Using Iron Ores of Kalabagh. I. Production of Limonite-Alkali Method

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The ammonium sulfate plant at Daudkhel based on pressure gasification of local coal containing sulfur of about 5.0% faced the problem of hydrogen sulfide removal from the process gas. After much deliberation a method of preferential water-washing under pressure (about 15.0 kg./cm^2) has been adopted to effect the removal of hydrogen sulfide along with some carbon dioxide. The efficiency of water-washing-out process ranges between 92.0 and 96.0% and this quantity of hydrogen sulfide is being utilized for the manufacture of sulfuric acid, 60° Bé (20.0 tons/day on 100.0% basis). The remaining 4.0~8.0% hydrogen sulfide constitute 0.1~0.2% of the process gas which is being removed by limonite in the boxes before and after CO-conversion. During normal run of the factory about 7600 Nm^3 gas per hour is being purified which requires about 600 kg. limonite per day. This calculation is based on 0.1% hydrogen sulfide in the gas and absorption efficiency nearly to maximum. Due consideration was also given to the fact that the spent limonite can be regenerated by air oxidation and used over again until sulfur content reaches over 40.0% in the limonite mass. In practice, the consumption will be slightly more than the mentioned quantity. At present imported limonite from European countries especially Holland and Denmark are in use in the factory at an approximate cost of about U. S. $ 45.00 per 1000 kg. In view of this recurring expenditure, it was felt necessary to exploit our own resources by suitable processing, if possible.

The first attempt was made in this regard to assess the availability of naturally occurring limonite in the country. One report⁽¹⁾ shows that the Yellow Ochre of Khewra has 71.6% hydrogen sulfide absorption capacity at maximum pH with respect to ferric hydroxide but other samples are limited within 40.0%. Further informations are lacking. The observations made in some explanatory experiments with oxide ores of Kalabagh, led to look for a method of processing the material to suit the purpose. From a study of available methods of limonite production, alkali method was chosen to be tried. A short review is presented below:

The general alkali methods⁽²⁾ described as the fusion of iron ores (FeS, FeS_2, Fe_2S_3 and oxides, etc.) with sodium carbonate or hydroxide⁽³⁾ to produce ferrite first then its hydrolysis to yield hydrated ferric oxide.

The thermal activation of iron oxide by fuller's earth in conjunction with sodium carbonate has also been recognized⁽⁴⁾.

Some other methods recommended the use of ammonia or alcohol⁽⁵⁾, steam⁽⁶⁾, lime, sodium carbonate⁽¹⁾, etc. on ferric chloride or some other iron salts.

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[*] Present adress: Natural Gas Fertilizer Factory, Fenchuganj, Sylhet, East Pakistan.

1) S. A. H. Jafri, M. Se, Thesis, Punjab University (W. Pakistan) (1956).
2) D. E. Redford, *Natural Gas Bull.*, **11**, No. 5, 13 (1947).
3) Gilbert and Fr. Seil, 776, 903 (1935).
4) R. G. Capall and R. C. Amero, U. S. Pat. 2433426 (1947).
5) Yu A. Klyachke et al., *Zavodskaya Lab.*, **13**, 901 (1947).
6) L. Reeves and Geofrey, Brit. Pat. 677645, 677690 (1952).

One patent[7] claims the use of 25~30% soda lye at 200°C for preparing desulfurizing material using " Boue Rouge " (Bayer process) in aluminum industry.

Another method[8] describes the use of ferric oxide residue from bauxite. Sodium carbonate was reacted upon to form sodium ferrate (Na_2FeO_4) which on subsequent hydrolysis produced hydrated oxide of iron.

Another patent[9] of Metallgesellschaft used the residual mud known as " Lux " or " Lauta " of aluminum industry and also the hydrates of iron in conjunction with 5.0% alkali for desulfurization of gas.

