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Abstract

Samples of ilmenite ore, 3 g each, were leached with 125 ml of a mixture of concentrated HCl–ethylene glycol at the boiling point of the leaching solution. The leaching times were in the range 70–130 h. The residues after leaching were analyzed by Energy Dispersive X-Ray Fluorescence (EDXRF) spectrometry. Only Fe and Mn were substantially leached out from the ore while other elements (Y, Zr, Nb, Sn and W) remained unleached.

1. Introduction

The southern part of Thailand is known to be the richest ore deposit region of the country. Of the minerals found in this region the most prominent is cassiterite, among the others are: tantalite–columbite, monazite, zircon and scheelite, to name but a few. The co-existence of these minerals is similar to other mineral deposits around the world [1,2].

The leaching of the titanium ore ilmenite with hydrochloric acid in order to upgrade it to synthetic rutile continues to be of interest [3,4], even though there have been reports of many other methods for achieving this, some of which have been adopted on a commercial scale [5]. The advantage of hydrochloric acid leaching is that it has no effluent disposal problem and the acid may be recycled.

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Girgin and Turker [3] have reported on the leaching of Fe from ilmenite by using: (1) concentrated hydrochloric acid and (2) mixtures of concentrated hydrochloric acid and organic solvents such as methanol, ethanol, and ethylene glycol at various acid concentrations. The temperature used in their studies was the boiling point of each corresponding mixture. The leaching period was 60 min; at 10 min intervals a small fraction of the liquid was drawn off and measured for Fe content by atomic absorption spectrometry. The results were that Fe was leached out best, after 60 min, by the mixture of concentrated hydrochloric acid–ethylene glycol with 9 M acid concentration. This mixture can leach Fe 2.5 times better than concentrated hydrochloric acid alone and 1.4 times better than an hydrochloric acid–ethanol mixture.

This report is complementary to the work of Girgin and Turker. Starting with their optimum conditions (i.e., using a concentrated HCl–ethylene glycol mixture with a 9 M HCl concentration as leachant and the leaching temperature at its boiling point), the experiments were carried out as a function of leaching time, from 70 h to 130 h. Analyses for the composition of the initial ore and the residue after leaching were carried out using an Energy Dispersive X-Ray Fluorescence (EDXRF) spectrometer. Ilmenite ore itself is only partially soluble in acid and the residue is the insoluble part of the ore. Since atomic absorption can only analyze samples in solution form, the analysis of the insoluble residue is thus beyond the atomic absorption capacity. This problem, however, can be handled quite readily by EDXRF spectrometry.

2. Experimental

2.1. Chemicals and equipment

Concentrated ilmenite was obtained from the Office of Mineral Resources Region 1 Songkla, Thailand. In appearance it is like a black sand with a grain size of approximately 60 mesh (0.25 mm) and was used in the experiments as received without any further modification.

The chemicals used were: hydrochloric acid (A.R., J.T. Baker), ethylene glycol (G.P.R., BDH Chemicals Ltd.), titanium dioxide (A.R., E. Merck), manganese dioxide (A.R., Carlo Erba), iron(III) oxide (AG, E. Merck), yttrium oxide, zirconium oxide, niobium oxide, tungsten oxide (all AG, Fluka). These metal oxides were used in the preparation of standards for quantitative determination of the corresponding metals in samples by EDXRF spectrometry. They were heated at 110°C for 3 h before use. Pure corn starch (CPC/Aji, Thailand) was used as a binder and pre-mixed with the ore samples or the standard metal oxides prior to pressing into pellets for quantitative analysis by EDXRF.

An orbital shaker (Adgle Kuhner, AG, Schweiz) was used for mixing corn starch and ore samples or standard oxides (5:1 ratio) into homogeneous mixtures. The maximum speed of this shaker is 500 cycle/min but the suitable speed in this experiment was set at 315–320 cycle/min. The mixtures were shaken for 24 h before being pressed into pellets. A die (SPECAC, Kent, England) and hydraulic press (Ring Press 00-25, Research and Industrial Instruments Co.) were used for pressing 4 g of mixed powder samples into disk-like pellets of 32 mm diameter to be used when acquiring EDXRF spectra. Each pellet was pressed at a pressure of 1.2×10^8 N m^{-2}.

The Energy Dispersive X-Ray Fluorescence (EDXRF) spectrometer (Spectrace 5000, Spectrace Instruments, Inc., Mountainview, California) is of the tube type. The excitation X-ray is generated from a tube using a Rh target. The detector is Si(Li) with a resolution of 164 eV for the Mn Kα line. This spectrometer is fully computerized and controlled by the software EDXRF version 1.35. The Central Equipment Division of the Faculty of Science acquired the XRD spectra the using an X-Ray Diffractometer (XRD) (Philips, PW3710 with Cu Kα radiation).

