MURSO PROCESS FOR PRODUCING RUTILE SUBSTITUTE

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Introduction

The present trends in the consumption of mineral rutile which is mainly used for the production of pigment by the chloride process, titanium sponge and welding electrodes show that the demand for the mineral will outstrip supplies very shortly. Australia which currently supplies more than 90% of the world's rutile requirements will have considerable difficulties in stepping up substantially its present production of about 360,000 tons of rutile concentrates per year due to economic, environmental and technical problems until new deposits of the mineral are discovered and developed. The shortfall in supplies of high TiO_2 feed material is expected to be of the order of 400,000 tons by 1975. This gap between demand and supply can only be filled by producing rutile grade (95+% TiO_2) material by upgrading ilmenite, the supplies of which are plentiful.

The problem of upgrading ilmenite is essentially one of cost and TiO_2 content which is acceptable to the consumers of natural rutile. During the past few years, a number of processes have been developed as a result of the potentially strong demand for a substitute for rutile. However, only very few of these, including the Murso process, meet the above requirements and are, as such, being considered for commercial exploitation.

The Murso Process

The Murso process which derives its name from the joint developers (Murphyores and CSIRO) was the first to upgrade ilmenite to a product containing 95-96% TiO_2. The other properties of the product i.e. particle size and chlorination characteristics are such that it can substitute successfully for natural rutile in its conventional uses. The process is capable of treating rock as well as alluvial deposits. Also, because of the selective nature of the process, chromite and other ferruginous impurities which occur in association with some ilmenite deposits can be magnetically separated from the upgrade after leaching without any significant loss of titanium values. Thus an ilmenite containing as high as 5.5% Cr_2O_3 in the feed material may be upgraded to a product containing 96% TiO_2 and less than 0.1% Cr_2O_3. In treating chrome contaminated ilmenites, the Murso process is unique because it is the only process so far reported which provides a method of converting this hitherto unsaleable material into rutile grade product.

Ilmenite is an extraordinarily inactive mineral from which the selective leaching of iron is rather difficult (1). Selective leaching of iron from natural ilmenite by hydrochloric acid has been proposed (2), but this involves the use of high acid concentrations and temperatures so that leaching operations have to be carried out under pressure and in two stages. The design and the materials of construction for leaching vessels also present considerable problems and efficient recovery of 32% HCl from chloride containing effluents by existing commercial processes is considerably more difficult and expensive than is the recovery of 20% HCl. The presence of ferric iron retards the leaching reaction as it is difficult to dissolve.

The core of the Murso process lies in converting ilmenite and other titaniferous ores into a material of high chemical reactivity, whereby iron associated with titanium is readily leached out with dilute acids, without the use of pressure and high temperatures. The enhanced reactivity is achieved by producing a "synthetic ilmenite" structure. While the x-ray diffraction pattern of the product is similar to original ilmenite, the micro-structure is quite different and consists of a large number of lattice defects, mainly sub-grain boundaries.

Prosser (3) has discussed the effect of changes in the mineralogical factors (i.e. crystal structure, inclusions, particle size, polycrystallinity, porosity, surface orientation, dislocations, dissolved impurities and non-stoichiometry) associated with a mineral phase, on its rate of reaction and a change as much as two orders of magnitude has been suggested. Experimental work done by the author on ilmenite prior to the publication of Prosser's paper and reported elsewhere (4) agrees with his findings.

Results in Figure 1 show that the rate of leaching of natural ilmenite in 20% HCl at 108°C is much slower than for ilmenite which has a large number of sub-grains.

The "synthetic ilmenite" structure is produced through the steps of oxidation and reduction. Figure 2 shows the microstructure of ilmenite at different stages of treatment. Thus in the Murso process, substantially all the iron values associated with titanium in the ore are oxidized to the ferric state. The ferric iron is then reduced to the ferrous state and the product so produced is leached in 20% HCl at 108-110°C at atmospheric pressure. After leaching, the solids are separated from the liquor, dried and calcined, and the ferrous chloride leach liquor is regenerated to produce hydrochloric acid which is recycled.

Oxidation

In the Murso process, oxidation has the following functions.

1. Introducing defects (grain-boundaries, micro-cracks, etc.) in the ilmenite grain.

2. Converting all the ferrous iron into ferric state which overcomes the problem of different ferrous to ferric ratios in ilmenites from different localities. Thus the process is capable of treating all ilmenites, irrespective of their origin.

3. Altering the equilibrium conditions, and the rate of reduction from ferric to ferrous state.

As may be seen in Figure 2 (b), the formation of subgrains in the main ilmenite grain starts at the oxidation stage and the oxidized material has a granular texture.

