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Hydrochloric Acid Leachability of The Sakarya-Karasu Ilmenite Concentrate

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Hydrochloric acid is used for upgrading ilmenite into synthetic rutile and in some instances to titania pigment. The quality of the titania pigment produced *via* this route is often inferior quality to those produced from sulphate and chlorination routes. The literature on hydrochloric acid leaching reports mainly 2 types of processing methods. Direct leaching without any further treatment is known to be ineffective as most ilmenites are highly insoluble in all strengths of hydrochloric acid. Therefore a pre-treatment in the form of both reduction and oxidation prior to reduction is applied to improve the solubility of ilmenite. Further improvement in ilmenite solubility was seeked by adding catalysts to the hydrochloric acid leach. In this study, the experimental details, analytical results and interpretations of the hydrochloric acid leachability of the Sakarya-Karasu ilmenite concentrate are discussed.

Key Words: Leachability, Sakarya-Karasu ilmenite.

INTRODUCTION

Direct leaching of ilmenite at atmospheric pressure is generally known to be very slow and in most cases only limited iron removal can be achieved even after long leaching times. There were attempts to increase the reaction rates. Such attempts have utilized elevated pressures and temperatures. The basis of the hydrochloric acid leach is expressed in the following reaction equation:

$$FeTiO_3 + 2HCl \rightleftharpoons TiO_2 + FeCl_2 + H_2O$$

Marshall and McMahon[1] leached a ground Norwegian ilmenite containing 45.1 % TiO_2, 11.3 % Fe_2O_3, 34.5 % FeO and 5.0 % MgO initially with 10 % hydrochloric acid for 1 h and then with 20-22 % hydrochloric acid for 7 h at boiling point. The treated product was upgraded to 73-78 % TiO_2. Kulling and Steinhausen[2] leached a similar ilmenite containing 44.3 % TiO_2, 33.9 % Fe, 5.3 % MgO and 0.3 % CaO with 37.7 % hydrochloric acid for 3 h at boiling point and obtained a product containing 88.4 % TiO_2, 1.2 % Fe and 0.6 % MgO + CaO. However, none of these products were pigment grade as the TiO_2 content of the final product was well below the required > 99 %.

Grohmann *et al.*[3] patented a process for the continuous digestion of ilmenite with concentrated hydrochloric acid at 65-105 ºC for more than 4 h. Their leaching process was done in a continuous flow system of two or more reactors of high mixing intensity at atmospheric pressure. The reactors were arranged in series with the reagents flowing in the same direction, with the temperature rising from 65 to 105 ºC due to the exothermic nature of the reaction. The final stage of leaching achieved a titanium extraction of 97 %. The resulting digestion solution was continuously withdrawn from the last reactor and processed further to obtain TiO_2 pigment.

EXPERIMENTAL

The direct acid leaching tests on Sakarya-Karasu ilmenite concentrate involved leaching with an azeotropic concentration, 20.24 % (w/v) HCl having a boiling point of 105 °C. The 20.24 % (or simply 20 %) HCl is the preferred acid concentration because hydrochloric acid with this concentration is readily and economically produced. The use of 20 % HCl is also encouraged by the fact that since the temperature at which leaching is done has a significant effect on leaching kinetics and titanium losses. On the other hand, the disadvantage of using 20 % HCl is that in a commercial operation it limits the concentration of ferrous chloride in the leach liquor to about 22 % w/w, which is below the upper solubility limit of ferrous chloride in hydrochloric acid. High pressure leaching has been proposed to allow the use of higher temperatures and higher acid concentrations, but such techniques require special construction materials and are expensive to implement. For the leach a charge of about 50 g of ilmenite and 350 mL of 20 % hydrochloric acid solution was placed in the flask that was heated until the liquor boil. The boiling time, excluding heat-up time, was 6 h in both tests. About 10 mL of liquor samples were collected at 1, 2, 4 and 6 h intervals for the determination of total iron dissolved in the solution. The withdrawn volume was compensated by the addition of same amount of fresh acid to the reactor. The dissolved iron content in the solution was determined by titrating with potassium dichromate.

