Proceedings of the International Seminar on Mineral Processing Technology - 2006, Chennai, India. pp. 512 - 518.

Microwave Acid Leaching of Beneficiated Ilmenite for the Production of Syntehtic Rutile

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Abstract

Beneficiated ilmenite is an intermediate product formed by the aqueous rusting of metallised ilmenite and separation of iron oxide. This product enriched with TiO_2 by the removal of metallic iron can further be upgraded by subsequent removal of residual iron by acid leaching for the production of synthetic rutile which is a preferred titanium feedstock for the preparation of TiO_2 pigment.

This paper presents the investigations on the microwave leaching of beneficiated ilmenite wherein heating is affected by microwave energy. The effects of leaching parameters such as temperature, concentration of acid, solid-liquid ratio and duration of leaching were studied on the preferential leaching of iron in hydrochloric acid and the parameters were optimized for the maximum dissolution of iron. The effect of particle size of the solid on the degree of removal of iron was also investigated. The studies indicated that the iron dissolution increased continuously with the residence time, acid concentration, temperature and the solid to liquid ratio with microwave heating. Finer particles showed better leachability than the coarser particles in terms of iron dissolution. The x-ray diffraction analysis of the leach residue further revealed the formation of rutile phase. Microwave energy heating had resulted in phenomenal decrease in the residence time just to 40 minutes compared to 6 hours required during conventional heating for the preparation of synthetic rutile with 93% TiO_2 and less than 3% residual iron.

INTRODUCTION

Ilmenite and rutile are the principal titanium minerals, which constitute majority of the titanium feedstock for the production of Titanium metal and titanium dioxide pigment. However, fast depletion of rutile deposits worldwide coupled with the increasing demand for the TiO_2 pigment necessitated many mineral industries to resort to synthetic rutile obtained by the upgradation of abundantly available ilmenite. Although a large number of technologies have been developed for the beneficiation of ilmenite, only a few indeed are in practice. These processes comprising essentially pyro and hydrometallurgical steps can be broadly grouped into a) partial reduction of iron oxide in ilmenite followed by acid leaching ; b) near total metallisation of iron oxide in ilmenite followed by aeration and leaching and c) complete reduction of ilmenite followed by electric smelting and acid leaching.

Becher process used successfully in Western Australia for the production of synthetic rutile involves the reduction of iron component of ilmenite to the metallic form and its subsequent removal as rust. The residual iron from the beneficiated ilmenite (product after rusting) was further removed by acid leaching for the production of synthetic rutile. The process has been found suitable for the ores that are high in titania and low in iron oxides and when a reactive low grade coal is used as the reductant.

A modified process essentially involving the above unit operations with additional step of oxidation of beneficiated ilmenite prior to leaching was developed by Mohan Das et.al (1997) for the preparation of high grade synthetic rutile.

Microwave energy, which is a part of the electromagnetic spectrum between the infrared ray and the radio frequency range with wavelengths between 1m and 1mm, has been found very effective in the speedy and efficient heating of minerals by Kingman et.al, (1998). In addition, microwave heating offers several other advantages such as high throughput, low reagent consumption and precise monitoring of the treatment process. Microwave leaching of electric arc furnace dust in caustic solution as studied by Xia et.al (2000) reported that the rates of recovery of Zinc was significantly higher under microwave conditions as compared to those observed with conventional leaching. Kelley et.al (1995) have studied the effect of microwave energy heating on the reduction of oxidized ilmenite and reported faster reduction kinetics under microwave heating. This paper presents the results of the studies on leaching characteristics of beneficiated ilmenite wherein, microwave energy was used for heating the solution instead of conventional heating.