2.2. Leaching of ore

The apparatus is similar to that used by Girgin and Turker [1]. The 250 ml round bottom flask contains 3 g of ore in 125 ml of leachant (91 ml of concentrated HCl + 34 ml of ethylene glycol) and a magnetic stirrer. The heating was furnished through a sand bath. The boiling point was 106–109°C. The leaching was carried out for various times: 70, 85, 100, 115, and 130 h. In the first hour of leaching the solution was greenish-yellow and subsequently turned to brownish-green. At the end of the leaching the residue was filtered and washed with water. After air drying the residue was weighed. All of the residues were grey in colour.

2.3. Samples analyses

The composition of the ore and the residues after leaching was analyzed by EDXRF. The pressed pellet can be considered as an infinitely thick sample [6]. In acquiring the EDXRF spectra each sample pellet was recorded four times by rotating the pellet 90° each time to ensure reproducibility of counting data [7]. The standard calibration graph method was employed for the quantitative analyses.

Intensity of the Kα line is used for Mn, Fe, Y, Zr, Nb, and Sn while the Lα line is used for W. There are two overlaps of lines among these elements; one is between Mn Kβ and Fe Kα, the other is Y Kβ and Nb Kα. To avoid the counting uncertainties of Fe Kα and Nb Kα, one could consider using the Fe Kβ and Nb Kβ lines, which are free of the overlapping problem. This alternative is, however, discarded due to the low counting of the two corresponding Kβ lines, which would have considerably larger statistical error in counting. Since the concentrations of Mn and Y are very low (Table 2) compared to Fe and Nb, respectively, this overlap problem should contribute only a very small error in reading the intensities of Fe Kα and Nb Kα lines. Furthermore, in the vicinity of Nb Kβ there is also the Compton peak of the Rh Kα line. This makes the selection of Nb Kβ even more unfavourable.

3. Results and discussion

3.1. Extraction efficiency

In an attempt to systematically compare the results from all the experiments, the extent of leaching (EF) was taken as the working parameter to be considered (Table 1).

Table 1
Summary of data from the leaching of ilmenite ore (3 g ore, 125 ml leachant)

Expt. no.	Leaching time (h)	EF (%)
1	70	49.0
2	85	46.9
3	100	53.2
4	115	55.1
5	130	36.1

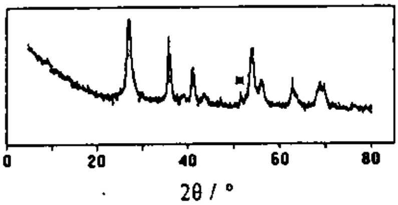

Fig. 1. XRD spectrum of the residue after leaching. The pattern is that of rutile, except that the asterisked peak is due to cassiterite.

3.2. Samples analyses

The XRD spectrum of the residue (Fig. 1) shows that its main composition is rutile with a trace of cassiterite, SnO_2. The amount of cassiterite in the residue as judged from XRD spectra varies from one experiment to the other: in some samples its peak (asterisked in Fig. 1) was seen clearly while in the others this same peak shows up only faintly.

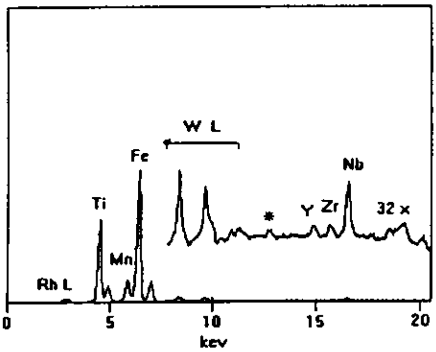

Fig. 2. EDXRF spectrum of ilmenite ore before leaching. * = sum peak of Fe K lines. Upper trace is enlarged 32-fold.

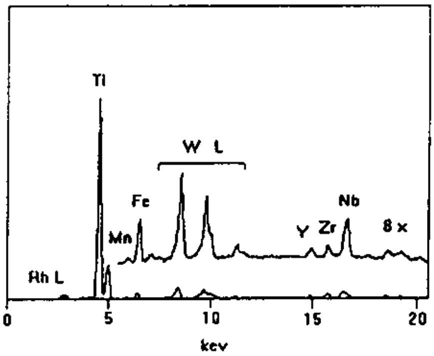

Fig. 3. EDXRF spectrum of the residue after leaching. Upper trace is enlarged 8-fold.