The rate and degree of leaching is dependent upon the changes in the micro-structure of ilmenite grain, and if the oxidation step is omitted, the rate of leaching is slow (Figure 1), consequently affecting the quality of the end product. The results show that a high degree of oxidation of ferrous to ferric iron ($> 90\%$) is required to produce a high TiO_2 ($\geqslant 95\%$) product.

Temperature of Oxidation

The oxidation is preferably carried out in a fluidized bed reactor below the sintering temperature of ilmenite which, though dependent on the chemical composition of the ore, is in most cases just above 1000°C. The rate of oxidation is temperature dependent also, and increases with increase in temperature as shown in Figure 3. Taking into consideration the above factors, as well as the fact that costly materials of construction would be requir-

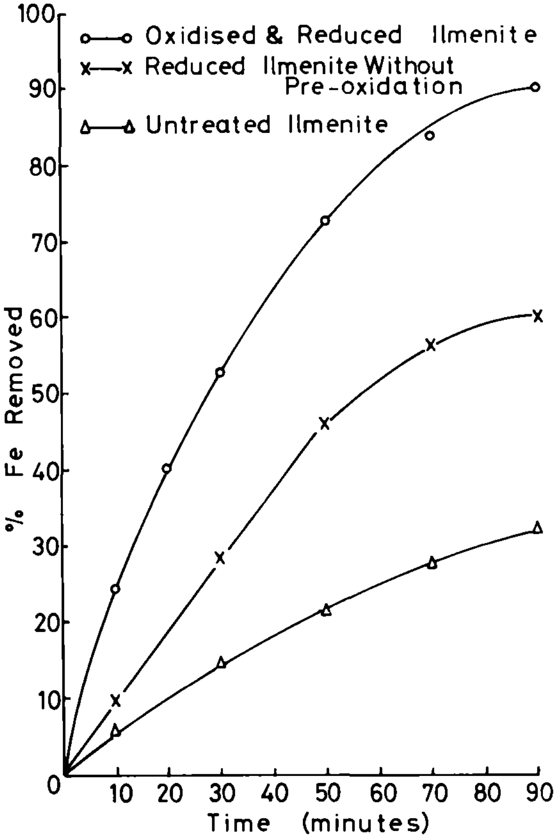

Figure 1. Effect of pre-treatment on the rate of leaching of ilmenite in 20% HCl.

Figure 2 (a) Photomicrograph of natural ilmenite x 200 using polarized light.

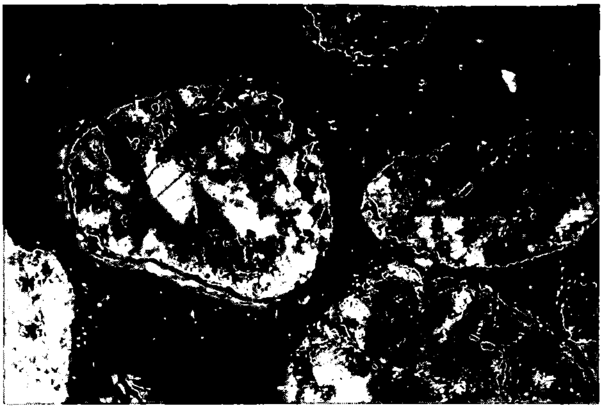

Figure 2 (b) Photomicrograph of oxidised ilmenite x 200 using polarized light.

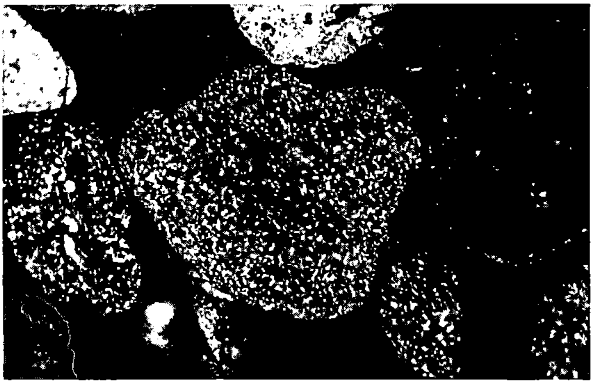

Figure 2 (c) Photomicrograph of oxidised and reduced ilmenite x 200 using polarized light.

ed for fluid bed reactors operating above 1000°C, sub-sintering temperatures are used and the typical oxidation temperature in the Murso process is 900-950°C.

