ISSN : 0974 - 7443 Volume 7 Issue 2

CHEMICAL TECHNOLOGY

An Indian Journal

Full Paper

Trade Science Inc.

CTAIJ 7(2) 2012 [61-65]

Reduction behaviour of different size fractions of a low grade ilmenite

Farhana Begum, Fahmida Gulshan, A.S.W.Kurny*

Department of Materials and Metallurgical Engineering, Bangladesh University of Engineering and Technology, Dhaka, (BANGLADESH)

E-mail: aswkurny@mme.buet.ac.bd

Received: 11th June, 2012 ; Accepted: 1st August, 2012

ABSTRACT

Sample of a low grade ilmenite (40 percent TiO_2) was divided into different size fractions by sieving and the reduction behaviour of the different size fractions was investigated. Sieve analysis showed that more than 95% of the ilmenite sample under investigation belongs to U. S. Sieve Nos. 100, 140 and 200. Chemical analysis results showed that the finer fractions contained a lower percentage of TiO_2 and a higher percentage of total iron. Finer fractions of the ilmenite sample were also observed to have a slightly higher sphericity. The three main size fractions of ilmenite were reduced with charcoal at 1050°C for 4 hours. Chemical analysis of the reduced samples revealed that finer fractions contain a lower amount of iron oxide although their pre-reduction iron oxides content was higher. The degree of reduction of iron oxides present in the ilmenite was found to be 79.36. 81.44 and 83.63% for the size fractions corresponding to U.S. sieve No. 100, 140 and 200 respectively. It was concluded that for the optimization of reduction parameters of ilmenite, a separate reduction procedure for each of the different size fractions is not necessary.

INTRODUCTION

Ilmenite and rutile are important minerals that contain titanium. Rutile is essentially naturally occurring titanium-dioxide and is relatively scarce. Ilmenite, on the other hand, is a mixed oxide of titanium and iron. Depending on the relative amounts of the different oxides of iron, the titanium content of ilmenite can be as low as 30 per cent. Ilmenites containing less than about 55 percent titanium dioxide are not considered suitable for industrial use.

Both rutile and ilmenite find wide applications in the manufacture of welding electrodes, ceramics, paints, white rubber and paper. Due to increasing demand, the known world deposits of rutile are fast depleting. This has forced scientists and technologists throughout the world to work on the development of processes[1] of enhancing the titanium dioxide content of the low grade ilmenites. In one of the processes for the enhancement of TiO_2 content of low grade ilmenite iron oxides in the ilmenite is selectively reduced to metallic iron and subsequently metallic iron contained in the reduced ilmenite is leached in a suitable acid. This upgraded ilmenite is known as synthetic rutile and is an acceptable substitute of natural rutile and high grade ilmenite.

Considerable efforts have gone into the optimisation of process parameters for reduction of iron oxides to enhance the TiO_2 content as much as possible. Effects of time and temperature of reduction, ilmenite –reducing agent ratio, prior oxidation, effects of catalysts, etc on the extent of reduction of iron oxides in the ilmenites have been investigated. This work concentrated on the reduction behaviour of the different size fractions of a low grade ilmenite collected from Kutubdia (an island in the Bay of Bengal) heavy mineral deposit in Bangladesh to see if separate reduction treatments of the different size fractions could enhance the overall extent of reduction. To the best of our knowledge, no such work has so far been reported. As a result this study on the reduction behaviour of different size fractions of a low grade ilmenite could be considered important for the commercial exploitation of low grade ilmenites.

EXPERIMENTAL

The sample of ilmenite was separated from the heavy minerals by physical means of separation. Sieve analysis was performed in a standard sieve shaker using 50 g sample and a shaking period of 15 minutes[2]. Since most of ilmenite was retained on US sieve No. 100, 140 and 200, subsequent investigations were conducted on these three fractions.

All the three fractions were analysed chemically by standard techniques[3] to determine the percentages of TiO_2, total iron and ferrous iron. Sphericity, a geometrical factor, of the three ilmenite size fractions was determined. For this purpose, the raw ilmenite samples were photographed under an stereoscope.

Sphericity of a particle was then calculated from the following formula.

$$\textbf{Sphericity} = \frac{d_n}{a} \qquad (1)$$

where, d_n = nominal diameter of the particle and a = length of its major axis.

Sphericity of at least seventy five grains of each size fractions was measured and the average value was taken as the sphericity of that particular fraction.

