EFFECT OF MECHANICAL ACTIVATION AND IRON POWDER ADDITION ON ACIDIC LEACHING OF PSEUDORUTILE

Güven YARKADAŞ, H.Özkan TOPLAN, Kenan YILDIZ

Sakarya Üniversitesi, Metalurji ve Malzeme Mühendisliği, 54187, Sakarya
kenyil@sakarya.edu.tr

ABSTRACT

This study presents the effect of mechanical activation on iron removal from pseudorutile to obtain synthetic rutile by hydrochloric acid leaching with or without iron addition as a reducing agent. Iron and titanium extraction efficiencies in leaching for 3 h without iron addition are 64% and 49%, respectively. After mechanical activation of pseudorutile for 30 min, iron and titanium extraction efficiencies increased to 82% and 62%, respectively. In case of iron addition to leaching step, mechanical activation has no prominent effect on the iron and titanium extractions. On the contrary, most of iron content in pseudorutile dissolved but titanium oxide remains at the solid part. Effect of iron addition to the leaching step was investigated with x-ray diffraction analysis of solid part.

Keywords: acidic leaching, mechanical activation, pseudorutile, rutile

PSEUDORUTİLİN ASİDİK LİÇİNE DEMİR İLAVESİ VE MEKANİK AKTİVASYONUN ETKİSİ

ÖZET

Bu çalışma, sentetik rutil elde etmek için, redükleyici olarak demir ilaveli veya ilavesiz sülfürik asit liçiyle pseudorutilden demirin giderilmesi üzerine mekanik aktivasyonun etkisini sunmaktadır. Demir ilave edilmeksizin 3 saatlik liç işlemlerinde demir ve titanyum ekstraksiyon verimleri sırasıyla %64 ve %49 dur. Pseudorutilin 30 dakikalık mekanik aktivasyonundan sonra demir ve titanyum ekstraksiyon verimleri sırasıyla %82 ve %62 ye çıkmıştır. Liç kademesine demir ilave edilmesi durumunda, mekanik aktivasyonun demir ve titanyumun ekstraksiyonlarına belirgin bir etkisi olmamıştır. Aksine pseudorutildeki demir içeriğinin çoğu çözünmüş ancak titanyum katı kısımda kalmıştır. Demir ilavesinin liç kademesine etkisi, katı kısmın x-ışını difraksiyon analizi ile incelenmiştir.

Anahtar Kelimeler: asidik liç, mekanik aktivasyon, pseudorutil, rutil

1. INTRODUCTION

Pseudorutile is an intermediate product of the weathering of ilmenite. It was identified a new compound with hexagonal symmetry and with composition $Fe_2Ti_3O_9$ as the main constituent of the altered product. In other words, pseudorutile is a new mineral intermediate between ilmenite and rutile in the natural alteration of ilmenite [1,2].

Titanium dioxide is an important intermediate in the manufacture of paints, pigments, welding-rod coatings, ceramics, papers and in other areas of chemical industry. White paints are primarily titanium dioxide and historically have been produced by two processes, the sulphate process which uses ilmenite ($FeTiO_3$) as a raw material, and the dry chlorination process which uses rutile (TiO_2) as a raw material. The sulphate process is well known and widely applied but is lengthy and costly. The dry chlorination process presently enjoys more favorable economics than the sulphate process and generates less waste material for disposal [3,4].

The production of synthetic rutile from ilmenite was widely investigated in literature. Besides acidic leaching of ilmenite [5-7] and alkaline leaching of ilmenite [8], the studies about the effects of mechanical activation on dissolution of ilmenite were presented in literature [8-11]. Mechanical activation of minerals by intensive grinding is a non-traditional way of influencing the processes in extractive metallurgy. The resulting creation of fine particles, the increase in specific surface area and the formation of defective structures accelerate leaching in hydrometallurgy. By introducing a high degree of structural disorder, the mechanical activation of minerals makes it possible to reduce their decomposition temperature [12-14].

This study presents the effect of mechanical activation on iron removal from pseudorutile to obtain synthetic rutile by hydrochloric acid leaching with or without iron addition as a reducing agent.

2. MATERIALS AND METHOD

2.1. Materials and characterization

Pseudorutile was obtained from Eczacıbaşı Doğa Madencilik Tic.A.Ş. TiO_2 and Fe_2O_3 contents in pseudorutile, analyzed by X-ray fluorescence (XRF) analysis, are 50.15% and 22.67%, respectively.

Mechanical activation of pseudorutile was performed in a planetary mono mill (Fritsch Pulverisette 6) under the following conditions: weight of the sample 10 g, weight and diameter of tungsten carbide (WC) balls 200 g and 10 mm, respectively, grinding bowl 250 mL WC, grinding time 30 min, speed of main disk 600 rpm, grinding process dry.

