Preparation of Titania from Ilmenite by Selective H$_2$S Sulfidization

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Experiments on preferential sulfidization of ilmenite in a static bed by hydrogen sulfide gas with a flow rate of about 20 cm$^3$ per min were conducted at 800$^\circ$, 900$^\circ$, 1000$^\circ$, and 1100$^\circ$C for different periods. Sulfidization (conversion of about 95 pct of the iron to its sulfide) at 1000$^\circ$C for 5 hr or at 1100$^\circ$C for 4 hr was considered quite suitable. The sulfidized samples were leached with boiling dilute hydrochloric acid and the influence of the concentration, amount of the acid, and the duration of leaching was studied. Leaching was most effective by employing 20 pct excess 2 N boiling hydrochloric acid for ½ hr. By this treatment, about 95 pct of the iron in ilmenite could be removed and a residue containing about 91 pct TiO$_2$ has been obtained. X-ray analysis revealed that TiO$_2$ in the residue has rutile structure. The merits of the process for commercial utilization have been mentioned briefly.

ILMENITE and rutile constitute the main sources for titanium and pigment grade titanium dioxide. Rutile with a much higher TiO$_2$ content is preferred over ilmenite, but its reserves are very limited. On the other hand, ilmenite is quite abundant in nature. Heavy mineral deposits containing ilmenite are found in Australia, India, the United States, South Africa, Canada, and Russia. In India, black beach sands of the south and southwest coast contain large quantities of ilmenite and a very small proportion of rutile. However, because of its high iron value, the mineral has to be upgraded to the rutile grade prior to its utilization for the production of the pigment or titanium metal.

In ilmenite, iron oxide and titanium dioxide are held chemically in a spinel form. As it is not possible to separate iron from titania in ilmenite by any physical method, drastic chemical treatment has invariably been applied to the mineral for its upgrading. The principal commercial processes currently in practice include 1) smelting with coke or coal$^{11-13}$ in an electric furnace, 2) leaching with acids under pressure$^{11-14}$ and 3) reduction of iron oxide followed by oxidation in the presence of a catalyst and subsequent removal of the oxide slurry.$^{15}$

In recent years, further development of existing processes and inventions of new methods have taken place. Jena and coworkers$^{16}$ leached ilmenite with hydrochloric acid under high pressure and at high temperatures to obtain a product containing about 98 pct TiO$_2$. Osaka Titan Co.$^{17}$ is producing titania by smelting ilmenite with coke in an electric furnace and subsequent leaching of the resultant titania rich slag with hydrochloric acid. A large number of investigations on the solid state reduction$^{18-34}$ of ilmenite (by carbon, hydrogen, carbon monoxide, or mixture of hydrogen and carbon monoxide) followed by iron removal either chemically or magnetically have also been carried out successfully. In a process which is in use at Laparte Titanium Ltd.$^{34}$ ilmenite is heated with reducing agents to convert the iron compounds to metallic iron which is subsequently separated by hydrochloric acid treatment or magnetic separation. It has been reported that the iron contained in ilmenite can be chlorinated$^{25-27}$ selectively in the presence of carbon monoxide. Another process for upgrading ilmenite developed at Titan Co. Inc.,$^{28}$ involves the treatment of the oxidized ilmenite with titanium tetrachloride and chlorine resulting in a product containing about 90 pct TiO$_2$. Preferential removal of iron from ilmenite by treatment with ammonium chloride$^{28,30}$ has also been reported in the literature.

Viswanathan Nayar$^{31}$ has reported the possibility of ilmenite beneficiation by high temperature conversion of the oxides of iron to iron sulfate in presence of hydrogen sulfide gas followed by acid leaching. Beneficiation of ilmenite by its treatment with sodium sulfate plus carbon$^{29-32}$ resulting in preferential sulfidization has drawn the attention of some investigators. Sulfidization with sulfur vapor$^{35,36}$ has also been attempted.

In the present investigation, upgrading of ilmenite, i.e., titania/iron separation by preferential sulfidization with hydrogen sulfide gas followed by dilute hydrochloric acid leaching has been studied on a laboratory scale.