The ilmenite fractions were reduced in a fixed bed reactor by charcoal. Each charge for reduction consisted of 50g of ilmenite mixed with an equal amount of charcoal of US sieve No. 30. Reduction was carried out at 1050°C for 4 hours. Details of the reduction setup can be found elsewhere[4]. After reduction, ilmenite was separated from charcoal. The reduced ilmenite was then analysed chemically for metallic iron and total iron. Optical microscopy of the reduced mass was also carried out to study the morphology of the iron precipitates.

RESULTS AND DISCUSSION

The result of sieve analysis is given in TABLE 1. It is found that the sample of ilmenite is distributed over a number of grains sizes. More than 95% of the ilmenite is seen to be retained on US sieve No. 100, 140, and 200; individual amount belonging to each of these sieves being 22.21%, 34.73% and 38.72% respectively. Only 4.68% was retained on the other sieves, which were not sufficient for further investigation. Investigations were therefore, conducted only on these three main size fractions.

TABLE 1 : Sieve analysis of the ilmenite sample

US Sieve No.	Mesh Opening, pm	% Retained on Sieve
70	210	4.32
100	149	22.21
140	105	34.73
200	74	38.72
270	53	0.36

TABLE 2 shows the chemical analysis of different size fractions of the ilmenite sample. It may be found that finer fractions contain a lower percentage of TiO_2. The percentage of total iron, on the other hand, is higher in finer fractions. Similar variation in the composition of finer and coarser size fractions of ilmenite has also been reported by Ahmed et al[5]. Although finer fractions of the ilmenite sample contain a higher percentage of total iron, percentage of ferrous oxide was actually found to be slightly lower in finer ilmenite size fractions. The ferric oxide content of the finer fractions is obviously higher.

TABLE 2 : Chemical analysis of different size fractions before reduction

Ilmenite Size Fraction	% TiO_2	% Total Fe	% FeO	% Fe_2O_3
U.S. Sieve 100	42.36	36.86	23.23	26.83
U.S. Sieve 140	41.38	37.98	22.85	28.91
U.S. Sieve 200	41.08	39.10	21.41	32.10

The sphericity of ilmenite of three different size fractions are given in TABLE 3. The sphericity of all three samples is found to lie in a narrow range, 0.829 – 0.849. However, finer size fractions are found to have a slightly higher sphericity than the coarser ones. This is possibly linked to the fact that finer fractions may have a longer history of weathering, erosion etc. during transport.

TABLE 3 : Sphericity of ilmenite particles of different size fractions.

Ilmenite Size Fractions	Sphericity
U.S. Sieve 100	0.829
U.S. Sieve 140	0.841
U.S. Sieve 200	0.849

Chemical analysis of the reduced samples (TABLE 4) shows that the percentage of metallic iron is 29.05, 32.05, 35.19 for ilmenite size fractions belonging to U. S. Sieve No. 100, 140 and 200 respectively. Comparison of TABLES 2 and 4 shows that the percentages of total iron in the reduced samples are higher as compared with the total iron content in the as-received sample. This is due to the removal of oxygen during reduction. The finer fractions after reduction are found to contain higher amount of total iron as before.

TABLE 4 : Chemical analysis after reduction. (Reduction Temp: 1050°C, Time: 4 hour)

Ilmenite Size Fractions	% Metallic Iron	% of Total Iron
U.S. Sieve 100	29.05	41.33
U.S. Sieve 140	32.05	43.57
U.S. Sieve 200	35.19	45.79

The extent or degree of reduction of an oxide sample can be defined as the fraction of oxygen removed during the reduction process and is given by

$$\mathbf{DOR} = \frac{\left(\mathbf{O}_2^i - \mathbf{O}_2^r\right)}{\mathbf{O}_2^i} \times 100 \qquad (2)$$

where, DOR = degree of reduction; O_2^i = initial oxygen content of the sample; O_2^r = oxygen content of the reduced sample.

Degree of reduction based on different forms of equation (2) has been used for iron ores[6]. In the case of ilmenite, oxides of both iron and titanium are present. Although TiO_2 is more stable than oxides of iron, it is possible, depending upon reduction temperature, time and atmosphere, that some of TiO_2 is reduced to lower oxides. However an earlier study[4] on reduction of ilmenite has shown that TiO_2 is not reduced during reduction for 4 hours at 1050°C. In the present case reduction of ilmenite was carried out for 4 hours at 1050°C and it can be assumed that loss of oxygen of ilmenite sample during reduction is due to the reduction of iron oxides only. Using this argument the degree of reduction of iron oxides in the ilmenite sample can now be defined as

$$\mathbf{DOR}_{Fe} = \frac{\left(\mathbf{O}_{2Fe}^i - \mathbf{O}_{2Fe}^r\right)}{\mathbf{O}_{2Fe}^i} \times 100 \qquad (3)$$

where, DOR_{Fe} = degree of reduction of iron oxides in ilmenite; O_{2Fe}^i = oxygen content of iron oxides in initial ilmenite; O_{2Fe}^r = oxygen content of iron oxide in the reduced sample.