Morphological analysis of pseudorutile after mechanical activation was analyzed by scanning electron microscopy (SEM, Jeol 6060 LV).

The phase analysis of pseudorutile and the solid products after leaching step were done by X-ray diffraction analysis (XRD, Rigaku Ultima).

2.2. Experimental procedure

Leaching of the pseudorutile was performed with 20% HCl at solid/liquid ratio of 1/40 at boiling temperature (110°C). The experiments were carried out using a 500 cm^3 three-necked glass reactor provided with a reflux condenser and magnetic stirring. The desired volume of hydrochloric acid was poured in the reactor, it was heated to the desired temperature and 5 g pseudorutile was added. In some experiments, 0.5 g iron powder was added after a certain time (30 min). After elapse of the reaction period, the slurry was filtered and the residue was washed with 100 cm^3 of 3% HCl. The washed residue dried at 110°C, calcined at 900°C for 1 h. The iron and titanium contents were determined in the filtrate by wet analytical methods.

3. RESULTS AND DISCUSSION

3.1. Characterization of pseudorutile

X-ray diffraction analysis of pseudorutile was given in Figure 1. The main component in the ore is pseudorutile. The other components in the ore were ilmenite (Fe_2TiO_3), rutile (TiO_2), pseudobrookite (Fe_2TiO_5) and fayalite (Fe_2SiO_4).

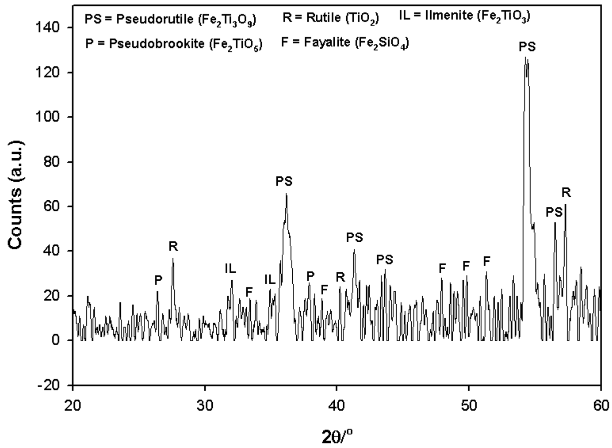
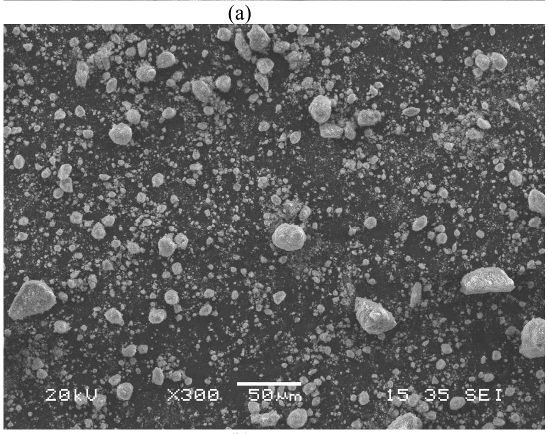


Figure 1. X-ray diffraction analysis of pseudorutile

(a)



(b)

Figure 2. Scanning electron micrographs of (a) non-activated and (b) activated pseudorutile for 30 min.

In Figure 2, scanning electron micrographs of non-activated and activated pseudorutile are shown. The particle size of non-activated pseudorutile was over 150 µm. The particle size of activated pseudorutile was less than 50 µm. The particle size was decreased and the surface area was increased with mechanical activation. Increasing the surface area of pseudorutile speeds up the kinetics of the leaching reactions.

3.2. Acidic leaching of pseudorutile

Pseudorutile is an inactive mineral from which the selective removal of iron is rather difficult. The reactivity of ilmenite can be enhanced by chemical reduction in solution using a suitable metal as a reducing agent.

Pseudorutile is dissolved in hydrochloric acid as follow,

$$Fe_2Ti_3O_9+12HCl \rightarrow 2FeCl_3+3TiOCl_2+6H_2O \quad (1)$$

It is pointed out [4] that this large amount of hydrochloric acid is impractical in hydrometallurgical processes from an economic view-point unless it can be recovered for recycling purposes.