At the end of the leach the hot liquor was filtered from the solids which were then washed with a 2 % (w/v) HCl and finally washed with water. The experimental conditions and oven-dried weights of the recovered solids are shown in Tables 1 and 2. The final filter cake was dried at 100 °C for 16 h and analyzed by XRF.

TABLE-1
EXPERIMENTAL CONDITIONS OF SAKARYA-KARASU ILMENITE FOR THE 20 % (w/v) HCl LEACH TESTS

Sample weight (g)	49.8
Reagent and Vol.	350 mL of 20 % (w/v) HCl
Stirring rate (rpm)	720
Heating temperature (ºC)	Boiling point
Maximum heating time (h)	6
Drying temperature (°C)	100
Weight recovered (g)	28

TABLE-2
XRF ANALYSES OF THE FEED AND 20 % HCl LEACHED
SAKARYA-KARASU ILMENITES AND METAL RECOVERIES

%	Feed ilmenite	Leached ilmenite	% Metal recovery
TiO_2	46.600	84.300	102*
Fe_2O_3	48.600	3.170	4
Mn_3O_4	0.329	0.036	6
Al_2O_3	0.691	0.823	67
SiO_2	2.510	4.480	100
MgO	4.440	1.020	13
CaO	0.216	0.203	53
K_2O	0.017	0.016	53
V_2O_5	0.214	< DL	0
Cr_2O_3	0.097	0.030	17
ZrO_2	0.062	0.117	106*
Nb_2O_5	0.013	0.022	95
SO_3	0.077	0.096	70
P_2O_5	0.015	0.036	135*
Cl	< DL	1.340	-
Na_2O	N/A	0.100	
Th (ppm)	15.000	< DL	0
U (ppm)	< DL	< DL	-
SUM	103.900	95.800	-

< DL = Less than the analytical detection limit;
*More than 100 % recovery value is attributed to the analytical precision.

RESULTS AND DISCUSSION

Liquor analysis: The variation in the total iron concentrations of the filtrates collected at set time intervals is presented Fig. 1 for the Sakarya-Karasu ilmenite. Although both samples were treated under the same conditions a distinct difference can be seen in the amount of iron dissolved in each case. This data show that the iron component of the Sakarya-Karasu ilmenite is distinctly soluble.

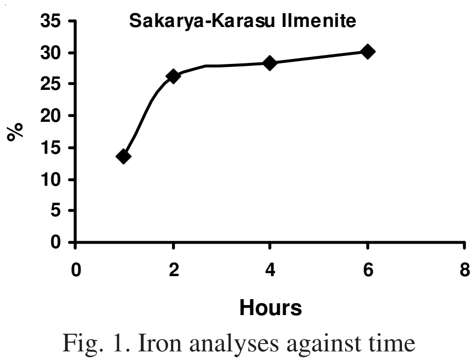

Fig. 1. Iron analyses against time

X-Ray diffraction determinations before and after leach: The XRD patterns of the acid leached Sakarya-Karasu residues were collected at set time intervals to monitor the variations in mineralogy. The patterns are shown in Figs. 2-5.