EDXRF spectra of ilmenite ore and residue are shown in Figs. 2 and 3. In Fig. 2 the three most intense lines, Fe Kα, Ti Kα and Mn Kα, are readily detected. There are other elements but these are at much lower concentrations (i.e., Y, Zr, Nb, W, and Sn). The same spectrum has to be enlarged by 32-fold to see the characteristic X-ray lines of these elements clearly in Fig. 2. (Since the energy of the Sn Kα line is 25.27 keV, Sn is not seen in Fig. 2. To see this line the spectrum must be acquired using a different set of parameters.) The concentrations of these metal impurities in the ilmenite ore as determined by the EDXRF method in this study are summarized in the first row of Table 2. Since Nb is present both in the ore and the residue it is quite natural to expect the presence of Ta as well in these samples, but Ta is close to W in the periodic table, so their characteristic X-ray lines (L lines) will be close together. In this case the concentration of W is much higher than Ta so the faint X-ray lines of Ta are buried under the shoulder of W lines, rendering them undetectable.

The EDXRF spectrum of the residue is shown in Fig. 3. The interesting feature is the high intensity of the Ti Kα line, while that of Fe Kα is barely seen, indicating that the residue is mainly TiO_2 with some impurities. This is in agreement with the XRD data, which show that it is rutile with a small amount of SnO_2 impurity (Fig. 1). The Sn Kα line is not covered in Fig. 3 but can be detected using another set of parameters. The

Table 2
Composition of ilmenite ore and the residues after leaching

Sample	Fe (%)	Mn (%)	Y (mg/kg)	Zr (mg/kg)	Nb (%)	Sn (%)	W (%)
Ilmenite	20.58	1.57	236	370	0.18	0.28	0.32
Expt. 1	5.64	0.45	314	740	0.31	0.43	0.69
Expt. 2	0.71	0.08	314	592	0.63	0.66	1.36
Expt. 3	0.78	0.11	412	798	0.35	0.92	0.90
Expt. 4	0.43	0.06	394	888	0.65	0.85	1.52
Expt. 5	0.53	0.06	472	962	0.59	0.73	1.47

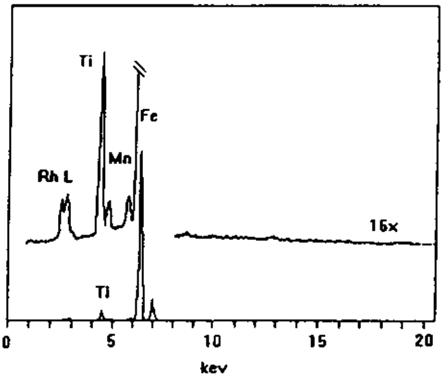

Fig. 4. EDXRF spectrum of the precipitate from filtrate. Upper trace is enlarged 16-fold.

X-ray lines of the other metal impurities are shown in the upper trace of Fig. 3, which corresponds to an 8-fold expansion of the intensity scale. The concentrations of these impurities in the residues as determined by the EDXRF method are summarized in Table 2.

Data on the composition of the residues after leaching, as shown in Table 2, indicate that the leachant works well in removing Fe and Mn from the ore. Concentrations of Fe and Mn drop from 20.58% and 1.57% to < 0.78% and < 0.11%, respectively. With the exception of the first experiment where the leaching time was the shortest, 70 h, the amount of Fe and Mn were not optimally reduced. The leachant is not capable of leaching out the other metals (i.e., Y, Zr, Nb, W, and Sn) from ilmenite. Support of this conclusion came from a qualitative study of the filtrate separated from the residue. Concentrated ammonia solution was added to the filtrate until complete precipitation was attained. The dark brown precipitate was filtered, air dried, and dried at about 100°C for a few hours. The dried solid was checked qualitatively with EDXRF showing only peaks of Ti, Mn, and Fe, as shown in Fig. 4.

The most prominent peak in Fig. 4 is that of Fe K lines, while those of Ti appear at much less intensity and those of Mn are even weaker. The most striking appearance is the complete absence of peaks from Y, Zr, Nb, W, which would appear in the region 8–20 keV, compared to Figs. 2 and 3, and Sn Kα at 25.27 keV. It can be concluded that these elements (Y, Zr, Nb, Sn and W) will remain in the residue intact. Most of the mass of Fe, Mn, and a small amount of Ti, was removed from the total mass of the ore, so the concentrations of these elements appear to increase, as shown by the data in Table 2.

The solubilities (or insolubilities) of the impurities elements in ilmenite as presented above are understandable from the chemical properties of the elements and their compounds. These elements, when co-existing in ilmenite, will be in the form of oxides or oxymetallates. In the leach solution at boiling point Fe and Mn oxides or oxymetallates are readily soluble. The oxides or oxymetallates of the other elements (Y, Zr, Nb, Sn and W) are considered refractory and resist attack by acids [8–11]. This would explain the phenomena observed in this study.

4. Conclusions

This study illustrates the capacity of the mixture HCl–ethylene glycol as leachant for Fe and Mn from ilmenite. The leachant has no effect on other elements present in the ore (i.e., Y, Zr, Nb, Sn, and W). This also illustrates the use of EDXRF for studying materials that are usually insoluble or hardly soluble, rendering their analysis by other instruments difficult or almost impossible.

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