In view of the above facts it was thought to produce the small quantity of limonite to meet the demand in this factory from local iron ore of Kalabagh by alkali method. Sodium hydroxide was considered to be suitable reagent for its possible use on recovery either in carbon dioxide removal plant of this factory or in the proposed soda-ash factory.

Experimental

There are several iron mines of different types of ores in this locality. The iron content of these ores varies within a wide range of 30.0~65.0%. The availability of high grade ore cannot be guaranteed. However, a better quality ore was selected for this purpose to avoid pretreatment and interference of gangue materials during processing. This sample was found to contain 56.5% Fe. A tentative analysis of the sample is given below:

Fe	56.5% (0.6% Fe^{2+})
SiO_2	5.0%
Al_2O_3	1.5%
CaO	2.2%
MgO	0.58%
S	0.32%

The underlying principle of this method was to heat an appropriate mixture of iron oxide ore and sodium hydroxide to produce sodium ferrite and hydrolyze in the subsequent step to obtain hydrated iron oxide along with the recovery of sodium hydroxide used. Alkali used for this purpose was of a commercial grade containing about 96.8% sodium hydroxide and over 2.0% sodium carbonate.

Preparation of Sodium Ferrite.—A known quantity (10 g.) of powdered and sieved (through a sieve of No. 100 French series) sample of iron ore was taken in a stainless steel tank (10×10×2 cm.) with 40.0% solution of sodium hydroxide, having 10.0% excess of the calculated quantity. The whole mass was mixed thoroughly, evaporated to dryness and heated at 200~225°C at least for 3 hr. to complete the reaction:

$$Fe_2O_3+2NaOH \longrightarrow Fe_2O_3,\ Na_2O+H_2O \qquad (1)$$

The reaction proceeded well to completion and resulted a hard mass adhering to the reacting vessel.

Preparation of Limonite.—The mass of sodium ferrite as prepared above was taken out of the vessel, grinded and sieved. The powdered mass (sometimes without crushing) was taken into a beaker, treated with water heated for one hour to effect hydrolysis according to the reaction:

$$Fe_2O_3\cdot Na_2O+H_2O \longrightarrow 2Fe(OH)_3+2NaOH \qquad (2)$$

On settling, the mixture was filtered on a Büchner funnel. The filtrate was the mixture of sodium hydroxide and sodium carbonate (in some cases sodium bicarbonate depending upon the mode of operation). The residue was ferric hydroxide with certain quantity of residual alkali. The mass obtained thus was blended with saw dust (wood shavings or pulp) for proper consistency, humidity (about 30.0%) and bulk density (approx. 0.8). This was then tested for its hydrogen sulfide absorption power* which was found comparable to the imported mass.

Results and Discussion

The progress of the above reactions was found satisfactory for the production of limonite but certain practical difficulties stood on the way e. g.:

1. The mass of sodium ferrite was found to stick to the reacting vessel and was difficult to remove it.
2. The hard mass of sodium ferrite was evassive to hydrolysis if not grinded and was much time consuming.
3. Filtration of hydrolysis product was difficult for its higher alkali concentration and slow rate of sedimentation of the hydrated oxide.
4. Recovery of alkali was incomplete.

However, to find out the optimum condition for the whole process, some experiments were carried out under different conditions of mass-alkali ratio, temperature and time of reaction. Active iron in the hydrolyzed product was the measure of yield. In all cases, grinded mass was hydrolyzed in boiling water for one hour. The results of the above experiments are presented in Table I.

From the results it may be concluded that:

1) The most suitable temperature for reaction 1 was from 200 to 225°C (curve 1 in Fig. 1). Next experiments were carried out at this temperature.

2) Heating for longer time over 3 hr. was found to be useless. Curve 2 in Fig. 1 indicates that the progress of reaction upto 3 hr. was steady but beyond this it was very slow.

3) Further, the effect of mass-alkali ratio

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[7] H. J. Zhibon, U. S. Pat. 2432071 (1947).

[8] S. Doldi, *Chemical Industria*, **29**, 140 (1947).

