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## KINETIC STUDIES ON THE DECOMPOSITION OF ILMENITE CONCENTRATE FROM SAND STONE FOR THE RECOVERY OF TITANIUM DIOXIDE

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Ilmenite concentrate from sand stone of D.G. Khan was selected for the recovery of titania. It was investigated that the maximum decomposition was done with a mixture of sulphuric acid and ammonium sulphate. Different factors, i.e. dilution, boiling time and pH were studied to effect hydrolysis. It was found that the maximum recovery was achieved at 3.5 times dilution for boiling 10 min. at pH less than 0.5 of the solution obtained after decomposition.

**Key words:** Ilmenite, Recovery, Titania

### Introduction

Titanium dioxide ( $\text{TiO}_2$ ) [1] is an important compound used widely in the manufacture of pigments. The important feature of its incorporation in the pigments of paints is that it confers durability on the paint. The element titanium occurs primarily in ilmenite and rutile. Both occur naturally in coastal black sands and in several hard rock ore deposits.

Ilmenite [2] found in sands are often altered by oxidation and leaching. As a result of these processes, the ratio of ferric to ferrous changes giving an indication of the extent to which weathering has occurred. At the same time the amount of iron tends to fall and the amount of titanium dioxide increases correspondingly.

In Pakistan, there are no major deposits of minerals containing considerable amount of titania. Laterite at Ziarat (Baluchistan) and bauxite and a high alumina clay at Nowa, District Attock, Punjab [3] contain upto 6% titania. The recovery of  $\text{TiO}_2$  from these deposits is not economically feasible. Sand stone deposits of D.G. Khan processed by Pakistan Atomic Energy Commission for the recovery of uranium leave behind ilmenite concentrate containing more than 26% of  $\text{TiO}_2$ . This concentrate has been selected to investigate the recovery of titania.

The literature survey enumerates various methods for the decomposition of Ilmenite to recover titania. Keeping in mind the facilities available for this work and comparative efficiencies of decomposition techniques, sulphuric acid and its mixture with ammonium salt has been selected for this investigation, the recovery of titania was effected through hydrolysis. Effects of dilution, temperature and pH were studied on hydrolysis to achieve maximum recovery of titania.

### Experimental

**Chemistry.** 10.00 g of the ilmenite concentrate under study was ground to minus 100 mesh and chemical analysis was carried out according to the standard methods [4-6]. The

results are:  $\text{SiO}_2$  3.52%,  $\text{TiO}_2$  26.37%,  $\text{Al}_2\text{O}_3$  13.60%,  $\text{Fe}_2\text{O}_3$  53.64%,  $\text{MnO}$  0.24%,  $\text{MgO}$  0.35%,  $\text{CaO}$  1.48%,  $\text{P}_2\text{O}_5$  0.00%,  $\text{Na}_2\text{O}$  0.50%,  $\text{K}_2\text{O}$  0.30% and moisture being 0.00%.

**Mineralogy.** Two thin sections were prepared from the powdered sample for this study. The minerals indentified are ilmenite, magnetite, haematite and a few grains of garnet. Ilmenite is recognised by its blue grey black colour whereas both magnetite and haematite show metallic lustre. According to rotational analysis, ilmenite is 30% and magnetite/haematite is 70%. According to wet chemistry the mineralogy corresponds to the chemical results. Independent ilmenite grains are visible under microscope but they are also associated with magnetite and haematite.

**Decomposition.** There are various methods [7-9] given in the literature for the decomposition of ilmenite. For this investigation, sulphuric acid and a mixture of sulphuric acid and ammonium sulphate have been selected for this investigation for the decomposition of the ore.

**Decomposition with  $\text{H}_2\text{SO}_4$ .** 10 Grams of the finely ground ilmenite concentrate minus 100 mesh ore is heated with 30 ml  $\text{H}_2\text{SO}_4$  of different concentrations for different intervals of time and at different temperatures in a partially covered vessel [10]. The results are given in Table 1.

**Decomposition with a mixture of  $\text{H}_2\text{SO}_4$  and ammonium sulphate.** 10 Grams [11] of the ilmenite concentrate minus 100 mesh is heated with 30 ml of the acid mixture of  $\text{H}_2\text{SO}_4$  and ammonium sulphate 15 ml of each of the reagent solutions of different concentration as is given in Table 2. The mixture was heated at  $192 \pm 3^\circ$  for various durations.

**Recovery of  $\text{TiO}_2$ .** 500 Grams [12] of the ilmenite concentrate heated with 1.5 litre acid mixture of 88% of  $\text{H}_2\text{SO}_4$  and 6.6%  $(\text{NH}_4)_2\text{SO}_4$  for a period of 2.0 hr. in a partially covered vessel at  $192 \pm 3^\circ$ . The undissolved solids are removed. 10.00g of iron powder was added. After about half an hour the mixture was cooled to  $60 \pm 5^\circ$  and kept at this temperature for about 5 hrs. The temperature was then lowered and the crystalized

FeSO<sub>4</sub> was removed. The solution was diluted to 2.5 litres and Titania was found to be 0.0416 g per ml spectrometrically [5]. To avoid the titania hydrolysis pH of this solution was maintained at 0.2 - 0.5. The effects of dilution, pH and boiling time on the recovery of titania were studied with this solution.

