

Pakistan Journal
of
Scientific and Industrial Research

Vol. 2, No. 4

October 1959

48 REDUCTION OF KALABAGH IRON ORE (CONTAINING FERRUGINOUS CLAY) WITH SUI GAS

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During the last phase of the Second World War, oxidic iron ores have been reduced in Germany to sponge iron in order to prepare a cheap catalyst for the Fischer-Tropsch synthesis.

After the war, the Hydrocarbon Chemicals Inc. of Newark, U.S.A., used successfully a fluidised bed* for this process and set up a plant with 20 tons daily capacity in Brownsville, (Texas). As sponge iron can immediately be converted into steel in an electric steel oven, it is a valuable raw material.

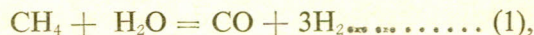
*In the fluidised bed the powdered ore (particle size upto 0.6 mm diameter) is whirled up by a strong current of hot gas, which after being freed from the water formed during reduction, is recycled. Reportedly, 400 cbm. of hydrogen are sufficient to produce 1 ton of sponge iron. The gangue, not being separated during reduction, must be removed afterwards by magnetic process.

The lower the reduction temperature, the larger and more active seems to be the surface of the produced sponge iron. Prepared at 480 °C., the sponge iron starts burning even at normal temperature, and has therefore to be wetted with oil during processing in air.

Russia also followed the above process, using carbon monoxide as reducing gas and 600°C. as the reaction temperature. Under these conditions, reportedly iron carbide, FeC₃, is formed, which is not pyrophoric and does not show much agglomeration of the particles.

A mixture of hydrogen and carbon monoxide has been used by the U.S. Steel Co., Chicago, Ill. The ore is used in the form of somewhat bigger particles and the

As a result of the experiences from the above reduction processes¹, a plant with 200 t/day capacity of sponge iron is working in Monterrey (Fierro Esponja S.A., Monterrey, Mexico) since the middle of 1958. The plant has been built by Kellogg Co., New York, and uses earth gas treated at first with steam according to the equation



the old well known reaction where the methane-steam mixture passes over heated ceramics. The small amount of carbon dioxide formed by the side reaction is removed and thus a

temperature raised to 850°C. Finally, A.D. Little, Cambridge, Mass., combined the partial oxidation of the earth gas into carbon monoxide and hydrogen with the reduction of the ore, and produced the required temperature by burning of the residual gas.

To use earth gas here in Pakistan for the reduction of iron ores is all the more important, not only for the lower expenditure on the plant itself (suggested to be only half of the blast furnace), but also because there is no suitable coal available for use either in a blast furnace or in the rotary kiln of the Krupp-Renn process. The indigenous coal is a brown coal having low caloric value but—what is worse—contains upto 10% sulphur, which on burning produces sulphur dioxide and (with moisture) sulphurous acid, thus rapidly damaging the whole iron equipment. Unfortunately, all attempts to upgrade the Kalabagh ore have been found unsuccessful or uneconomic so far. (2,3) The problem therefore was to find out as to how the low grade Kalabagh iron ore containing ferruginous clay and with an average iron content of 34% would behave when treated with Sui gas, because in the direct reduction processes using gas, only the best oxidic iron ores with 50 and more per cent iron have so far been used.

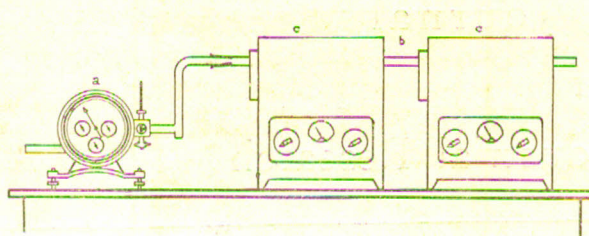


Fig. 1—Diagrammatic sketch of arrangement of furnaces for reduction of Kalabagh iron ore with Sui gas
 gas with 85% hydrogen and 15% carbon monoxide is produced, representing an even higher reduction potential than earth gas alone.

The experiences gained at this large scale production plant have been so advantageous that another plant with 500 tons daily capacity will soon be set up. Thus for the first time, this fluidised bed reduction competes favourably with the old blast furnace.¹

Sui gas, as such, was used in the following experiments because there was no equipment available for upgrading it by steam treatment according to equation (1) given above.

The apparatus, as given in Fig. 1, consisted of a gasometer (a) to maintain a constant speed of the passing gas and a glass or porcelain tube (b) going through two (Gallenkamp type) combustion furnaces (c) with a maximum temperature of 1400°C. The connection between the gasometer and the glass tubing consisted of a K.P.G. ground glass joint arrangement, which allowed rotation of the tube from time to time. By this means, it was hoped to ensure that all particles of the ore came into intimate contact with the passing gas. From the X-ray analysis, however, one drew the conclusion that this goal could be reached only approximately.

The first oven acted as a pre-heater for the passing gas because in its absence the temperature inside the tube drops several hundred degrees centigrade below the temperature indicated by the oven's own thermometer, due to the cooling effect of the passing gas. With the use of the pre-heating oven, however, the iron ore placed in the middle of the second oven was actually at the temperature indicated by the oven.

On passing Sui gas through powdered Kalabagh iron ore at temperatures ranging from 600°C. to 1200°C. for different periods of time and separating the reduced product magnetically, it was found that after half an hour reaction at 600°C., the non-magnetic portion became optimal at 20% of the used ore instead of reaching the expected 60%. Starting with an average sample containing 34% iron and 66% gangue, the removal of 20% (practically iron-free) gangue should raise the iron content to 42.5%; it was, however, found to be 53%. This rather poor result is readily understood when we take into consideration the minerals constituting the Kalabagh ore. In Table 1, the different minerals present in an average sample of the ore are shown, as found by Qurashi et al.⁴

Assuming that the oxides limonite and hematite would have lost only water and oxygen, while the carbonate siderite would have decomposed with the development of carbon dioxide and subsequently reduced to metallic iron, the iron content—after removing 20% gangue—would rise to 53% in accord with the experiment. It follows that most probably the chamosite remained essentially unaffected by the gas treatment. Being an iron magnesium alumino-silicate, wherein the iron might not only be a kation of that salt but may also form coordinative linkages, it cannot be expected to be affected by methane.