While calculating O_{2Fe}^r it is assumed that iron, other than in metallic form, is present in the reduced ilmenite as FeO only. Study on iron ore[7] has also shown that if degree of reduction is more than 40% (which is true in the present case as will be seen later), then no metallic iron is produced before all higher oxides are reduced to FeO. TABLE 5 shows the initial and final values of oxygen contents of iron oxide (s) in different size fractions of ilmenite. The degree of reduction (DOR_{Fe}) based on equation (3) for the three size fractions is presented in the forth column of TABLE 5. It is clear from the table that although finer ilmenite grains contain a higher amount of oxygen associated with iron, these fractions actually contain a lower amount of oxygen in the reduced mass. Consequently the degree of reduction is seen to be higher in the finer fractions. In other words, under the reduction conditions used, the finer fractions of ilmenite gets reduced at a faster rate.

TABLE 5 : Initial and final oxygen content of iron oxide and degree of reduction

Ilmenite Size Fractions	% of Total O_2 Combined with Iron before reduction	% of Total O_2 Combined with Iron after reduction	Degree of reduction
U.S. sieve No. 100	13.21	2.73	79.33
U.S. sieve No. 140	13.74	2.55	81.44
U.S. sieve No. 200	14.38	2.35	83.66

Optical micrographs on cross-sections of reduced ilmenite of different size fractions are given in Figure 1. Metallic iron is clearly visible as the bright phase, the rest of the phases are grayish, void and fissures being dark in appearance. In general, metallic iron appeared as parallel platelets (Figure 1). This is because of the original laminar morphology of ilmenite and hematite phases in ilmenite grains. But in finer fractions of ilmenite, iron particles were coarser than those in coarser fractions. In a substantial number of grains in finer ilmenite fraction, especially those with void and fissures, iron particles coalesced and took up a globular morphology. This relatively thicker morphology of iron particles in finer fractions is due to the fact that finer particles get reduced at a faster rate and thus allow more time for the iron atoms to diffuse and coalesce.

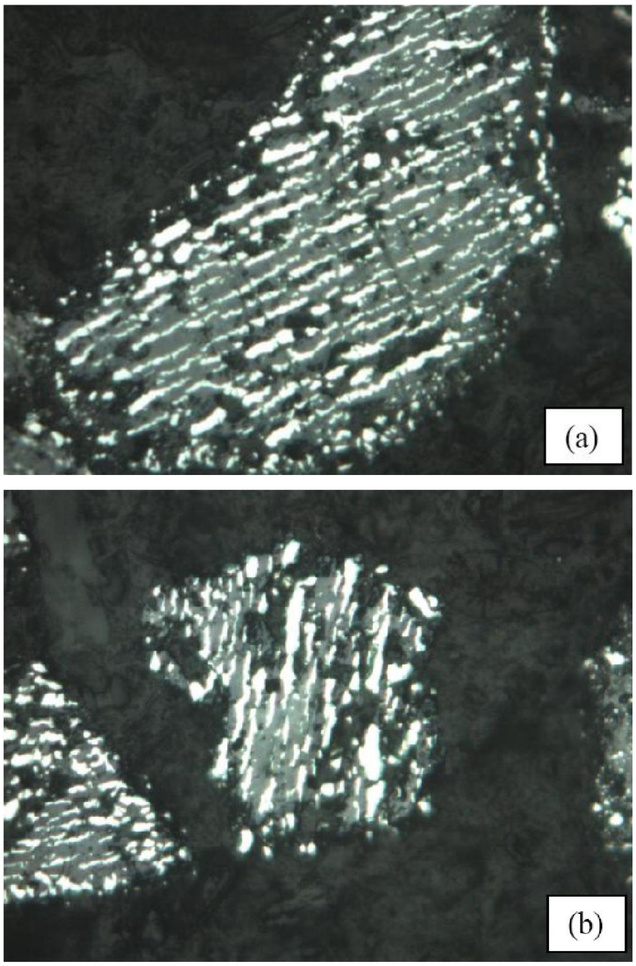

Figure 1 : Micrographs of the ilmenite particles after reduction for 4 hours at 1050°C. (a) U. S. sieve No.100, (b) U. S. sieve No. 200.