[9] Brit. Pat. 452504 (1943); *Rec. Brev. Belg.*, 871 (1943).

* Activity test is given in Appendix.

TABLE I. PRODUCTION OF LIMONITE UNDER DIFFERENT CONDITIONS

Experiment	Variable		Yield, %	Remark
Fe/NaOH, 1.3 Reaction time, 1 hr.	Temp. °C :	100	48.0	Brown hard mass, easily breakable
		150	70.0	Brown hard mass
		200	82.0	Less brown hard mass
		225	84.5	Less brown hard mass
		250	85.3	Lesser brown harder mass breaks with difficulty
		300	86.0	
Fe/NaOH, 1.3 Temp., 200°C	Reaction time, hr.	2	90.0	Brown hard mass
		3	93.1	Brown hard mass
		3	95.2*	Brown hard mass
		6	94.5	Brown hard mass
		12	94.5	Harder mass
Temp., 225°C Reaction time, 3 hr.	Mass/alkali ratio	1.40	79.5	Brown hard mass
	(Fe/NaOH)	0.90	95.5	Brown hard mass
		0.75	96.0	More brown hard mass

* This experiment was done at 225°C.

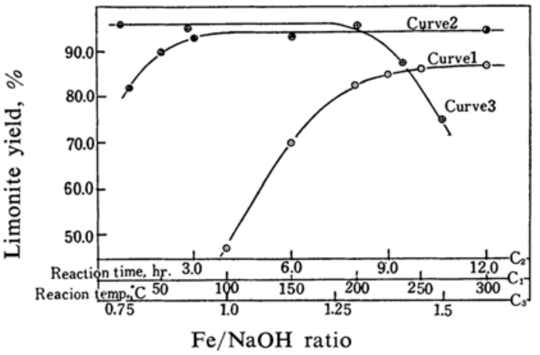

Fig. 1. Yield of limonite under different conditions.
—⊙—⊙— C_1 Temperature-yield
—◬—◬— C_2 Time-yield
—⊕—⊕— C_3 Fe/NaOH ratio-yield

was distinct arround stoichiometric ratio. The reaction at stoichiometric ratio was 79.5% while with 10.0% excess of alkali it was 95.2%. But with more excess the effect was insignificant (curve 3, Fig. 1).

4) Finally, the optimum condition for this reaction was found to be:

a) Alkali: 10.0% excess of stoichiometric ratio.
b) Temperature: 200~225°C.
c) Reaction time: 3~4 hr.

The first difficulty of adherence of mass to the reacting vessel could somehow be eliminated by stirring thoroughly during evaporation to dryness but the process became laborious. The carbonate (sometimes bicarbonate) content in recovered alkali solution was much high in this case.

Since the reaction[1)] was considerably satisfactory, more attention was paid to alkali recovery. To effect maximum alkali recovery without causing deterioration of limonite quality, special stress was given to the hydrolysis under different conditions of temperature and water/mass ratio. Attempt was also made to recover more alkali by passing carbon dioxide in the solution but as it will be seen later, it did not claim any superiority over the others. In all the cases, the recovery reached towards a limiting value upto which it might be economical. However, these results are presented in Tables IIa and IIb.

In view of the difficulties experienced during this work, the macaronies (solid) of 6~10 mm. diameter were prepared from the paste of powdered ore and sodium hydroxide for smooth handling, dried and treated in the same way as those of previous experiments. Some of the results of those experiments are presented in Table III. Some changes in experimental conditions were also tried.

It was interesting to note here that the recovery of alkali as hydroxide was prominent and considerably higher than the recovery with other method tried earlier (cf. Table IIa). This treatment was definitely an improvement over the other in respect of easier handling and slightly better overall recovery (with higher percentage of sodium hydroxide). Limonite quality was more or less the same as prepared otherwise.