It was, therefore, thought advisable to roast the ore prior to the methane treatment in order to decompose the chamosite into compounds susceptible to reduction. The reduction of ore, previously done by roasting in passing air at 650°C., yielded a magnetic portion with 56% iron content, which increased to 60.2% while roasting was carried at a raised temperature of 750°C. A further rise in the reaction temperature was therefore indicated. Actually, when both roasting and reduction were carried out between 950-1000°C. with a flow of 12 cft./hr of Sui gas, an explosive reaction took place. A cloud of carbon dust came out of the tube and caught fire. The experiment was therefore at once stopped and the ore cooled in the methane atmosphere. It

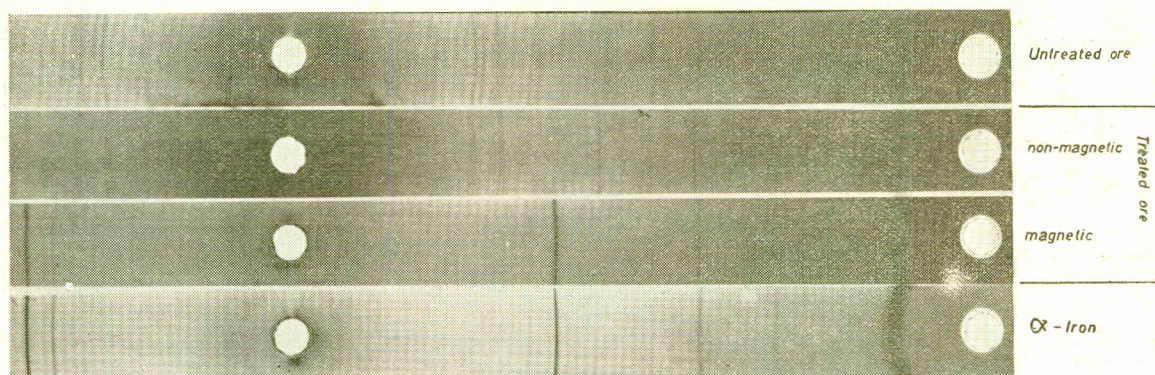


Fig. 2.—X-ray patterns of the magnetic and non-magnetic fractions of the treated ore, showing the efficient reduction of ore into sponge iron by the roasting and Sui gas treatment.

was found that the used glass tube had softened and was firmly combined with the partly sintered ore so that only parts of the ore could be properly removed. The parts of the ore on the side where the gas entered looked like tarred coke. These lumps were very light in weight and easily powderable between the fingers. When brought in contact with the horse-shoe magnet they were found to be strongly magnetic. The magnetic portion—constituting over 90%—yielded 93% iron as chemically determined.

TABLE 1.—PERCENTAGE MINERAL COMPOSITION OF THE MEAN SAMPLE BY X-RAY ANALYSIS.

Constituent Minerals	Weight % from X-ray analysis	Corrected value	Contribution to iron content
Limonite ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O} \cdot n\text{H}_2\text{O}$) ..	8	7	4.5
Hematite ($\alpha\text{-Fe}_2\text{O}_3$) ..	16	14	9.8
Siderite (FeCO_3) ..	24	22	10.6
Chamosite* $3(\text{Fe}, \text{Mg})\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot n\text{H}_2\text{O}$..	32	30	8.4
$\text{TiO}_2, \text{Cr}_2\text{O}_3$ etc. ..	5	6	<1
Quartz ..	5	6	..
Kaolinite, Bohimite ..	10 ± 5	15	..
Total ..	100	100	33.8 ± 0.5

*Chamosite is a ferruginous clay and the formula given is, therefore, only approximate. It may contain 24-32% iron and an average figure of 28% has been used in the table.

Fig. 2 shows the X-ray powder diffraction patterns of the untreated ore (used in this experiment) at the top, and underneath are the corresponding patterns of the magnetic and non-magnetic portions of the roasted and reduced ore, and of α -Iron for comparison. Except for a very faint line at $d=2.45 \text{ \AA}$ (Table 3-a) the magnetic fraction of the treated ore compares in all details with the α -iron pattern. Due to the sintering of the tube, no proper yield determination was possible. However, this experiment shows the feasibility of reducing the Kalabagh iron ore, containing ferruginous clay, with Sui gas after decomposing the chamosite by roasting at 950-1000°C. in passing air. Under special conditions, a material is formed which in its behaviour and appearance closely resembles sponge iron.

These special conditions could not be maintained throughout the layer of ore in the tubes we had for use. One essential condition seems to be the high speed of the passing gas, another surely that of temperature at 950-1000°C. At 12 c.ft./hr., a few lumps of sponge iron are always formed besides sintered material which, after magnetic separation, yields a magnetic portion of an iron content of 78-86%. The exothermic character of the reduction reaction may account for the explosion. When this additional reaction heat is carried away quickly enough by the passing gas, no sintering occurs and the sponge-iron material is formed, as in the foremost part of the layer of ore. Behind these first parts, sintering