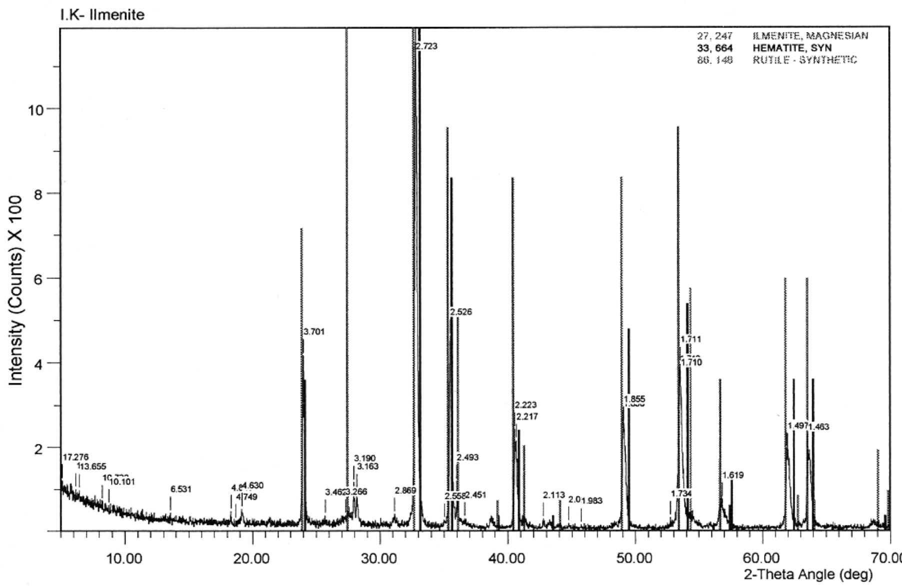

Fig. 2. XRD pattern of the direct leach product at the end of 1 h reaction time

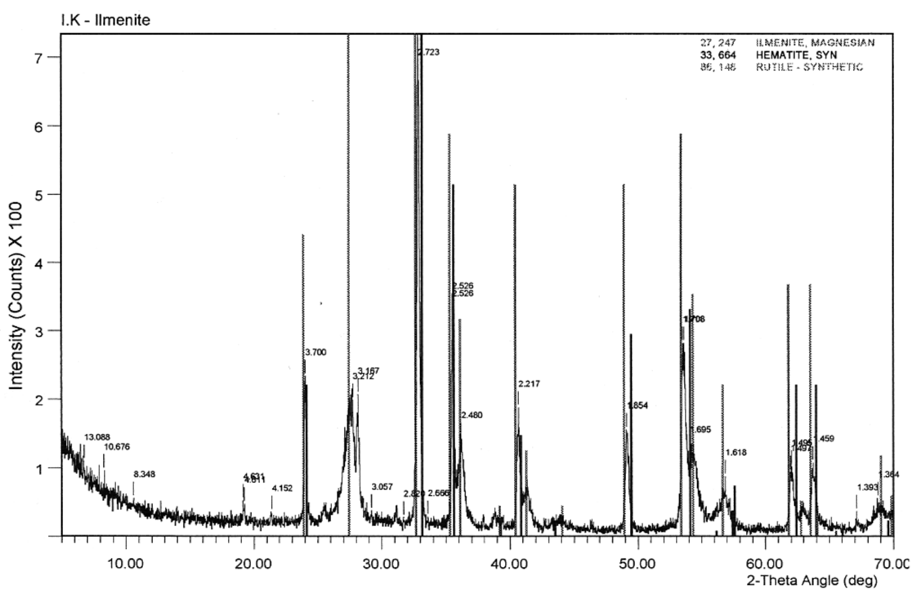

Fig. 3. XRD pattern of the direct leach product at the end of 2 h reaction time

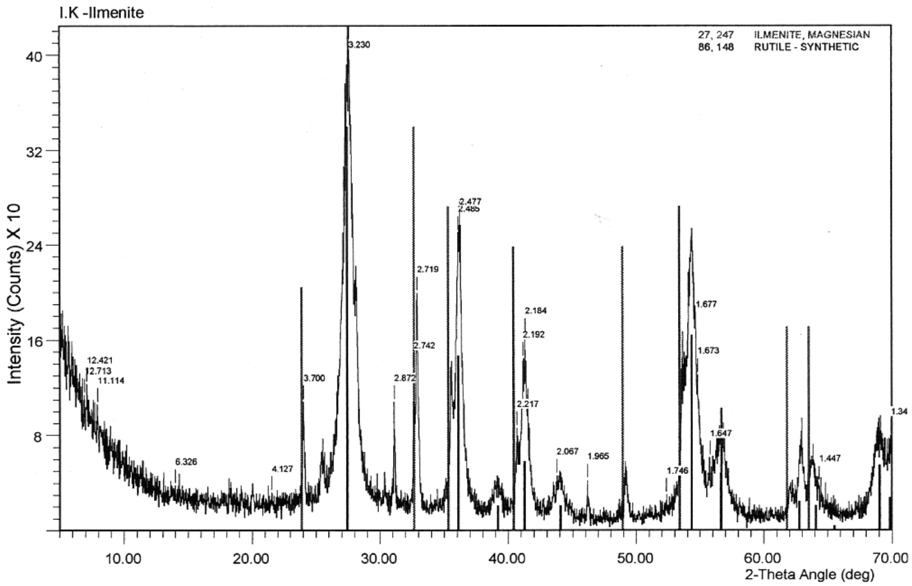

Fig. 4. XRD pattern of the direct leach product at the end of 4 h reaction time

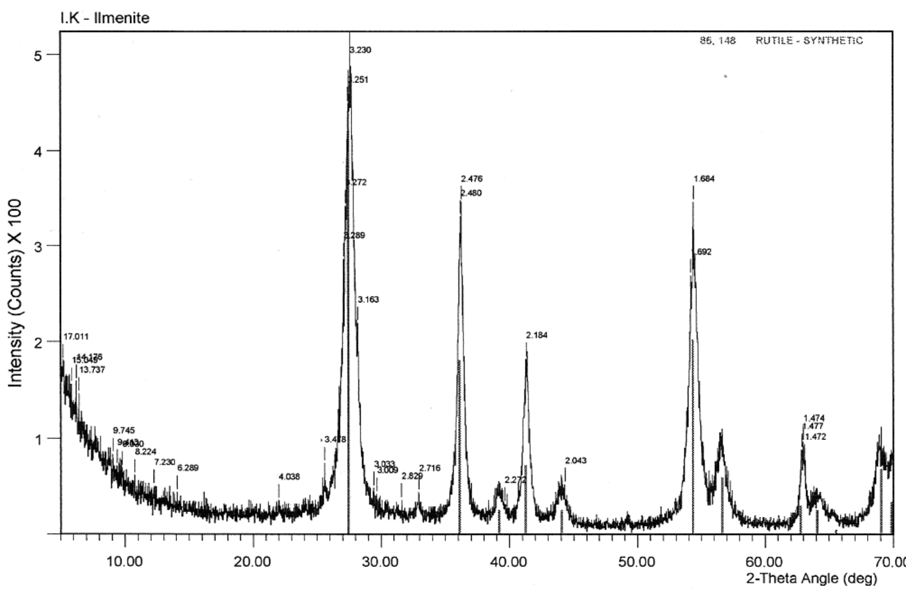

Fig. 5. XRD pattern of the direct leach product at the end of 6 h reaction time

The mineralogic variations as a result of acid leach were monitored from their XRD patterns. The XRD pattern after 1 h leaching was dominant by the mineral phases found in the original ilmenite. At this stage only insignificant amount of rutile was formed. However, in time ilmenite and hematite gradually disappeared and rutile appeared. At the end of 6 h leaching the conversion to rutile was nearly completed. However, the broad base peaks and low counts per second (y-axis) indicate the final product was only poorly crystalline.

Effect of acid concentration on the solubility of iron from ilmenite: Leaching experiments were conducted to determine the effects of hydrochloric acid concentration on the dissolution kinetics of the Sakarya-Karasu ilmenite concentrate.

The experimental conditions and oven-dried weights of the recovered solids are shown in Table-3. While the XRF analyses of the different concentration of HCl acid leaching is presented in Table-4 (Fig. 6).