Reduction characteristic of ilmenite can depend upon numerous factors including size and shape characteristics of ilmenite particles, composition, presence of different phases and their morphologies, presence of defects like voids, cracks etc. As for the size of the ilmenite particles, it will significantly affect the reduction rate if the reaction is diffusion controlled. It has been shown[9,10] that reduction of ilmenite at higher temperature, as is used in the present study, is controlled by the diffusion of reductant through the product layer. It is therefore expected that finer ilmenite particles with shorter diffusion length will have higher rate of reduction.

Particles with similar average volume will have different thickness or diffusion length depending upon their shape characteristics. In the present study, the shape characteristic of ilmenite particles has been expressed in terms of sphericity. Sphericity of a particle is expected to affect the overall rate of reduction. A sphericity of one means that the particle has the shape of a sphere and hence the lowest surface area to volume ratio. This particle will obviously have lower flux of reductant through it. Particles with lower sphericity will be elongated in shape and hence have higher surface area. This will lead to higher diffusion rate in particles with lower sphericity. It has been already seen (TABLE 3) that ilmenite of lower size fractions has slightly higher sphericity. Therefore, shape characteristics of finer ilmenite particles are not favourable for higher rate of reduction.

Merk and Pickles[9] and Jones[10] have shown that the presence of manganese oxide and magnesium oxide reduces the rate of reduction of ilmenite. Ahmed et al have shown that finer fractions of ilmenite collected from a nearby source contain slightly higher percentage of both MnO and MgO[5]. Thus the difference in the impurity content can not contribute either to the higher reduction rate of finer fractions found in the present study. In fact both shape characteristics and MnO and MgO content of finer ilmenite particles are expected to have a negative effect on their reduction rate.

It can thus be said that the higher degree of reduction of finer ilmenite fractions observed in the present study is mainly due to shorter diffusion length in finer particles. The effect of faster diffusion in finer particles on the reduction rate more than offsets the negative effect of their higher sphericity and higher MnO and MgO contents. It may be mentioned that optical microscopy could not reveal any detectable difference in type and extent of defects among the different ilmenite size fractions which could be attributed to their difference in reduction behaviour.

The present study has shown that although finer fractions of this low grade ilmenite contain higher percentage of iron oxides, they actually get reduced at a faster rate. As a result the reduced samples of finer fraction contain a lower amount of iron in the oxide form. Thus from the view point of optimization of reduction process, adaptation of separate reduction procedure for each of the size fractions is not necessary. However the leaching behaviour of each of the three major fractions may be investigated to find out if they show any difference in leaching characteristics related to iron removal.

CONCLUSIONS

1- Finer size fractions of the ilmenite sample contained lower percentage of TiO_2 and higher total amount of oxides of iron.
2- Finer fractions have a higher degree of reduction with the consequence that finer fractions actually contain lower amount of iron oxide after reduction. It is concluded that as far as the optimization of reduction parameters of the given sample is concerned, a separate reduction procedure for each of the fractions is not necessary.

Higher reduction rate of finer size fractions of ilmenite sample is believed to be principally due to shorter diffusion length in these finer particles.

REFERENCES

[1] Annie George, P.N.Mohan Das; Journal of Scientific and Industrial Research, **44**, 443-450 **(1985)**.
[2] American Foundrymen's Society, Foundry Sand Handbook, **7**th Edition, **(1963)**.
[3] B.C.Agarwal, S.P.Jain; A Text Book of Metallurgical Analysis, 3rd Edition, Khanna Publishers, Delhi **(1996)**.
[4] A.S.M.A.Haseeb, M.Z.Huq, A.S.W.Kurny; Trans.Instn.Min.Metall. (Sect. C: Mineral Process. Extr.Metall.), **106**, C39-C43 **(1997)**.
[5] S.Ahmed, T.Pal, S.Mitra; J.Geol.Soc.India, **40**, 29-41 **(1992)**.
[6] R.Haque, H.S.Ray, A.Mukherjee; Trans.Indian Inst.Met., **44(5)**, 403-407 **(1991)**.
[7] D.G.Dam Gonzales, J.H.E.Jeffes; Ironmaking and Steelmaking, **14(5)**, 217 **(1987)**.
[8] M.I.El-Guindy, W.G.Daveptort; Metall.Trans, **1**, 1729 **(1970)**.
[9] R.Merk, C.A.Pickles; Canadian Inst.Min.Metall., **27(3)**, 179 **(1988)**.
[10] D.G.Jones; Trans.Int.Min.Metall., **83**, 1 **(1974)**.