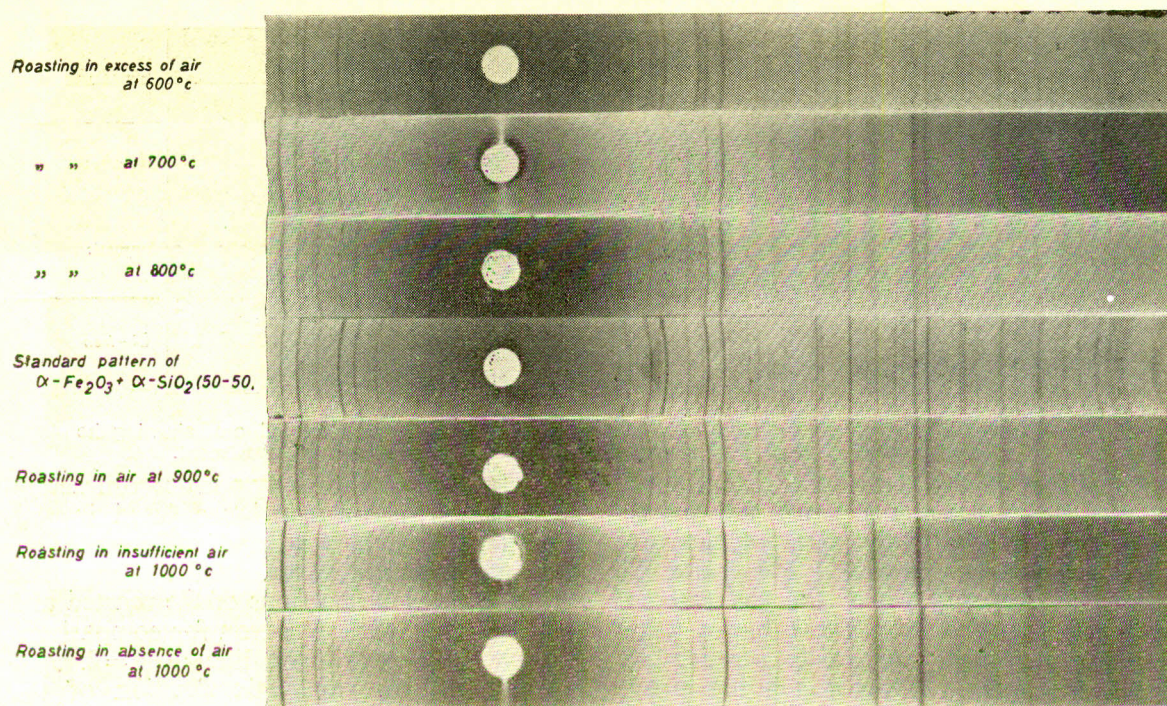


Fig. 3 Series of X-ray patterns of ore roasted at several different temperatures, both with and without air

takes place and prevents a proper magnetic separation. The ideal conditions according to the opinion of the present authors are therefore to be obtained in the fluidised bed, where the utmost speed of the gas can be maintained so that the whirled up particles may be reduced and cooled before agglomeration happens.

At lower speeds of the passing gas e.g. 8 cb. ft./hr. where sponge-iron-like lumps are no more formed, the sintering of treated ore could be reduced to a minimum. Using a porcelain tube, the treated ore could be brought out quantitatively and yield determinations became possible. The following questions had to be answered:

1. At what temperature and after how much time of roasting in the air is the optimum decomposition of chamosite obtained?
2. What are the decomposition products of chamosite?
3. Are all of them susceptible to subsequent reduction?

From the investigations that the Bureau of Mines, Washington, has already carried out² it is known that the iron-bearing minerals are finely distributed throughout the gangue. Roasting might convert them all into reducible iron compounds, and subsequent reduction into metallic iron, but sintering of the gangue may carry away both into the non-magnetic portion. Therefore, it had also to be found out in what forms the iron occurs in the non-magnetic portion?

To answer all these questions fully, X-ray analysis had to be carried out because $\alpha\text{-Fe}_2\text{O}_3$ as well as Fe_3O_4 are magnetic and it is not possible chemically to determine metallic iron in the presence of these two oxides or even other iron compounds quantitatively. These X-ray analyses have been carried out by L. Ahmad, S.H. Rizvi and M.M. Qurashi.

The previous investigations by these authors^{4,5} had shown that heating the ore without passing air at 450°C., 600°C. and 800°C., or with steam at 300-450°C. modified the chamosite lattice, yielding Fe_3O_4

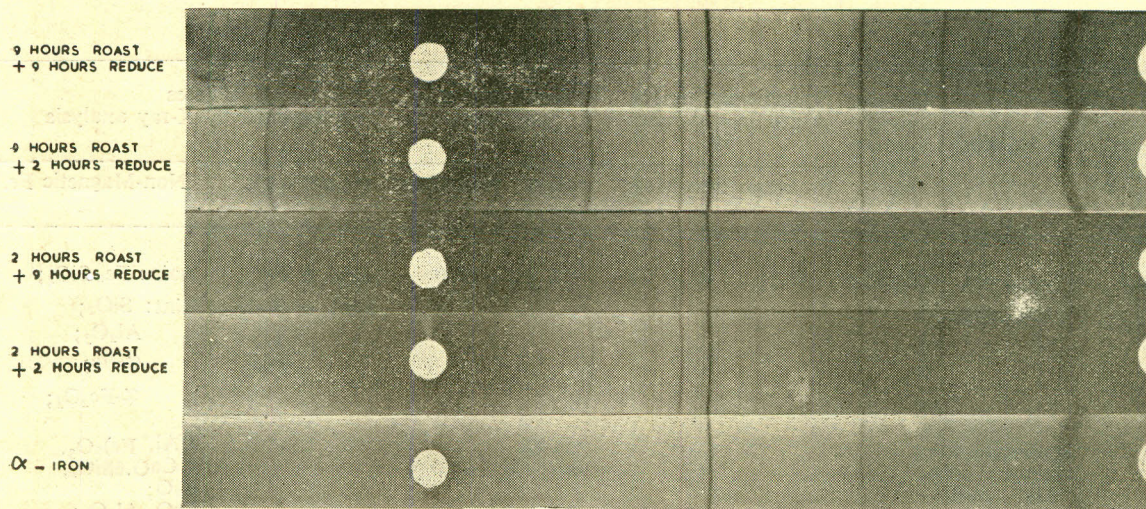


Fig. 4. (a)