Iron metal is used as a reducing agent to promote the leaching of pseudorutile in hydrochloric acid. The reactions taking place after adding of iron powder are as follows:

$$Fe + 2HCl \rightarrow FeCl_2 + H_2 \quad (2)$$

$$Fe+2FeCl_3 \rightarrow 3FeCl_2 \quad (3)$$

$$Fe + 2TiOCl_2 + 4HCl \rightarrow 2TiCl_3 + FeCl_2 + 2H_2O \quad (4)$$

A portion of the added Fe powder dissolves in HCl forming ferrous chloride and hydrogen gas. The dissolved ferric chloride will be reduced by Fe powder to form ferrous chloride. The oxidation reaction of Ti^{3+} to Ti^{4+} is assumed to be accompanied by reduction of the ferric iron (hematite) in the ore to the soluble ferrous chloride as follow:

$$2TiCl_3 + Fe_2O_3 + 2HCl \rightarrow 2TiOCl_2 + 2FeCl_2 + H_2O \quad (5)$$

After addition of Fe powder, the amount of total Ti in solution and the hydrolysis of $TiOCl_2$ takes place as follow[4]:

$$TiOCl_2 + H_2O \rightarrow TiO_2 + 2HCl \quad (6)$$

In Figure 3, titanium and iron extraction efficiencies in acidic leaching of pseudorutile without addition of Fe powder as reducing agent and the effect of mechanical activation on this process were given. As seen from the figure, mechanical activation increased the extraction efficiencies for titanium and iron. Without mechanical activation of pseudorutile, the extraction efficiencies for iron and titanium in acidic leaching for 180 min were 64% and 47%, respectively. These values increased to 81% for iron and 61% for titanium in same leaching conditions after mechanical activation of pseudorutile.

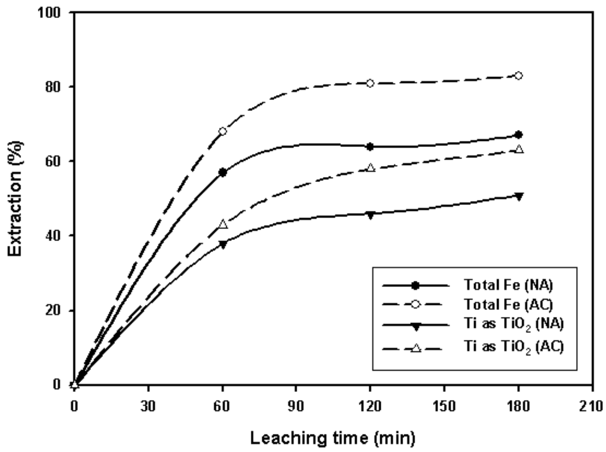


Figure 3. Acidic leaching of pseudorutile without Fe addition (NA: non-activated, AC: activated ore)

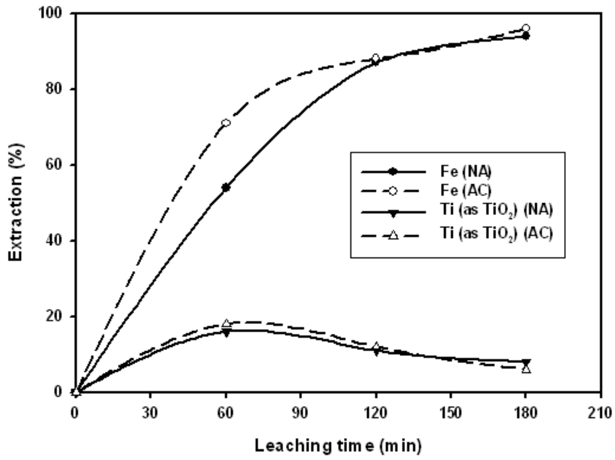


Figure 4. Acidic leaching of pseudorutile with Fe addition (NA: non-activated, AC: activated ore)

Titanium and iron extraction efficiencies in acidic leaching of pseudorutile with addition of Fe powder as a reducing agent were given in Figure 4. The main purpose of Fe addition to aciding leaching of pseudorutile, as mentioned in the reactions (2-6), is to provide TiO_2 in the solid part and the removal of iron from the ore into the solution. As seen from Figure 4, iron extraction from the ore was increased, on the contrary titanium was not dissolved and precipitated as TiO_2. The mechanical activation has no prominent effect on iron and titanium extractions in acidic leaching of pseudorutile with iron addition. About 8% of titanium was dissolved from the ore but about 93% of iron dissolved in acidic leaching and the removal of iron from pseudorutile was achieved with acidic leaching after Fe addition. The phase analysis of solid parts for two samples after the leaching of pseudorutile were carried out with x-ray diffraction analysis. This analysis is given in Figure 5.