The oxidation reaction is exothermic (ΔH_{1173} =-27.61 K Cal/gm. mole of ilmenite) but the heat of reaction is not sufficient to maintain the ilmenite at the oxidation temperature. The heating of the charge is achieved by fuel injection in the fluid bed with an excess of air to give approximately 10% oxygen in the fluidizing gas. This does not affect the rate of oxidation as shown in Figure 3.

Reduction

The reduction of oxidized ilmenite is carried out firstly to convert ferric iron to the ferrous state, the solubility of the latter being higher, and secondly to create further changes in the micro-structure of the ilmenite grain. The process of formation of sub-grains which starts at the oxidation stage continues, and a large number of small grains are formed (Figure 2c). After the reduction treatment, there are hundreds of crystalline individual grains within an original grain. The change of micro-structure during oxidation and reduction means that whereas individual crystals of untreated ilmenite average perhaps 200 μ in diameter, the average diameter of pseudobrookite crystals formed after oxidation is only perhaps 20 μ and after reduction the ilmenite crystals are less than 5 μ in diameter.

Microscopic studies show that much of each original grain after reduction has approximately the same crystallographic orientation. However, even the region of approximately similar orientation shows a shadowy granularity due either to strain or to small actual differences of crystalline orientation. X-ray diffraction studies provide no evidence of increased strain after treatment and it is probable that the shadowy granularity is an actual polycrystalline texture with a very slight difference in the crystal orientation, and probably pseudomorphing the granularity of the pseudobrookite phase formed during oxidation.

While a number of studies (5-9) have been carried out on the reduction of ilmenite to metallic iron, very little data is available on the reduction of ferric iron in oxidized ilmenite to the ferrous state; this being the region of interest to the Murso process.

Results show that the reduction of oxidized ilmenite is a step-wise process and occurs in two well defined stages of ferric to ferrous, followed by ferrous to metallic iron. The rate of reduction and equilibrium conditions in the first stage are much more favourable than in the second stage.

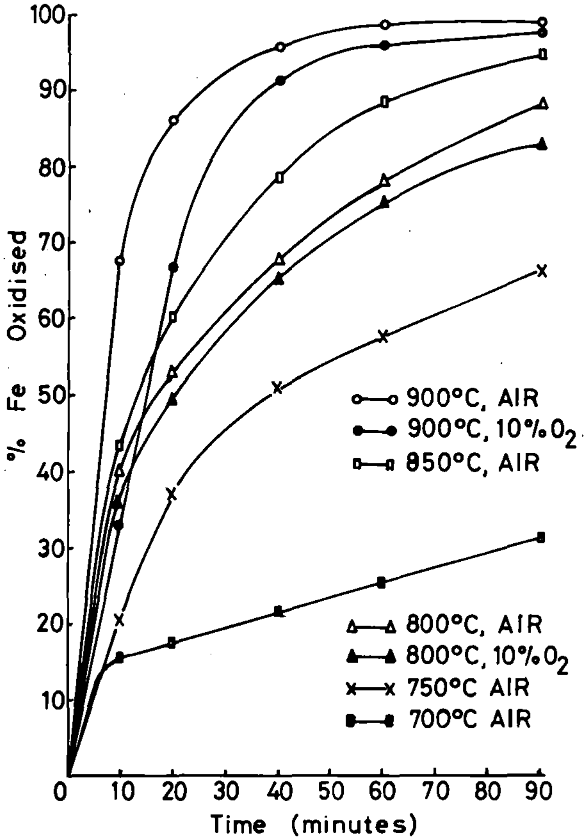

Figure 3. Effect of temperature and partial pressure of oxygen on the rate of oxidation of ilmenite.

Reduction Temperature

Like oxidation, the rate of reduction is also temperature dependent and increases with increase in temperature as shown in Figure 4. The equilibrium also becomes more favourable at higher temperatures. In operating a full scale plant, however, the actual temperature is governed by considerations similar to the oxidation step i.e. sintering of ilmenite and materials of construction for reactors. Added to this is the fact that the reaction is only slightly exothermic(-16.4 Cal./gm of the oxidized ilmenite) and it is difficult to provide heat in a system where strong reducing conditions are required. Considering the above factors, the optimum temperature of reduction as determined from experimental work for the Murso process is 850-900°C.

In view of the very favourable equilibrium for the partial reduction of oxidized ilmenite, a high utilization of the reductant is achieved, particularly in a two stage process. Experiments show that in two stage simulated tests, using hydrogen as a reductant, hydrogen utilization in excess of 75% is achieved. The favourable equilibrium also obviates the need for high purity hydrogen. A gas mixture consisting of hydrogen, carbon monoxide, carbon dioxide and water vapour i.e. a gas composition which may be economically produced by steam reforming of naptha or natural gas is as effective as hydrogen, as shown in Figure 4. A typical reductant gas composition is 70% H_2, 13% CO, 13% CO_2 and 4% water vapour.