Figure 2 presents the curves showing the extent of alkali recovery on hydrolysis of sodium ferrite under different conditions. Curves B, C and D^1 show the influence of

TABLE IIa. RECOVERY OF ALKALI BY HYDROLYSIS OF SODIUM FERRITE

Sample	No. of Washings	Water/mass ratio	Recovery of alkali expressed as Na %				Remark
			NaOH	$NaHCO_3$	Na_2CO_3	Total	
A	1	14	27.9	—	22.7	50.6	Hydrolysis of ferrite at room temperature, 35°C (without grinding)
	2	10	13.0	—	10.4	23.4	
B	1	8	29.0	—	28.8	58.0	Hydrolysis carried out at 85°C after grinding
	2	8	7.6	—	7.3	14.9	
	3	8	2.0	—	1.4	3.4	
	4	8	1.1	—	0.8	1.9	
C	1	8	32.2	—	30.7	62.9	Hydrolysis carried out at 100°C after grinding
	2	8	5.5	—	4.6	10.1	
	3	8	1.7	—	1.4	3.1	
D	1	8	29.4	—	20.9	50.3	First step hydrolysis at room temperature and subsequent washing after passing CO_2 in it (at room temperature) after grinding.
	2	8	—	4.5	13.9	18.4	
	3	8	—	6.18	1.35	7.53	
	4	8	—	3.1	0.38	3.48	

TABLE IIb. EXTENT OF ALKALI RECOVERY WITH VARIED WATER/MASS RATIOS

Water/mass ratio	Recovery of alkali (Na %)				Remark
	A	B	C	D	
8	—	58.0	62.9	50.3	A, B, C and D represent the A, B, C and D of Table IIa respectively.
14	50.6	—	—	—	
16	—	72.9	73.0	68.7	
24	74.0	76.3	76.1	76.23	
32	—	78.2	—	79.71	

TABLE III. RECOVERY OF ALKALI BY HYDROLYSIS OF SODIUM FERRITE MACARONIES (SOLID)

Experiment	No. of washing	water/mass ratio	Recovery of alkali (Na %)			Remark
			NaOH	Na_2CO_3	Total	
1. Ferrite reaction at 200°C for 24 hr.	1	5	47.5	23.2	70.7	These expts. were carried out according to methods D in Table IIa without CO_2. These are represented by curve E in Fig. 2.
	2	5	3.6	5.9	9.5	
	3	5	1.9	1.5	3.4	
		15	53.0	30.6	83.6	
2. Ferrite reaction at 225°C for 24 hr.	1	5	50.8	20.5	71.3	Symbols ◬, △ and ▲ are for 1, 2 and 3 sets of expts. respectively.
	2	5	5.5	5.0	10.5	
	3	5	0.6	0.8	1.4	
		15	56.9	26.3	83.2	
3. Ferrite reaction at 225°C for 3 hr.	1	5	47.6	21.7	69.3	
	2	5	8.6	4.0	12.6	
	3	5	1.1	1.0	2.1	
		15	57.3	26.7	84.0	

temperature on the progress of hydrolysis. Though at the beginning, higher temperature enhances the hydrolysis but at the later stage with water-mass ratio about 24, all the results tend to reach a limiting value. Beyond this, hydrolysis was very slow. For a recovery of alkali lower than 70.0%, heating has a favorable effect but for higher recovery heating effect is insignificant. From the curve D^2 it was clear that the interaction of carbon dioxide did not offer any improvement.

The curves A and D^1 have shown marked influence of grinding on the progress of hydrolysis at the initial stage. An increase of 13.0% alkali recovery was observed due to grinding at water/mass ratio 16, and thus, the grinding was always preferred before hydrolysis.

Curve E, indicates the better recovery of alkali where procedure D without carbon dioxide was followed. However, the recovery over 80.0% was considered to be uneconomical.