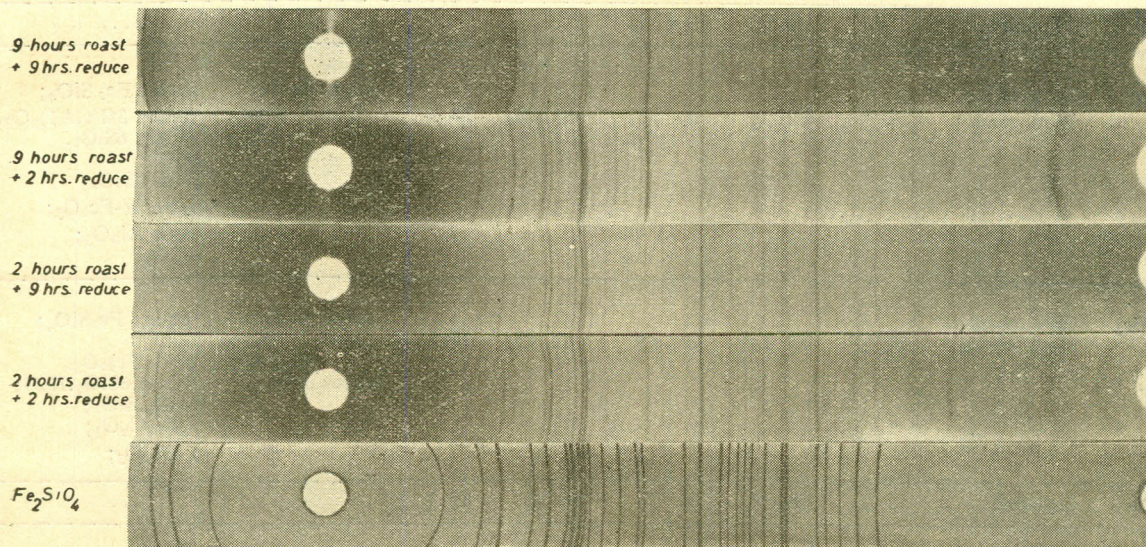


Fig. 4.(b).— Patterns of (a) magnetic fraction and (b) non-magnetic fraction of the iron ore subjected to roasting and reduction for various lengths of time. Comparison patterns of α -iron and Fe_2SiO_4 are also included.

principally. Fig. 3 However, in a current of air—as done in the present experiments—the chamosite breaks down yielding mainly α - Fe_2O_3 and SiO_2 as shown in the X-ray patterns of Fig. 3.

Sometimes there are also some faint lines of Fe_3O_4 but this is probably due to the fact that, in spite of periodical rotation of the tube, the gas does not always flow uniformly through all parts of the layer of ore. Thus, by roasting in passing air, a much simpler product was formed and it was found that the

characteristic lines of chamosite disappear completely only when the roasting had been carried out above $950^\circ C$. These observations already answer the first question and the first part of the second one qualitatively but not quantitatively because there are also several other lines besides the iron oxides, most of them being characteristic of iron ortho-silicate, Fe_2SiO_4 . Unfortunately the roasted ore being a mixture of several compounds allowed no exact quantitative determination of the components. Much more informative patterns

TABLE 2.

Exper. No.	Treatment*.	Gaseous loss during treatment.	Chemically determined iron content in		Iron yield in % of theory		Phases determined by X-ray analysis	
			Fr. Magn.	Non-Magn.	Magn.	Non-Magn.	Magnetic Fr.	Non-Magnetic Fr.
6a ₁	9 hrs. roast. 9 hrs. reduct.	32.5%	83 %	19.4 %	79.3	20.0	main: α -Fe faint: α -Fe ₂ O ₃ ; C; SiO ₂ .	main: Fe ₂ SiO ₄ ; faint: SiO ₂ ; Al ₂ O ₃ ; α -Fe; α -Fe ₂ O ₃ ;
	non-magn. Fr. reduced for 2 hrs. more				in all 85.6 %			3(Al, Fe) ₂ O ₃ . 4 CaO.6SiO ₂ . H ₂ O; FeO. Al ₂ O ₃ ;
6a ₂	repeated	36.5%	92 %	17 %	83.3%	16.5 %
6a ₃	repeated	..	84 %	19.6 %
6b	9hrs. Roast. 2hrs. reduct.	26 %	72 %	27 %	65.6%	34.1 %	main: α -Fe; faint: Fe ₃ C; SiO ₂ ;	main: Fe ₂ SiO ₄ ; faint: 3(Fe,Al) ₂ O ₃ . 4CaO. 6SiO ₂ . H ₂ O; Fe ₃ C; SiO ₂ ; α -Fe; α -Fe ₂ O ₃ ; FeO. Al ₂ O ₃ ; Al ₂ O ₃ ;
6c ₁	2hrs. roast. 9hrs. reduct.	33 %	83.2%	20.4%	80.4%	20.5 %	main: α -Fe; faint: SiO ₂ ;C; Fe ₂ SiO ₄ ; traces of Fe ₃ C;	main: Fe ₂ SiO ₄ ; faint: 3(Al, Fe) ₂ O ₃ . 4 CaO.6SiO ₂ .H ₂ O; Al ₂ O ₃ .SiO ₂ ; FeO.Al ₂ O ₃ ; α -Fe ₂ O ₃ ;
6c ₂	repeated.	32 %	84 %	15 %	83 %	15.1 %
6d	2 hrs. roast. 2 hrs. reduct.	26 %	70 %	27.1 %	74.1 %	30.5 %	main: α -Fe; faint: Fe ₃ C; SiO ₂ ; C;	main: Fe ₂ SiO ₄ ; faint: SiO ₂ ; Al ₂ O ₃ ; 3(Al, Fe) ₂ O ₃ . 4CaO.6 SiO ₂ .H ₂ O; FeO.Al ₂ O ₃ ; Fe ₃ C;
6e	1 hrs. roast. 4 hrs. reduct.	30 %	78 %	20.5 %	78.7 %	21.5 %
6f	1 hr. roast. 2 hrs. reduct.	26 %	69 %	26.3 %	69 %	30.9 %
6g	1/2 hr. roast. 2 hrs. reduct.	22 %	60 %	23.7 %	78.7 %	24 %

* The speed of the passing gases throughout the experiments was 8 c. ft/hr. through a tube of approx. 1.5 cm. diameter.