Leaching

Having produced "synthetic ilmenite," the next step in the upgrading process is to remove iron oxide (and the oxides of manganese, magnesium and aluminium which invariably substitute iron oxides in the ilmenite lattice) selectively with a minimum of loss of titanium values and without substantial change in the particle size of the end product. The conditions of leaching should be mild so as not to impose serious limitations on the materials of construction for the leaching vessels. The leachant used, besides being reasonably cheap, should also be such that it can be regenerated from the iron compound produced in the leaching step, so as to leave no effluent disposal problems, the latter being one of the main reasons for the change from the sulphate to the chloride route for manufacturing titanium pigment. In view of the above factors, hydrochloric acid was found to be the most satisfactory leachant.

Since the oxides to be removed from the ilmenite lattice constitute approximately 45% of the grain and are chemically bound with TiO_2, the dissolution of these could result in the disintegration of the original grain during leaching, if conditions favourable to the reconstitution of the rutile structure are not available.

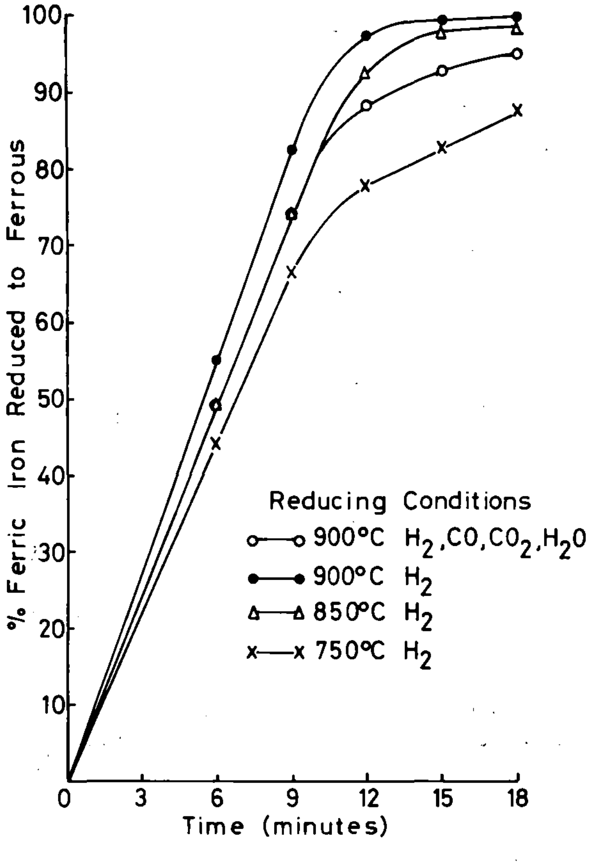

Figure 4. Effect of temperature and reducing gas composition on the rate of reduction of oxidised ilmenite.

The main factors which affect the above are acid strength and temperature of leaching.

Experiments show that the rate of dissolution of iron increases with increase in acid concentration and so does the amount of titanium in solution. However, the titanium which goes into solution in the initial stages of leaching precipitates as the acid concentration of the solution goes down. The rate of leaching and hydrolysis of titanium are also temperature dependent and the higher the temperature, the higher are the rates of leaching and hydrolysis of titanium at a given acid concentration. The optimum conditions for leaching in the Murso process were found to be 20% HCl and a temperature of 108-110°C at atmospheric pressure. In practice, a 20% excess of 20% HCl over the stoichiometric amount required for leaching iron and other acid soluble non-titaniferous values is used, and in batch-wise leaching, leaching time of 3-4 hours is required.

The hydrolysis of titanium during leaching results in a certain amount of fine TiO_2 being produced. Figure 5, showing the amount of titanium in solution against the weight of fines produced, suggests that the hydrolysis phenomenon is quite complex as some of the titanium is precipitated as fine suspension from solution while the majority of it is deposited within the pores of the grain. It would appear that the reaction during leaching is a topotactic one, as the leached product has a well defined rutile structure and is quite stable.

The hydrochloric acid leaching of "synthetic ilmenite" removes oxides of manganese, magnesium, vanadium and to a certain extent aluminium along with iron. The rate of removal of manganese and magnesium follow very closely that of iron. A typical analysis of the upgrade is 96% TiO_2, 1.5% Fe_2O_3, 0.07% MnO, 0.08% MgO and 0.05% V_2O_5.

The low amounts of manganese, magnesium and vanadium in the upgrade are a distinct asset of the Murso process over some other processes where these impurities are not removed, as they are undesirable in the feed material for chlorination.