MATERIALS AND EXPERIMENTAL METHODS

Beneficiated Ilmenite

Beneficiated ilmenite used for the present investigation was prepared by aeration rusting of reduced ilmenite and subsequent separation of rust and beneficiated ilmenite from aqueous solution. The preparation of beneficiated ilmenite was reported in detail elsewhere by Mohan Das et.al.(1995). The major constituents of the above intermediate product was analysed by standard chemical analysis. The chemical composition of the beneficiated ilmenite is shown in Table 1. The results of the sieve analysis of the above product are given in Table 2. It can be seen that bulk of the mineral particles are in the size range (0.1 - 0.5) mm.

Table 1: Major Constituents of Beneficiated Ilmenite

Constituents	% By Weight
TiO_2	78.86
Total iron	13.89
Metallic iron	0.257

Table 2: Sieve Analysis of Beneficiated Ilmenite

Size Range (mm)	% By Weight	Cumulative weight percent retaining
-1 + 0.71	0.721	0.72
-0.71+0.50	11.747	12.47
-0.50+0.355	15.189	27.66
-0.355+0.250	20.106	47.76
-0.25+0.180	25.675	73.44
-0.180+0.125	21.360	94.80
-0.125+0.09	3.679	98.48
-0.09+0.063	0.993	99.47
-0.063	0.530	100.00

Microwave Digester

A PC controlled microwave digester, (ETHOS SEL, Milestone, Italy) was employed for carrying out the leaching studies. Microwave digester with Teflon coated heating cavity has 12 Teflon vessels rotating inside the cavity. A safety shield made up of HTC plastic covered these vessels. Samples for the leaching experiments were taken in these vessels. The temperature and duration of microwave heating were controlled and monitored by a sensor provided in the digester. Rotating magnets driven by motors generated a rotating magnetic field below the microwave cavity. Stirring effect within the vessel was achieved by placing a magnetic spin bar. A ventilation provision provided in the digester enables the cooling of the sample after the experiment.

Instrumental Methods of Analysis

X-Ray Diffraction Studies

The X-ray diffraction studies were carried out by the powder diffraction technique using Philips X-ray Difractometer with CuK_α monochromatic radiation. The characteristic peaks in the diffractogram were indexed using the standard values of d-spacings. The result of the XRD analysis of the beneficiated ilmenite is shown in Table 3.

Table 3: XRD Analysis of Beneficiated Ilmenite

2Theta	d(A^0)	Description	Assignment
25.37	3.507	Strong	Brookite
32.47	2.755	Medium	Pseudobrookite
35.59	2.519	Weak	Iron oxide
40.91	2.204	Weak	Brookite
48.21	1.885	Medium	Brookite

Table 4: XRD Analysis of Leach Residue of Rusted Ilmenite

2 Theta	d (A^0)	Description	Assignment
25.40	3.503	Strong	Brookite
27.58	3.230	Weak	Rutile
32.50	2.752	Medium	Pseudo-brookite
36.45	2.463	Weak	Rutile
37.20	2.414	Weak	Brookite
40.96	2.201	Weak	Iron oxide
48.26	1.884	medium	brookite
51.91	1.759	Weak	Brookite
56.19	1.636	Weak	Iron oxide

Scanning Electron Microscopy

The Scanning electron microscopic investigations of the beneficiated ilmenite and microwave leached samples were carried out using GEOL JSM 5600. The samples were fixed on to an adhesive tape pasted over the stud. Gold was sputtered on the mineral sample and the micrographs was taken at the required magnification depending on the surface selected for the studies.

EXPERIMENTAL METHODS

About 30 mL of 7M HCl and 5 g of beneficiated ilmenite were taken in a Teflon vessel of the microwave digester and heated to the required set temperature. Leaching of the sample was continued for 30 minutes duration in the microwave digester. After the leaching, the contents in the Teflon vessels were cooled and filtered. The residue was washed with water and dried in an oven. The residue was analysed for total iron and TiO_2 content. Leaching parameters such as temperature, residence time, acid concentration and solid-liquid ratio were optimised by varying one of the parameters while all the other parameters remained unaltered.