*Effect of dilution.* 50.00 ml of the solution containing 2.08 g of TiO<sub>2</sub> was taken each time and was diluted with 50, 75, 100, 125, 150, 175 and 200 ml of water and boiled for 10 minutes in each case. During cooling, the TiO<sub>2</sub> hydrolysed and settled. The precipitate was filtered, calcined at 1000° and weighed.

TABLE 1. PERCENTAGE DECOMPOSITION OF ILMENITE CONCENTRATE PERCENTAGE CONCENTRATION OF H<sub>2</sub>SO<sub>4</sub>.

S. No.	Temp. °C	Time (hrs)	20	30	40	50	60	70	80
1.	100°	1.0	4.2	10.3	12.0	13.2	11.3	10.0	7.3
		1.5	4.5	12.3	14.5	13.5	11.3	10.2	7.2
		2.0	5.1	13.2	14.8	13.5	11.0	10.3	7.8
		2.5	5.7	13.8	16.1	15.1	11.0	10.1	7.0
		3.0	5.7	14.5	16.1	15.8	10.9	10.0	6.9
2.	150°	1.0	5.6	20.1	20.4	24.6	17.7	15.0	10.2
		1.5	6.1	23.3	24.3	24.8	17.9	14.8	10.3
		2.0	6.2	25.5	25.8	25.3	17.3	14.0	10.2
		2.5	6.5	28.6	29.0	26.2	16.9	14.0	10.4
		3.0	6.6	30.0	31.0	27.3	16.9	13.8	10.0
3.	200°	1.0	8.0	40.1	45.2	47.3	35.8	26.0	11.2
		1.5	8.5	45.8	48.3	47.9	35.6	18.2	11.0
		2.0	9.3	45.8	50.1	48.1	35.4	17.3	11.0
		2.5	10.5	46.3	50.4	49.0	30.8	15.3	10.9
		3.0	11.5	46.3	50.6	49.0	30.0	15.0	10.9

TABLE 2. DECOMPOSITION WITH ACID MIXTURE. (WT. OF THE ORE) TAKEN 10 g, VOLUME OF THE ACID MIXTURE 30 ml TEMPERATURE 192 ± 3°).

S. No.	Concentration of acid mixture (%)		Percentage Decomposition after (hrs.)				
	H <sub>2</sub> SO <sub>4</sub>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	1.0	1.5	2.0	2.5	3.0
1.	96	13.2	15.2	22.6	26.4	26.6	26.6
	96	6.6	20.5	24.8	28.7	29.0	29.3
	96	3.3	14.8	15.2	16.4	17.2	17.8
2.	88	13.2	35.7	48.4	50.1	50.2	50.1
	88	6.6	40.5	52.8	79.3	79.0	78.3
	88	3.3	23.2	26.6	26.8	26.8	26.9
3.	80	13.2	27.3	30.9	31.2	31.4	31.4
	80	6.6	28.2	34.3	35.1	35.2	35.3
	80	3.3	17.6	20.2	20.8	20.7	20.8
4.	72	13.2	18.7	24.6	25.0	25.0	25.0
	72	6.6	20.6	21.3	21.8	21.9	22.0
	72	3.3	14.4	14.8	14.9	15.0	15.3

The results are given in Table 3.

*Effect of boiling time.* 50.00 ml of the solution was taken, diluted 3.5 times with 125 ml of H<sub>2</sub>O and boiled for different intervals of time. The amount of TiO<sub>2</sub> hydrolysed on cooling was filtered, calcined at 1000° and weighed. The results are tabulated in Table 4.

*Effect of pH.* 50.00 ml of the solution at pH 0.5 was taken, diluted to 175 ml and boiled for 10 min. after adjusting the pH 0.5, 0.7, 1.0, 1.2, 1.5, 1.8 and 2.0. On cooling, hydrolysed titania was filtered, calcined the weighted. The results are given in Table 5.

TABLE 3. EFFECT OF DILUTION. (VOLUME OF THE SOLUTION TAKEN 50 ml.; TIME OF BOILING 10 min.; AMOUNT OF TiO<sub>2</sub> 2.0 g).

S. No.	Vol of H <sub>2</sub> O added (ml)	Amount of TiO <sub>2</sub> hydrolysed (g)	% of TiO <sub>2</sub> hydrolysed (%)	% of TiO <sub>2</sub> retained in the soln. (%)
1.	50	1.400	67.31	32.69
2.	75	1.484	71.30	28.70
3.	100	1.692	81.35	18.65
4.	125	1.796	86.35	13.61
5.	150	1.686	81.06	18.94
6.	175	1.120	53.85	46.15
7.	200	0.844	40.58	59.42

TABLE 4. EFFECT OF BOILING TIME (VOLUME OF THE SOLUTION TAKEN 50 ml, WATER ADDED 125 ml, AMOUNT OF TiO<sub>2</sub> PRESENT 2.08 g).