TABLE 3 (a).—COMPARISON OF THE PATTERNS OF α -Fe AND THE MAGNETIC FRACTION AFTER REDUCTION.

Magnetic Fraction ..	2.45(VF)	2.23(W)	2.025(S)	1.58(VF)	1.44(M)	1.285(W)	1.175(S)
Standard α -Fe pattern ..		2.23(W)	2.025(S)	1.58(VF)	1.44(M)	1.285(W)	1.175(S)

TABLE 3 (b).—X-RAY ANALYSIS OF THE NON-MAGNETIC FRACTION FROM THE DOUBLE (AIR AND SUI GAS) TREATMENT.

Non-magnetic fraction	Standard data of Fe_2SiO_4	α - SiO_2	$3(\text{Al}_2\text{Fe})_2\text{O}_3$ $4\text{CaO} \cdot 6\text{SiO}_2 \cdot \text{H}_2\text{O}$	$\text{FeO} \cdot \text{Al}_2\text{O}_3$
F 5.20	5.2(70)		5.0(40)	
—	4.37(10)	4.26(35)		4.69(20)
F 3.98	3.96(70)		3.97(40)	
—	3.78(30)			
M 3.55	3.54(90)		3.48(40)	
F 3.33		3.343(100)	3.41(20)	
—			3.28(40)	
F 3.20				
F 3.10				
F 3.07				
F 3.03	3.04(70)			
S 2.92			2.90(100)	2.87(60)
—	2.886(40)			
S 2.83	2.822(100)		2.82(60)	
F 2.75				
F 2.71			2.68(60)	
W 2.64	2.626(80)			
S 2.57	2.562(90)		2.60(60)	
—			2.53(40)	
S 2.50	2.495(100)			
S 2.445	2.461(60)	2.458(12)		2.45(100)
W 2.40	2.403(60)		2.40(80)	
—	2.350(40)			
F 2.33				
M 2.30	2.302(80)	2.282(12)	2.30(40)	
W 2.19	2.190(70)	2.237(6)	2.16(40)	
F 2.05	2.07(60)	2.128(9)	2.11(60)	
M 2.03	2.042(60)		2.06(60)	2.02(80)
—	1.984(40)	1.980(6)		
W 1.95				
F 1.92	1.938(40)			
—			1.88(70)	
W 1.84	1.837(70)			
W 1.83		1.817(17)		
F 1.78				
S 1.775	1.775(100)			
M 1.700	1.703(60)		1.70(20)	
W 1.675	1.677(70)			
W 1.665		1.672(7)		
M 1.635	1.648(70)	1.659(3)	1.64(80)	1.64(16)
M 1.635	1.625(70)			
W 1.600	1.605(70)			
F 1.585	1.589(30)		1.58(50)	
S 1.575	1.574(70)			
—	1.537(50)	1.541(15)	1.54(50)	1.56(40)
M 1.525	1.523(80)			
M 1.515	1.515(80)			
F 1.460	1.461(40)		1.46(60)	
S 1.445	1.446(70)	1.453(3)	1.44(20)	
W 1.430	1.428(70)			1.43(80)
W 1.420	1.419(40)			
W 1.410			1.41(60)	
—	1.399(70)		1.39(60)	
—	1.395(20)			
W 1.375	1.372(70)	1.382(7)		
M 1.345	1.340(80)	1.374(20)	1.35(20)	

were obtained from the separate magnetic and non-magnetic fractions when the roasted ore was reduced with Sui gas and the treated ore separated magnetically. This has been done in a series of experiments 6a-g., the results of which are presented in Fig. 4 and Tables 2 and 3.

The first interesting data is the gaseous loss the ore suffers during treatment. In Table 2 these losses are given together with the yields of iron in the magnetic and non-magnetic fractions for the various hours of roasting and the subsequent reduction.

One can see that the gaseous loss seems to depend mainly on the reduction time. Irrespective of whether the roasting was carried out for 9 hrs., as in experiment (6a₁), for 2 hrs. as in experiment (6c₀), or even for 1 hr. as in (6e), the gaseous loss reaches 30% when the reduction is carried out for at least 4 hours and increases to 33 to 35% in 9 hours.

On the other side, when the reduction lasts only for 2 hours, the loss drops to 26%, irrespective of whether the ore has been roasted for 9 hours as in experiment (6b), for 2 hours as in (6d), or only for an hour as in experiment (6f). Half an hour's roasting followed by 2 hours reduction gives a still lower loss of 22% (6g), and when there is no roasting at all but only reduction for 1/2 an hour, we have a loss of only 16.4%.

This means that half an hour's roasting causes an increase in the gaseous loss from 16.4 to 22% when two hours' reduction follows. An hour's roasting brings the loss almost to the maximum because, while two hours' reduction brings about losses of 26% (6f) a prolongation to 4 hours (6e) raises the loss to 30%. In the repeated experiment 6a₂ the gaseous loss was highest i.e. 36.5%, most probably due to incidentally favourable conditions in the layer. However, the highest iron content of 92% in the magnetic portion had also been received. This parallelism prevails throughout the series of experiments so that one can say the higher the gaseous loss the higher the iron content in the magnetic portion.