Optimisation of Acid Concentration

Beneficiated ilmenite samples were leached with HCl. The concentration of the acid was varied at 6M, 7M, 9M and 11.3M (concentrated acid), while the other variables such as temperature, residence time and solid liquid ratio were kept constant. The samples of residue after leaching were filtered, washed, dried and analysed. The effect of acid concentration on the dissolution of iron from beneficiated ilmenite is shown in Figure 1.

Optimisation of Leaching Temperature

Microwave leaching experiments were carried out at temperatures 60, 70, 80, 90 and 100 o C for studying the effect of temperature on the dissolution of iron from beneficiated ilmenite.All the leaching experiments were carried out for 30 minutes with 7M HCl, at solid – liquid ratio of 1: 6 (w/v). The variation of iron dissolution as a function of temperature is shown in Figure 2.

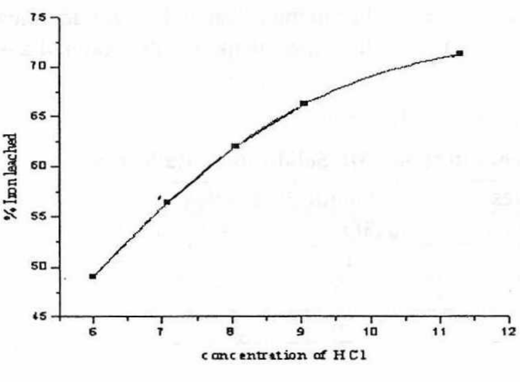

Fig. 1: The Effect of Acid Concentration on the Dissolution of Iron

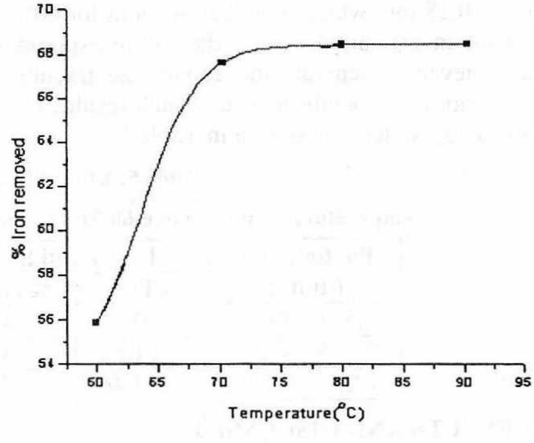

Fig. 2: Dissolution of Iron as a Function of Temperature

Optimisation of Residence Time

For optimising leaching time, the other three parameters such as acid concentration, temperature and solid-liquid ratio were kept constant and the residence time was varied at 5, 10, 20, 40 and 50 minutes. Figure 3 shows the effect of residence time on the removal of iron from beneficiated ilmenite during microwave leaching.

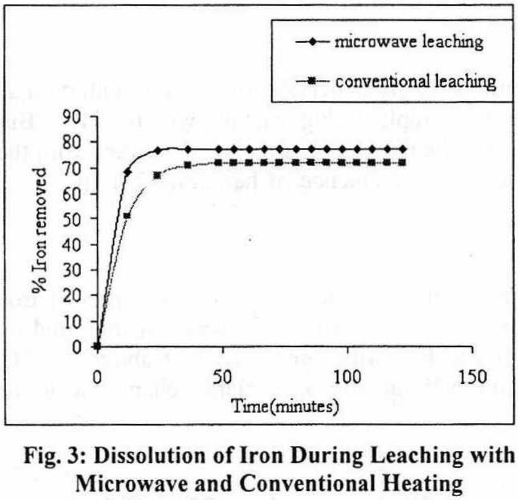

Fig. 3: Dissolution of Iron During Leaching with Microwave and Conventional Heating

