above results, 70.0% acid was found to be most suitable for the reaction. Another set of experiments was carried out with this acid to ascertain the optimum quantity. Those results are shown in Table VI and also by Fig. 2 (curve IV).

From the above Tables V and VI, 40 ml. sulfuric acid (70%) was found to be the requisite quantity for 10.0 g. spent limonite. Some experiments were also carried out with 5.0 kg. sample. The results were found satisfactory. The similar difficulties of iron hydroxide filtration as with the oxide ores were also encountered here. The advantages in this case were that the reaction temperature was lower while the progress was better. The over-all recovery of limonite was 80.0% by this method (considering the loss during processing).

Recovery of Sulfur.—The residue obtained after digestion of spent limonite with sulfuric acid contained mainly sulfur, iron oxide and little organic matters. The approximate compositions was found to be:

Sulfur	75.0%
Iron oxide	20.0%
Others	5.0%

TABLE V. EFFECT OF SULFURIC ACID CONCENTRATION ON THE PROGRESS OF REACTION WITH THE SPENT LIMONITE

Sample taken, 10.0 g. Quantity of acid used, 40 ml.
Time of reaction, 10 min. Water added for dilution, 100 ml.

Concn. of sulfuric acid, % (by wt.)	Acid ratio $\left(\frac{\text{Quantity used}}{\text{Stoichiometric quantity}}\right)$	Observed temp., °C before diln.	Observed temp., °C after diln.	Reaction, %	Remark
15.0	1.06	No remarkable rise of temperature		53.9	—
30.0	2.34	—		58.0	Muddy liquid
50.0	4.47	40	35	68.5	Slurry
60.0	5.75	50	45	76.5	Thin paste
70.0	7.22	65	50	89.0	Thin paste
80.0	8.9	70	60	89.5	Thick paste
97.0	11.4	75	90	90.0	Pasted and charred
70.0†	7.22	65	65	83.5	Thin paste
70.0	7.22	60	55	79.5	Thin paste The sample was not regenerated.

† 100 ml. water was used for dilution in two portions of 50 ml. each.

TABLE VI. EFFECT OF QUANTITY OF ACID ON THE PROGRESS OF REACTION

Sample taken, 10.0 g. Concn. of acid used, 70.0%
Reaction time, 10 min. Water used for dilution, 100 ml.
Temperature, to boiling

Quantity of acid used ml.	Acid ratio $\left(\frac{\text{Quantity used}}{\text{Stoichiometric quantity}}\right)$	Reaction, %	Remarks on reaction product before dilution	Remarks on reaction product after dilution
14.0	2.52	71.0	Paste	Easily decantable (sp. gr. 1.05)
25.0	4.5	79.5	Paste	Easily decantable
40.0	7.2	87.2	Thin paste	Easily decantable
50.0	9.0	89.0	Pasty liquor	Decantable
100.0	18.0	90.0	Muddy	Decantable with time (sp. gr. 1.19)

The impure sulfur thus recovered was purified to about 90.0% by melting out process. For further purification any standard method could be adopted.

In view of the above observations, it appears fairly agreeable to operate such plant. It is, of course, not free from difficulties. The main difficulty with this method that it is a lengthy process. It is always difficult to realise movement of such type of materials through the process equipments. However, it may be concluded that 80.0% of the spent limonite can be recovered by this method. The rest 20.0% make up limonite may be supplemented by producing it from local iron ores preferably "siderite".

Summary

A method of limonite production has been developed in this laboratory and it was produced from both "Kalabagh iron ores" and "spent limonite" by using local sulfuric acid (60° Bé). Ammonium sulfate, by-product, was also recovered. The process comprised of (i) digestion of the raw materials with 70.0% sulfuric acid, (ii) ammonia treatment of the resultant ferric sulfate solution to produce ferric hydroxide and (iii) careful drying and blending of ferric hydroxide (and oxide) to the desired consistency. The over-all recovery of spent limonite was found to be 80.0%. A material balance sheet is also presented. For the production of 20.0% make-up limonite "siderite" iron ore is suggested to be of use.

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Pak-American Fertilizer Factory
Daudkhel, West Pakistan

Appendix

Flow Diagram: The material balance of the limonite production (by sulfuric acid method) could be shown by following flow diagram (1.0 kg. iron oxide ore basis).

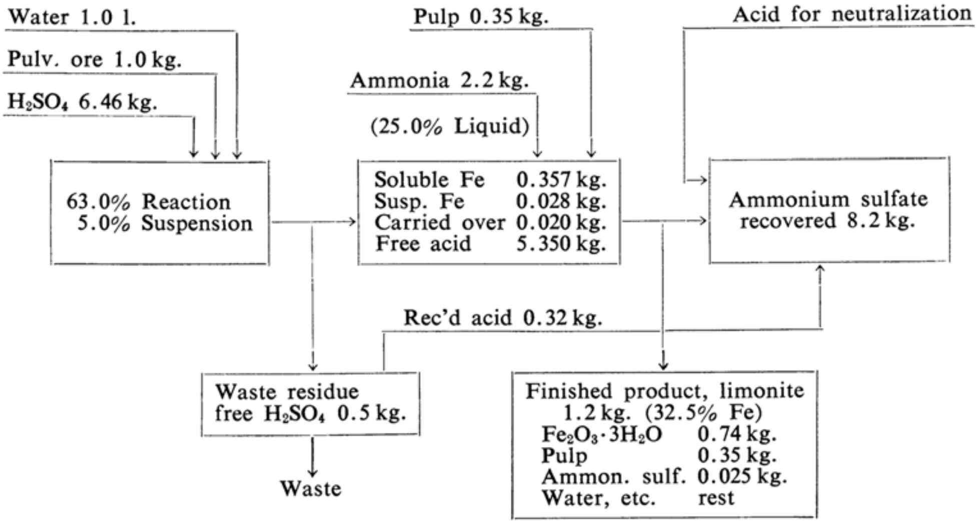

Fig. 3. Material flow diagram of limonite production (acid method).