EXPERIMENTAL

The ilmenite used in the present investigation was a concentrate from the beach sands of Manavalakurichi (southern coast of India), containing 54.2 pct TiO$_2$, 14.20 pct Fe$_2$O$_3$, 1.25 pct Al$_2$O$_3$, 26.60 pct FeO, 0.40 pct MnO, 0.07 pct Cr$_2$O$_3$, 0.16 pct V$_2$O$_5$, 1.03 pct MgO, 0.12 pct P$_2$O$_5$, 0.80 pct ZrO$_2$, and 0.68 pct SiO$_2$. Sieve analysis (BS) of the said concentrate was as follows: 0.5 pct +44 mesh; 16.5 pct -44 to +60 mesh; 65.8 pct -60 to +100 mesh; 13.7 pct -100 to +150 mesh; and balance -150 mesh. Hydrogen sulfide gas was produced by reaction between dilute hydrochloric acid and iron pyrite. Chemically pure grade acid was used for leaching.

Sulfidization of ilmenite was carried out in a one-end closed 30 mm diam silica tube as shown in Fig. 1. Each time 10 g of ilmenite sample was taken in an alumina boat and inserted up to the closed end of the
silica tube whose open end was fitted with a rubber stopper. A silica tube and a pyrex glass tube introduced into the reaction tube through the rubber stopper, served as the inlet and outlet, respectively, for the hydrogen sulfide gas. The gas was prepared by the reaction of dilute (about 2 N) hydrochloric acid with sticks of iron pyrites. In the initial period the reaction tube was flushed with a rapid stream of hydrogen sulfide and subsequently its rate was controlled to about 20 cu cm per min by adjusting the flow of the acid. The reaction tube was then inserted into a preheated kanthal-wound, resistance furnace fitted with an on-off device and the desired temperature was maintained within ±5°C. Sulfidization was studied as a function of temperature (800°C to 1100°C) and time (1 to 16 hr). At the end of the experiment, the boat was cooled under hydrogen sulfide to room temperature and then weighed. At each temperature, the experiment was repeated for a suitable cumulative period to constant weight.

The samples sulfided to the maximum possible degree (95 pct Fe converted to sulfide) were leached with boiling hydrochloric acid in a pyrex flask fitted with a reflux condenser. The influence of the concentration and amount of acid as well as time of leaching was studied. The amount of acid removed was estimated from analysis of the leach liquor (titration against KMnO₄) and the residue gravimetrically determined. The best product obtained was chemically analyzed and also examined by X-ray diffraction using the powder technique.

RESULTS AND DISCUSSION

The process under investigation for upgrading ilmenite involves two principal steps: 1) preferential sulfidization of iron oxide by H₂S at a high temperature and 2) subsequent leaching of the sulfidized product in boiling dilute hydrochloric acid. Complete preferential sulfidization of iron in the ilmenite (used in the present work) should, theoretically, result in a weight increase of 7.33 pct. Results obtained in the two stages are discussed below.

Effect of Temperature and Time on Sulfidization

Fig. 2 shows the effect of temperature and time on sulfidization of the ilmenite. Preferential sulfidization of iron appears to take place at a considerable rate up to about 95 pct (represented by 7 pct weight increase) and beyond this the rate seems to be extremely slow. About 95 pct sulfidization is achieved in 12, 8, 5, and 4 hr at 800°C, 900°C, 1000°C, and 1100°C, respectively. Leaching studies were carried out with samples sulfidized at 1000°C.

Effect of Concentration of Acid on the Leaching of the Sulfidized Ilmenite

Results of leaching tests using different concentrations (varying from 0.5 to 4 N) of boiling (about 105°C) dilute hydrochloric acid, for 1 hr are shown in Table I. In these tests the amount of acid used was 30 pct in excess of the stoichiometric amount needed for complete dissolution of the iron present in the sample. It is obvious that with increase in acid concentration, the recovery of iron increases up to 2 N HCl, beyond which there is no improvement in leaching.

Effect of Quantity of Acid Used for Leaching

Leaching results using different quantities of 2 N boiling hydrochloric acid for 1 hr are presented in Table II. Iron recovery increases with the quantity of acid up to 20 pct in excess of the stoichiometric amount.

Effect of Leaching Time

Sulfidized samples were leached with boiling 20 pct excess acid of 2 N concentration from 15 min to 1 hr. From Table III, it is evident that ½ hr is adequate for leaching, beyond which there is no significant change in iron removal. Thus, the recommended conditions for upgrading