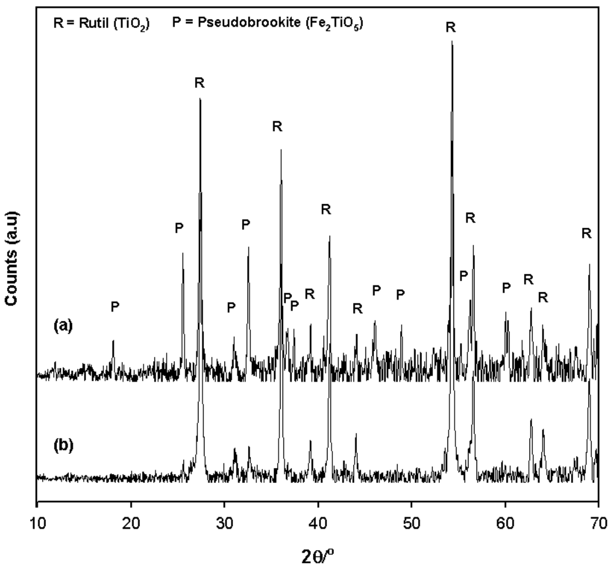


Figure 5. X-ray diffraction analysis of the solid products: (a) calcined solid part, no Fe addition; (b) calcined solid part, with Fe addition.

As seen from Figure 5, the main phases in the solid after acidic leaching of pseudorutile without Fe addition are rutile (TiO_2) and pseudobrookite (Fe_2TiO_5). On the other hand, the main phase in the solid after acidic leaching of the ore with Fe addition is rutile. Pseudobrookite is small contents in the solid and the solid with high rutile content was obtained by acidic leaching with Fe addition.

4. CONCLUSIONS

The addition of iron during acidic leaching of pseudorutile produces Ti^{3+} in solution and expected to have a main role in accelerating the leaching of pseudorutile. About 93% of iron was removed from the ore and the resulting solid has a high content rutile (more than 90%) and a small quantity of pseudobrookite (less than 7%). Mechanical activation of pseudorutile as a pre-treatment accelerated the leaching of the ore, espescially in case of no-Fe addition to the leach step.

Acknowledgement

This study was supported financially by Sakarya University (Project No: BAPK 2007-01-08-005)

REFERENCES

[1] I.E.Gray, A.F.Reid, "The structure of pseudorutile and its role in the natural alteration", The American Mineralogist, Vol 60, pp.898-906, 1975.

[2]www.handbookofmineralogy.org/pdfs/pseudorutile.pdf

[3] E.A. Abdel-Aal, I.A. Ibrahim, A.A.I. Afifi, A.K. Ismail, "Production of synthetic rutile from Egyptian ilmenite ore by a direct hydrometallurgical process", 2nd International Conference on Processing Materials for Properties, TMS (The Minerals, Metals & Materials Society), pp.955-960, 2000.

[4] I.A. İbrahim, M.H.H.Mahmoud, A.A.I.Afifi, B.A. El-Sayed, "Direct hydrochloric acid leaching of an Egyptian ilmenite ore for production of synthetic rutile", Hydrometallurgy 2003 – 5th International Conference in Honor of Professor Ian Ritchie – Volume I: Leaching and Solution Purification, TMS (The Minerals, Metals & Materials Society), pp.555-564, 2003

[5] E.Olanipekun, "A kinetic study of the leaching of a Nigerian ilmenite ore by hydrochloric acid", Hydrometallurgy, 53, 1-10, 1999.

[6] T.Ogasawara, R.V.V. Araujo, "Hydrochloric acid leaching of a pre-reduced Brazilian ilmenite concentrate in an autoclave", Hydrometallurgy, 56, 203-216, 2000.

[7] B.Liang, C.Li, C.Zhang, Y.Zhang, "Leaching kinetics of Panzhihua ilmenite in sulfuric acid", Hydrometallurgy, 76, 173-179, 2005.

[8] A.M.Amer, "Alkaline pressure leaching of mechanically activated Rosetta ilmenite concentrate", Hydrometallurgy, 67, 125-133, 2002.

[9] C.Li, B.Liang, L.Guo, Z.Wu, "Effect of mechanical activation on the dissolution of Panzhihua ilmenite", Minerals Engineering, 19, 1430-1438, 2006.

[10] C.Sasikumar, D.S.Rao, S.Srikanth, B.Ravikumar, N.K. Mukhopadhyay, S.P.Mehrotra, "Effect of mechanical activation on the kinetics of sulfuric acid leaching of beach sand ilmenite from Orissa, India", Hydrometallurgy, 75, 189-204, 2004.

[11] C.Li, B.Liang, S.P.Chen, "Combined milling – dissolution of Panzhihua ilmenite in sulfuric acid", Hydrometallurgy, 82, 93-99, 2006.

[12] P.Balaz, Extractive Metallurgy of Activated Minerals, Elsevier Science B.V., Amsterdam, 2000.

[13] G.Yarkadaş, K.Yıldız, "Effect of mechanical activation on alumina extraction from alunite ore and its thermal behavior", Mineral Processing and Extractive Metallurgy (TIMM C), 117(3), 175-178, 2008.

[14] G.Yarkadaş, K.Yıldız, "Effects of mechanical activation on the soda roasting of chromite", Canadian Metallurgical Quarterly, 48(1), 69-72, 2009.