The X-ray analysis shows that in passing air, the main decomposition compounds of chamosite are α -Fe₂O₃ and silica. So the gaseous loss must stem from the water formed during the reduction of Fe₂O₃. An explanation for the 16.4% gaseous loss during the reduction of the original ore without prior roasting has already been given on the basis that only the first three minerals in Table 1 have been reduced to metallic iron. As soon as the decomposition of the chamosite starts during roasting, there is a large increase in the gaseous losses.

The second important data is the iron content in the non-magnetic portion because it represents the economic loss in the process and it is therefore necessary to determine :

- (a) in what compounds is iron present in the non-magnetic fraction ?
- (b) How have these compounds been brought into the non-magnetic fraction ?
- (c) how can this be prevented ?

The various phases found in the X-ray analysis, as given in Table 2, reveal that the main iron-bearing compound in the non-magnetic fraction is iron ortho-silicate. From the series of experiments 6a-d, with various roasting and reduction times, one can see that this iron ortho-silicate must have been formed during roasting and that it is susceptible to reduction with Sui gas. Thus when the roasting (9 hour as in 6a) is followed by a much shorter reduction time (2 hours only as in 6b), there is an increase of about 14% of iron-ortho-silicate in the non-magnetic fraction in comparison to 9 hours reduction in (6a). The same high percentage of iron, namely 30.5%, in the non-magnetic fraction occurs when 2 hours' roasting is followed by only 2 hours' reduction (6d). However, when an ore roasted for 2 hours in experiment 6c, where the same amount of iron ortho-silicate must have been formed as in 6d, is reduced for 9 hours these 30.5% iron content drops to 20%. In this context, it is worthwhile to mention that a repeated reduction of the non-magnetic fraction as in experiment 6a for

further 2 hours, furnished again a magnetic portion and raised the overall yield of metallic iron from 79.3 to 85.6%. This provides positive proof that the iron compounds present in the non-magnetic fraction are susceptible to reduction.

Besides this main compound, iron ortho-silicate, faint lines of α -iron, α -Fe₂O₃ are also observed in the X-ray patterns of the non-magnetic fraction. Both being magnetic, their presence in the non-magnetic portion can only be understood by assuming that the magnetic particles become surrounded by sintered gangue and are hence too heavy to be picked up by the magnet.

In the patterns of the non-magnetic fraction, a dozen other lines, most of them faint, remain still outstanding. A search in the A. S. T. M. card index shows that they may be due to a number of different phases the principal amongst them are ; SiO₂; (Al,Fe)₂O₃. 4CaO.6SiO₂.H₂O; FeO.Al₂O₃ and high temperature forms of Al₂O₃.

While iron ortho-silicate is reducible and its iron content thus transferable to the magnetic fraction, the iron particles included in sintered gangue represent an irrecoverable loss until sintering can be prevented. The results of the experiment 5 already give some indication of how sintering can be prevented. The lumps resembling sponge iron and yielding a magnetic fraction consisting of α -iron of 93% purity have been formed—as already mentioned—only with a fairly high speed of the passing gas. The gasometer, giving only a volume of 12 c. ft. per hour which passes through the apparatus, reveals little about the actual speed with which this volume passes through the narrow gaps of the layer of the ore. The speed of the reducing gas should be high enough to carry away the reduction heat so quickly that no sintering can happen. The most favourable conditions to achieve this would be obtained in a fluidised bed oven.

The same considerations are to be applied in case of the magnetic portion of the ore.

The main component is of course, α -iron, but besides it, there are sometimes the lines of α -Fe₂O₃ and more often those of iron carbide, silica and carbon. Unreduced α -Fe₂O₃ can come into the magnetic portion either because the methane did not come into contact with it in the thick layer of the ore, or in the sintered gangue it is included in such a way that the weight of the whole particle allows it to be picked up by the magnet. The presence of silica as well as the rather low iron content of the magnetic fractions, which does not exceed 86.5%, support this assumption. Thus an examination of the magnetic fraction also shows that the prevention of sintering is decisive for the economy of the whole process.

In experiment 6e, the roasting time has been restricted to one hour and subsequent reduction for 4 hours is sufficient to produce practically the same yields as with longer treatment. It follows that the roasting time of 1 hour is sufficient to break down chamosite and may even be further reduced to half an hour (6g). Not so the reduction time. Two hours reduction (as in 6f) leaves 10% iron unreduced in the non-magnetic fraction, while the same reduction time used for an ore which has been roasted only for $\frac{1}{2}$ hour gave practically the same 78.7% iron yield as in theory of experiment 6a₁ and 6e. Obviously iron ortho-silicate cannot be considered simply as a decomposition product of chamosite because its ratio is apparently increasing with the roasting time, while the breakdown of chamosite occurs between 950 to 1000°C. in a very short time. Therefore it probably comes through another reaction e.g. of iron oxide with silica. If so, the roasting time should be kept as short as possible to just get the decomposition of chamosite into α -Fe₂O₃ and silica, because the less iron ortho-silicate is formed the shorter can be the reduction time. Since sintering can happen during roasting as well as during reduction, the roasting should preferably be carried out in a fluidised bed too.

Summary

The reduction with Sui gas of Kalabagh iron ore containing ferruginous clay is possible

if the clay (chamosite) is decomposed by prior roasting. This roasting has to be carried out at temperatures above 950°C. otherwise the characteristic lines of chamosite do not disappear completely from its X-ray pattern. Furthermore it has to be carried out in a current of air of a sufficiently high speed. Only under the above conditions the main decomposition products are α -Fe₂O₃ and silica, while simple heating furnishes Fe₃O₄ and a much more complex pattern of the roasted ore. The shorter the roasting time the better, because iron ortho-silicate is formed with long roasting times. It cannot be considered to be simply a decomposition product of chamosite but is probably formed out of iron oxides and silica.