S. No.	Time of boiling in (min.)	Amount of TiO <sub>2</sub> hydrolysed (g)	% of TiO <sub>2</sub> hydrolysed (%)	% of TiO <sub>2</sub> retained in solution (%)
1.	5	1.311	63.03	36.97
2.	10	1.783	85.72	14.28
3.	20	1.402	67.40	32.60
4.	30	0.813	39.09	60.91
5.	40	0.677	32.55	67.45
6.	50	0.504	29.04	70.96
7.	60	0.501	24.09	75.91

TABLE 5. EFFECT OF PH VOLUME OF THE SOLUTION TAKEN 50 ml; AMOUNT OF TiO<sub>2</sub> PRESENT 2.08 ml, VOLUME MADE 175 ml; TIME OF BOILING 10 MIN.

S. No.	pH	Amount of TiO <sub>2</sub> hydrolysed (g)	% of TiO <sub>2</sub> hydrolysed (%)	% of TiO <sub>2</sub> retained in solution (%)
1.	0.50	1.007	48.41	51.59
2.	0.70	1.010	48.58	51.42
3.	1.00	1.055	50.72	49.28
4.	1.20	1.058	50.87	49.13
5.	1.50	1.066	51.25	48.75
6.	1.80	1.074	56.63	48.37
7.	2.00	1.097	52.74	47.26

### Results and Discussion

Chemical analysis of the ilmenite concentrate presented in Table 1 and mineralogical identifications show that it consists mainly of magnetite, ilmenite, haematite and garnet. Independently visible ilmenite grains constitute about 30% of the concentrate. There is a small amount of garnet and the rest are magnetite and haematite. The ilmenite grains are also associated with magnetite, haematite and garnet grains as well.

Preliminary experiments for selecting a suitable decomposing agent were conducted keeping in view the facilities available for this work. Sulphuric acid and a mixture of sulphuric acid and ammonium sulphate in varying molar proportions were studied. Out of these mixtures of ammonium sulphate 6.60% sulphuric acid 88% showed encouraging results. Better results with mixture of ammonium sulphate and sulphuric acid were due to fact that  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{TiOSO}_4 \cdot \text{H}_2\text{O}$  formed during the reaction is more stable than  $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ .

Decomposition of ilmenite concentrate was performed by heating ilmenite with different concentrations of  $\text{H}_2\text{SO}_4$  at various temperatures and for different time interval. The results of decomposition with  $\text{H}_2\text{SO}_4$  are represented in Table 1 and it was found that when 10 g of the minus 100 mesh ore was attacked with 40% of  $\text{H}_2\text{SO}_4$  at  $200^\circ$  for 3 hrs. the decomposition was maximum. It was observed that on heating for such a prolonged period of time and at such a high temperature, fuming started which resulted the highest decomposition to 50.6% but at the same time the copious fumes of  $\text{SO}_2$  and  $\text{SO}_3$  gases evolved during the reaction.

The other method applied for decomposition of ilmenite concentrate that is the decomposition with an acid mixture of  $\text{H}_2\text{SO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$  which yielded better results than  $\text{H}_2\text{SO}_4$  alone. Different compositions of the acid mixture were tried as is given in Table 2. 10 Grams of the material under study was treated with 30 ml of the acid mixture at a temperature  $192 \pm 3^\circ$ . It was observed that the maximum decomposition i.e., 79.3% was obtained by the attack of 88% of  $\text{H}_2\text{SO}_4$  and 6.6%  $(\text{NH}_4)_2\text{SO}_4$  for 2 hrs.  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{TiOSO}_4$  was leached with water from the decomposed ilmenite concentrate and titania was precipitated by hydrolysing this solution. The pH of this solution was maintained 0.5 at which the hydrolysis at room temperature does not take place. The effect of dilution, boiling time and variation of pH on the hydrolysis of  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{TiOSO}_4$  were studied.

The effect of dilution was studied by keeping the

boiling time constant for 10 mins. There was no appreciable change in the pH of the solution. The results presented in Table 3 show that the dilution favours the precipitation and is maximum when the solution is diluted 3.5 times. On further dilution, the precipitation begins to decrease. Thus the optimum conditions for the achievement of the best results are: (i) 3.5 times dilution; (ii) 10 min. boiling time as in Table 4.

Effect of boiling time was also studied by varying the time from 5 min. to 1 hr. by diluting the solution 3.5 times. The best time of boiling for maximum precipitation obtained was 10 min. as given in Table 4.

Similarly the variation of pH from 0.5 - 2 effected the precipitation. But the results are not as encouraging as in case of dilution because the maximum precipitation at pH 2 is 54.85% and beyond this pH, the other oxides of group III start to precipitate. The results of Table 4 and 5 clearly indicate that the maximum precipitation i.e., 85.72% takes place at 3.5 times dilution and boiling for 10 min.

Precipitated  $\text{TiO}_2$  was quite white in colour but when it was dried it developed a slight brownish tinge which was due to the presence of iron. Some complexing agent such as ethylene diamine tetra acetate were tried to eliminate the traces of colouring impurities but these efforts were not successful. This aspect of titania recovery needs further investigation.

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