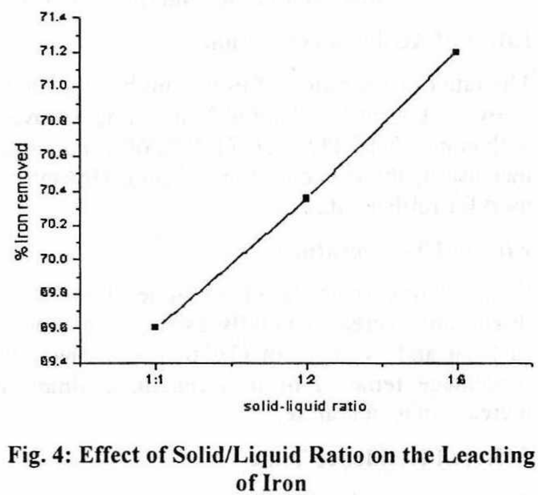

Fig. 4: Effect of Solid/Liquid Ratio on the Leaching of Iron

Optimisation of Solid - Liquid Ratio

In order to study the effect of relative amounts of solid and liquid on the degree of iron dissolution during microwave leaching, experiments were carried out at solid - /liquid ratios of 1:1. 1:2 and 1: 6 (w/v). All the leaching experiments were carried out at 90 ° C , for 60 minutes in 7 M HCl. The results are shown in Figure 4.

Effect of Particle Size on Leaching

Rusted ilmenite samples of different sieve fractions were leached at optimum conditions derived from the above experiments. Three different sieve fractions, namely, -0.5+0.355, -0.355+0.25 and – 0.25+0.18 mm which, together account for 60% of the bulk of the beneficiated ilmenite was taken up for the investigations. In another set of experiments, the bulk of the beneficiated ilmenite was ground and sieved to separate the above size fractions, which were subsequently leached under identical conditions. The analysis of the leach residue obtained in each of the experiments for the residual iron and TiO_2 content are shown in Table 5.

Table 5: Effect of Particle Size on Leaching

Temperature. - 90°c; Time-60 Min.; Acid Concentration-7M; Solid-Liquid Ratio-1: 6

Particle size (mm)	Unground Samples		Ground Samples	
	%TiO_2	%Total Iron	%TiO_2	%Total Iron
-0.5 +0.355	90.51	4.43	91.45	3.25
-0.355 +0.25	91.52	4.21	92.64	3.32
-0.25 +0.18	92.46	3.99	93.16	3.17

RESULTS AND DISCUSSION

The selective leaching of iron present both in the form of ferrous ($FeO.TiO_2$, ilmenite) and ferric ($Fe_2O_3.TiO_2$, Psuedobrookite) state in the beneficiated ilmneite can be described by the following chemical reactions.

$$2\,FeO.\,TiO_2 + 2HCl \rightarrow Fe^{2+} + TiO_2 + 2Cl^- + 2OH^-$$

$$Fe_2O_3.TiO_2 + 3\,HCl \rightarrow 2\,Fe^{3+} = TiO_2 + 3\,Cl^- + 3\,OH^-$$

The main parameters that can influence the rate of this reaction are particle size, acid concentration, temperature, solid liquid ratio, and the residence time.

Effect of Acid Concentration

The rate of dissolution of iron from beneficiated ilmenite strongly depended on acid concentration as shown in Figure 1. About 49% iron was removed from the sample during leaching with 6M HCl. But with conc. HCl (11.3 M), 71.27% of iron was removed. The removal of iron was increased with the increase in the concentration of acid. However, in view of convenience of handling, 7M HCl was used for further studies.

Effect of Temperature

Figure 2 represents the effect of leaching temperature on the dissolution of iron. The rate of iron dissolution increases rapidly as the temperature of leaching increased. This was also reported by Jackson and Wadsworth (1976) and Sinha (1984). It can be further observed that above 80 ° C, percentage removal of iron remained almost constant without any appreciable change with the increase in temperature.

Effect of Residence Time

As seen from the Figure 3, even at a residence time of 10 minutes, about 70% of the iron in beneficiated ilmenite was removed by leaching in presence of microwave heating compared to only

50% removal in the corresponding period during leaching with conventional heating. Investigations further suggest that any further increase in the residence time beyond 15 minutes had no significant effect on the iron removal.