This iron ortho-silicate has been found to be reducible to metallic iron by Sui gas. In the reduction process, the speed of the current of Sui gas plays an important role. Sponge-iron-like lumps—the magnetic portion of which is α -iron of 93% purity—are formed only with a high speed of the gas and are not found when the speed is lower.

According to the assumption of the present authors, the reduction of the iron oxides, being an exothermic reaction, furnishes so much surplus heat at 1000°C. that sintering occurs. Thus further reduction of reducible compounds included in the gangue is prevented and metallic iron in the gangue is carried away into the non-magnetic fraction. A high speed of the gas, however, might both reduce and carry away the reaction heat thus preventing sintering. In the tubes used in the present experiments, the ore having a particle-size of approximately 0.5 cm. tends to remain in a thick layer. A quick penetration of the gas through all parts of this layer cannot therefore be secured. The present authors are of the opinion that the most favourable conditions for roasting as well as reduction would be available in a fluidised bed.

Experimental

1. *The apparatus.*—As shown in Fig. I the gas and air used was measured by a gasometer and then passed through a long glass or

porcelain tube, going through the length of two Gallenkamp-type furnaces heatable up to 1400°C. With a flow of 12c.ft/hr. of the gas the temperature inside the tube when placed in only one oven was found to be 860°C. in the middle when the heating element was placed and dropped down to 500, 360, 280, 140C and 80°C. respectively at successive distances of 5 cm each towards the entrance. The oven's own thermoelement indicated 1000°C. all the time. To avoid this large temperature drop, the first oven was simply used as a pre-heater for the gas and the ore was placed in the middle of the second oven where the temperature was now found in agreement with that indicated on the oven's own thermoelement.

The connection between the gasometer (filled with water, the gas being used undried) and the tube consisted of a K.P.G. (Schott and Gen.) ground glass arrangement, which allowed rotation of the tube from time to time by hand. By this means, it was hoped to ensure that all particles of the ore came into contact with the passing gas. However, the X-ray analysis of the treated ore revealed that this could not always be attained reliably by such occasional rotations.

2. *The ore.*—The ore used was an average sample from Kalabagh, already analysed by M. M. Qurashi et al., containing 34% iron distributed among four different minerals as shown in Table I. This ore, which is easily powderable, had a particle size of 0.5 cm. and was completely non-magnetic.

3. *Treatment of the ore with Sui gas.*—100 gs. of the ore were placed in the middle of the second furnace and both furnaces heated up to 600°C. (with Sui Gas passing) for half an hour, two hours and finally for 6 hours. The ore was then cooled in the earth gas atmosphere and magnetically separated by means of a small horse-shoe magnet. Both the magnetic and the non-magnetic fractions were treated a second time with the magnet but the second application produced no further separation. These three experiments were also carried out at 700, 800 and 900°C. The result was practically the same as obtained at 600°C.

With half an hour's duration, the optimal yield of the non-magnetic fraction was achieved, i.e., 20gs. These 20gs.—20% by weight—of the ore were found to be practically iron free. The removal of 20% gangue from a 34% iron-bearing ore should rise the iron content in the remaining magnetic portion up to 42.5%; actually the iron content was found to be 53%.

Assuming that only limonite, hematite and siderite would have been reduced to metallic iron, the losses of water, carbon dioxide and oxygen would total to about 16.4%. The overall loss therefore would be 36.4% and the iron content in the then remaining magnetic portion would be 53.1%, again in good agreement with the found value.

53% iron in 63.6 g. of the magnetic portion correspond to 33.7 g. of iron which are in accord with the theoretical value of 34 g.

4. *Roasting of the ore in air at 650° and 750°C. prior to reduction with Sui gas.*—110 gs. of the ore were heated up to 650°C. in a current of air (12 c.ft./hr.) for 4 hours and then Sui gas was passed through with the same speed, at the same temperature, and for the same time. Result: 68.8% magnetic portion containing 56% iron. The same experiment carried out at 750°C. yielded:

48% magnetic portion with 60.2% iron
= 28.9 g.

52% non-magnetic portion with 18% iron
= 9.4 g.

Total = 38.3 g. theory: 37.4 g.

5. *Roasting the ore in air at 950°-1000°C. and subsequent reduction with Sui gas at the same temperature.*—100 gs. of the ore were heated in a 12 c. ft./hr. current of air up to 950°-1000°C. for 3 hours. Then the temperature was lowered to nearly 800°C. and Sui gas was passed through with the same speed. The temperature was then raised again to 950°-1000°C. within the next 5 minutes, when all of a sudden an explosion occurred. A big cloud of carbon dust came out of the tube and caught fire. The experiment was at once stopped and the ore cooled down in a current of Sui gas.

It was found that the glass tube used had become soft and the partly sintered ore was very firmly attached with the tube so that only parts of the ore could be removed. The parts of the ore at that side where the gas entered looked like tarred coke. These lumps were very light in weight and easily powderable between the fingers. Treatment with the horse-shoe magnet showed that they were strongly magnetic, and the magnetic portion constituting practically all of it—contained 93% iron as determined chemically. From the rest of the ore, approximately 50 g. could be freed from glass fragments. This was powdered and also magnetically separated; the magnetic portion was found to contain 74% iron. The determination of yield, however, was not possible.

In Fig. 2, the X-ray pattern of the untreated and the treated ore each split off into a magnetic and non-magnetic portion are shown side by side with that of α -iron. Quantitative evaluation of these patterns confirms the figures of 93% iron in the magnetic fraction. The non-magnetic fraction gives a complex pattern, the predominant phase in which was identified to be iron ortho-silicate, Fe_2SiO_4 . A dozen other lines, most of them being faint, remain outstanding. A search in the A. S. T. M. card index suggests that they are due to a number of different phases, the principal amongst them are SiO_2 ; $3(\text{Al}, \text{Fe})_2\text{O}_3 \cdot \text{CaO} \cdot 6\text{SiO}_2 \cdot \text{H}_2\text{O}$; $\text{FeO} \cdot \text{Al}_2\text{O}_3$; and high temperature forms of Al_2O_3 .