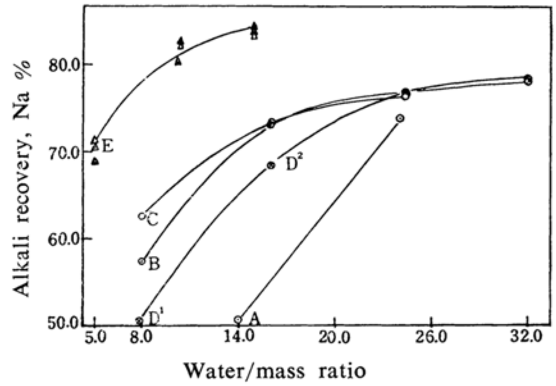

Fig. 2. Extent of alkali recovery on hydrolysis of Na-ferrite.

A	Hydrolysis at 35°C (without grinding)
B	Hydrolysis at 85°C (with grinding)
C	Hydrolysis at 100°C (with grinding)
D^1	Hydrolysis at 35°C (with grinding)
D^2	Further hydrolysis of D^1 after passing CO_2
E	Hydrolysis of macaronies (D^1 without CO_2)

Summary

An industrial process of limonite production has been developed in this laboratory using local iron oxide ore of Kalabagh by alkali method. Sodium hydroxide was allowed to react with pulverized ore at 200~225°C to produce sodium ferrite. This product was then hydrolyzed to obtain hydrated ferric oxide (limonite) and alkali in aqueous solution. The method was further modified in the light of some operational difficulties.

Hydrolysis was carried out under varied conditions for maximum recovery of alkali and the recovery upto 80% found to be economical. A graphical representation of this recovery was also given.

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Appendix

Activity of Limonite.—The activity of limonite was determined by its hydrogen sulfide absorption capacity and subsequent liberation of elementary sulfur on regeneration according to overall reaction:

$$Fe_2O_3(H_2O)_x + 3H_2S \rightarrow Fe_2S_3(H_2O)_x + 3H_2O$$

$$Fe_2S_3(H_2O)_x + 3/2O_2 \rightarrow Fe_2O_3(H_2O)_x + 3S$$

In other words, free sulfur liberate on air oxidation was the measure of activity of limonite. The experimental arrangement was as shown in Fig. 3.

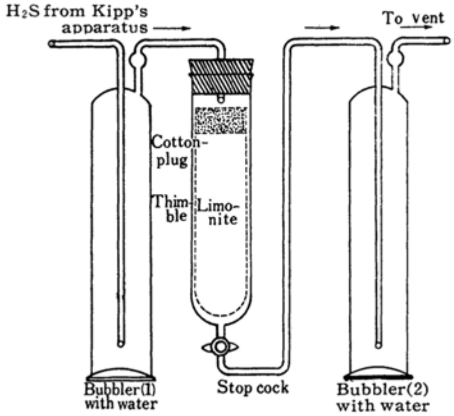

Fig. 3. H_2S absorption system for activity test of limonite.

Procedure.—Ten grams limonite was taken in a thimble and it was moistened thoroughly. A cotton plug was placed at the mouth of the thimble. The thimble was then placed into a cylindrical separating funnel having an internal diameter 16 mm. This was connected to the bubblers containing water according to the diagram. Hydrogen sulfide was generated in a Kipp's apparatus. Moist gas was passed through the limonite bed for a considerable period of time. When the rate of gas flow shown by two bubblers almost the same, the stop-cock was then closed for 3 min. If there was no bubble in bubbler (1) during this period, the hydrogen sulfide absorption by limonite was considered to be complete. The impregnated limonite was then oxidized by passing air through the same system for 12 hr. at the rate of 60 l./hr. using suction pump. The oxidation was complete during this period.

The thimble was taken out and dried at 80°C. The dry mass was then extracted with carbon disulfide (CS_2) in a Soxhlet apparatus. The extracted sulfur was weighed directly.

All the tests were carried out under identical conditions. The activity of natural "Bog ore" (imported from Holland and Denmark) and the limonite produced by the above method was comparative. Ninety-seven per cent iron content of limonite (produced) was found to be active.