Effect of Solid-Liquid Ratio

The weight percentage dissolution of iron as a function of solid –liquid ratio is shown in Figure 4. It is evident from the above figure that the percentage dissolution increased with the decrease in solid liquid ratio as observed by Biswas et.al (1994) during their investigations on the conventional leaching of Bangladesh ilmenite in HCl before and after roasting.

The Effect of Particle Size and Grinding

The effect of particle size of the beneficiated ilmenite and that of grinding on the dissolution of iron in HCl is shown in Table 3. The extent of iron dissolution in the acid increased with the decrease in particle size. The same phenomenon was observed by Biswas et.al (1994) and Olanipekun (1999) during their investigations on conventional leaching of raw ilmenite in hydrochloric acid. The above results further indicate that the extent of iron removal was higher with the ground samples compared to unground samples of same particle size range. This observation was in full agreement with the findings of Sasikumar et.al (2004) who have demonstrated that the milled samples in addition to increase in the surface area and owing to other factors such as structural disorder, enhanced strain, liberation of select crystal faces are more amenable to leaching compared to unmilled samples.

The microwave irradiation has shown great advantage on the removal of iron from the point of view of kinetics and the quality of the final product compared to the results obtained with conventional heating. The acceleration of reaction rate under microwave assisted leaching was justified due to the following facts as suggested by Al-Harahsheh et.al (2004):

- The existence of non-thermal effect reduces the activation energy for the reactions.
- The super heating effect occurring during dielectric heating is making the temperature independent of reaction conditions.
- Large thermal current generated during microwave heating result in increased temperature gradient between the solid and the liquid to assist the mass transport at the interface.
- Increase in the surface area due to cracks initiated when solid particles contain more than one phase with different heating rates.

XRD Analysis

XRD analysis of the rusted ilmenite showed the presence of majority of the peaks corresponding to brookite/ Anatase phases. A few minor peaks corresponding to rutile were also seen in the diffractogram. The appearance of peaks due to iron oxide in the pattern also indicates that the removal of iron oxide during rusting was incomplete. A similar mineralogical phase characteristics were seen in the case of leached samples. However, the intensity and number of peaks due to iron oxide in the leached samples were less essentially due to the removal of iron phase during leaching.

SEM Studies

The scanning electron micrograph of beneficiated ilmenite prior to oxidation (Fig. 5a) clearly shows the needle like iron oxide admixture along with the ilmenite grains. The iron oxide phase formed during the corrosion of metallic iron was found adhered to the crevices and voids created by the removal of metallic iron. The reoxidation of the beneficiated ilmenite had resulted in the formation of cracks across the solid grains of ilmenite (Fig.5b). Scanning electron micrographs (Fig. 5c to 5d) of the leached products illustrate the progress of iron removal from beneficiated ilmenite during leaching as evident from large number of cavities and voids in the micrographs.

CONCLUSIONS

Synthetic rutile of about 94% TiO_2 and less than 3% residual iron could be obtained under optimum conditions of leaching of beneficiated ilmenite employing microwave heating instead of conventional heating. The microwave irradiation has shown great advantage on the removal of iron from the point of view of kinetics and the quality of the final product compared to the results obtained with conventional heating. While the increase in acid concentration, temperature and residence time had positive effect on the degree of the iron removal; the increase in solid to liquid ratio had a negative effect. Freshly ground samples have shown greater amenability for acid leaching compared to unground samples of same particle size. The advantage of reoxidation of beneficiated ilmenite prior to acid leaching for improving the leachability of the solid could be well explained by the formation of cracks across the grains (as supported by the micrographs) which in turn aid the penetration of the acid.

ACKNOWLEDGEMENT

We would like to thank Director, RRL, Trivandrum for providing the facilities for carrying out the work. We also thank Department of Science and Technology, Ministry of Science and Technology , Govt. of India for the financial assistance with which the work was carried out. Thanks are due to Dr. Shyamaprasad and Dr. Peter Koshy for helping in the XRD and SEM investigations.

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