TABLE-3
EXPERIMENTAL CONDITIONS OF THE DIFFERENT CONCENTRATION HCl LEACHED TESTS

Condition	10 % HCl	20 % HCl	32 % HCl
Sample weight (g)	50	50	50
Reagent used	350 mL of 20 % (w/v) HCl	350 mL of 20 % (w/v) HCl	350 mL of 32 % (w/v) HCl
Stirring rate	720 rpm	720 rpm	720 rpm
Heating temp. (°C)	Boiling point	Boiling point	Boiling point
Max. heating time (h)	6	6	6
Filtrate recovered	260 mL or 295 g	275 mL or 310g	280 mL or 300 g
Drying temp. (°C)	100°C	100°C	100°C
Weight recovered (g)	37	28	27

TABLE-4
XRF ANALYSES OF THE DIFFERENT CONCENTRATION HCl ACID LEACHING

%	FEED	Sakarya-Karasu ilmenites					
		10 % HCl	10 % leach recovery	20 % HCl	20 % leach recovery	32 % HCl	32 % leach recovery
TiO_2	46.600	52.100	83	84.300	102*	85.700	99
Fe_2O_3	48.600	39.500	60	3.170	4	2.000	2
Mn_3O_4	0.329	0.339	76	0.036	6	0.027	4
Al_2O_3	0.691	0.668	74	0.823	67	0.807	63
SiO_2	2.510	3.880	114	4.480	100	4.730	102
MgO	4.440	4.060	68	1.020	13	1.060	13
CaO	0.216	0.189	65	0.203	53	0.204	51
K_2O	0.017	0.009	39	0.016	53	0.012	38
V_2O_5	0.214	0.135	47	< DL	0	< DL	–
Cr_2O_3	0.097	0.068	52	0.030	17	0.027	15
ZrO_2	0.062	0.067	80	0.117	106*	0.137	119
Nb_2O_5	0.013	0.013	74	0.022	95	0.027	112
SO_3	0.077	0.070	67	0.096	70	0.119	83
P_2O_5	0.015	0.031	153	0.036	135*	0.035	126
Cl	< DL	0.152	–	1.340	–	0.845	–

%	FEED	Sakarya-Karasu ilmenites					
		10 % HCl	10 % leach recovery	20 % HCl	20 % leach recovery	32 % HCl	32 % leach recovery
Na_2O	N/A	N/A	–	0.100	–	N/A	–
Th (ppm)	15.000	36.000	–	< DL	–	27.000	–
U (ppm)	< DL	< DL	–	< DL	–	< DL	–
SUM	103.900	101.300	–	95.800	–	95.700	–

< DL = Less than the analytical detection limit;
*More than 100 % recovery value is attributed to the analytical precision.

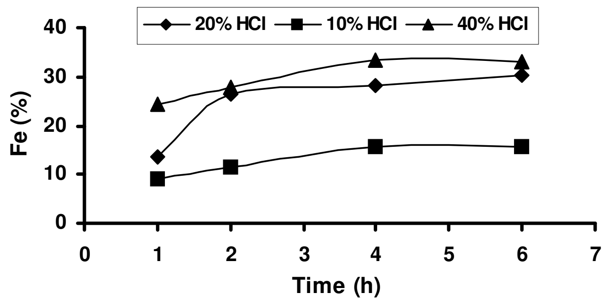

Fig. 6. Effect of acid concentration on the solubility of iron from ilmenite. Pulp density 12.5 %

Conclusion

This investigation has detailed the leaching behaviour of the Sakarya-Karasu ilmenite concentrate and its oxidation and reduction heating products in hydrochloric acid solutions and accounted for the success of ilmenite upgrading processes which employ mineral pretreatment steps of oxidation and reduction followed by hydrochloric acid leaching. The significant findings are summarized below: (**i**) Feed material was prepared from Sakarya-Karasu ilmenite and the hydrochloric acid concentration, oxidation/reduction heating and solids on the leaching rate were studied. (**ii**) The Sakarya-Karasu ilmenite is a typical ilmenite-hematite exsolution assemble. (**iii**) Overall selective ferrous iron removal from the ilmenite rich phase leached at a low per cent solids was observed. (**iv**) The oxidized and reduced product was nearly closed reactive than the Sakarya-Karasu ilmenite concentrate.

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