6. *Studies on the formation of iron ortho-silicate and its behaviour against Sui gas at 950°-1000°C.*—These experiments were carried out in a porcelain tube, which stood upto the temperature of 1000°C. without combining with the ore. Thus yield determinations were possible. The speed of the gas was 8 c.ft./hr.

6a.₁—*Roasting for 9 hours and reduction for 9 hours.*—80 g. of the ore were roasted in a current of air (8 c.ft/hr) for 9 hours at 950-1000°C. Cooled down in air and reduced the next day with Sui gas under the same conditions again for 9 hours. Cooled in methane atmosphere and brought out quantitatively. Received : 54.0 = 67.5% of the starting ore. The loss is, therefore, 26 g. = 32.5%.

Magnetic portion : 26 g. with 83% iron
= 21.58 g. = 79.3% of theory.

Non-magnetic portion : 28 g. with 19.4%
= 5.43 g. = 19.9% of theory.

Total	..	27.01 g
theory	..	27.2 g

12 g. of the non-magnetic portion were again treated with Sui gas for 2 hours at the same temperature and magnetically separated. Received : magnetic portion 0.46 g. with 74.9% iron = 0.8 g. iron for the whole amount of 28 g. non-magnetic portion. The overall yield of iron would rise to 85.6 % of theory. This experiment shows that there is still some component in the non-magnetic fraction susceptible to further reduction.

This experiment was repeated twice with the following results :

6a₂.—Used ore : 100 g.

Treated Ore : 63.5 g. Loss : 36.5 g.

Magnetic portion : 30.8 g. with 92% iron
= 28.34 g. = 83.3% of theory.

Non-magnetic portion : 33.0 g. with 17% iron
= 5.61 g = 16.5% of theory.

Total	..	33.95 g.
theory	..	34.0 g.

6a₃.—Magnetic portion with 84% iron

Non-magnetic portion with 19.6% iron

6b.—Roasting for 9 hours Reduction for only 3 hours.—

Used ore : 100 g.

Treated Ore: 74 g. Loss : 26 g. = 26%
Magnetic port. 31 g. with 72% iron
= 22.32 . = 65.6% of theory.

Non-magnetic port. 43 g. with 27% iron
= 11.61 g. = 33.3% of theory.

Total	..	33.93 g.
theory	..	34.0 g.

6c₁.—Roasting for 2 hours reduction for 9 hours.—

Used ore : 50 g.

Treated ore: 33.5 g. Loss: 16.5 g. = 33%

Magnetic portion: 16.4 g. with 83.3% iron
= 13.66 g. = 80.3 % of theory.

Non-magnetic portion: 17.1g.with 20.4%iron
= 3.49 g. = 20.5% of theory.

Total	..	17.15 g.
theory	..	17.0 g.

6c₂. = Repeated.—

Used ore : 50 g.

Treated ore : 34g. Loss 16 g. = 32 %
Magnetic portion : 16.8 g. with 84 % iron
= 14.11.g. = 83% of theory.

Non-magnetic portion: 17.2 g. with 15% iron
= 2.58 g. = 15.1 % of theory.

Total	..	16.69 g.
theory	..	17.0 g.

6d.—2 hours roasting and 2 hours reduction.—

Used ore : 50 g.

Treated ore : 37 g. Loss : 13 g. = 26 %
Magnetic portion : 17.8 g. with 78.8 % iron
= 12.6 g. = 74.1 % of theory.

Non-mag. portion: 19.2g.with 27.1% iron
= 5.2 g. = 30.5% of theory.

Total	..	17.8 g.
Theory	..	17.0 g.

6e.—1 hour roasting 4 hours reduction.—

Used ore : 50 g.

Treated ore : 35 g. Loss : 15 g. = 30%
Magnetic portion : 17.2 g. with 78 % iron
= 13.4 g. = 78.7 % of theory.

Non-mag. portion : 17.8 g. with 20.5% iron
= 3.65 g. = 21.5 % of theory.

Total	..	17.05 g.
theory	..	17.0 g.

6f.—1 hour roasting 2 hours reduction.—

Used ore : 50 g.
 Treated ore : 37 g. Loss : 13 g. = 26%
 Magnetic portion : 17 g. with 69% iron
 = 11.73 g. = 69 % of theory.
 Non-mag. portion: 20 g. with 26.3% iron
 = 5.26 g. = 30.9% of theory.

Total .. 16.93 g.
 theory .. 17.0 g.

6g.—1/2 hour roasting 2 hours reduction.—

Used ore : 100 g.
 Treated ore : 78 g. Loss : 22 g. = 22 %
 Magnetic portion : 44.6 g. with 60% iron
 = 26.76 g. = 78.7 of theory.
 Non-mag. portion : 33.8 g. with 23.7% iron
 = 8.01 g. = 24% of theory.

Total .. 34.86 g.
 theory .. 34.0 g.

References

1. Nachrichten aus Chemie and Technik Bd 6 No. 17/18 264, 1958, u. Bd. 7 No. 3, 17/18 1959.
2. Preliminary beneficiation tests on Pakistan Iron ore. July 1958 United States Bureau of Mines.
3. A. H. Chotani, Sadiq A. Ahmad, Ishtiaq Ali, S. H. Rizvi and M. M., Qurashi, Pakistan J. Sci. Ind. Research, I, 293 (1958).
4. M.M. Qurashi, S.H. Rizvi, and M. Latif Ahmad, Pakistan J. Sci. Ind. Research, I, 265 (1958).
5. S.H. Rizvi and M.M. Qurashi, Pakistan J. Sci. Ind. Research, I, 185 (1958).
6. Howard R. Amundsen, Agha H. Hashim, A. Hai and S. H. Rizvi, Pakistan J. Sci. Ind. Research, I, 207 (1958).