Regeneration of Hydrochloric Acid

The regeneration of hydrochloric acid from ferrous chloride liquors is based on the principle of hydrolysis of a metal chloride to give hydrochloric acid and the corresponding metal oxide. Since the chlorides of iron, manganese, magnesium, and titanium, which go into solution are all readily hydrolyzable, hydrochloric acid can be easily regenerated from the leach liquor. Based on the above principle, many commercial processes e.g. Woodall-Duckham, Otto, and Lurgi, are in operation and produce

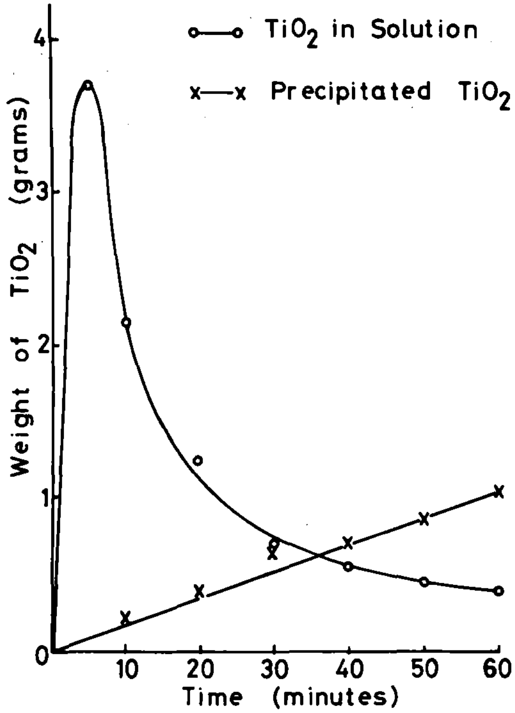

Figure 5. TiO_2 in solution against TiO_2 precipitated from solution during leaching.

19 - 20% HCl economically.

Pilot Plant Tests

The Murso process has already been tested in a small scale pilot plant. Oxidation and reduction tests were conducted in a 30 cm. diameter fluid bed reactor and the leaching in a 50 litre vessel. While most of the tests were batch tests, some continuous oxidation and reduction experiments were also conducted.

The upgrade has TiO_2 content and particle size equivalent to natural rutile and chlorinates much faster than natural rutile because of its much larger surface area (upgrade 8.4 m^2/gm, rutile 0.32 m^2/gm). Also, the degree of chlorination of the upgrade in a batch test is much higher than rutile because of its high porosity. Small scale chlorination tests at 950°C and chlorine flow of 16.5 cm/sec gave a chlorine conversion of 99%, and the carry over loss of the solids was of the order of 1.8%. These results compare very favourably with the tests on natural rutile. Also, the material has been used satisfactorily as a coating on welding electrodes. These tests confirm that the upgrade may be used as a substitute for natural rutile.

Acknowledgements

The author would like to express his thanks to G. Dark for his technical assistance. Thanks are also due to D. Waugh, E. Foley, A. Turnbull, G.H. Taylor, E.S. Pilkington, J. Hamilton and many other members of CSIRO and Murphyores Staff. The author is grateful for the cooperation of the Division of Mineral Chemistry of CSIRO and the mangement of Murphyores for permission to publish this paper.

References

1. Tikannen, M.H., Tyynela, T. and Vuoristo, E., "Reducing Pressure Leaching of Ilmenite Concentrate," Proceedings of the International Symposium on Unit Processes in Hydrometallurgy, The Metallurgical Society of AIME, Vol. 24, February, 1963, pp. 269-283.

2. Lo, C. and Mackey, T.S., "Beneficiation of Ilmenite," U.S. Patent No. 3,193,376, July 6, 1965.

3. Prosser, A.P., "Influence of Mineralogical Factors on the Rates of Chemical Reaction of Minerals," Proceedings of the Ninth Commonwealth Mining and Metallurgical Congress, The Institution of Mining and Metallurgy, London, Vol. 3, 1969, pp.59-79.

4. Sinha, H.N. and Waugh, D.M., "A Process for the Beneficiation of Titaniferous Ores," British Patent No. 1,225,826, March 24, 1971, (Application date May 1, 1967).

5. Shomate, C.H., Naylor, B.F. and Boericke, F.S., "Thermodynamic Properties of Ilmenite and Selective Reduction of Iron in Ilmenite," U.S. Bureau of Mines, Report of Investigations No. 3864, May, 1946.

6. Walsh, R.H., et al., "The Reduction of the Iron Values of Ilmenite to Metallic Iron at Less than Slagging Temperatures," Transactions of the Metallurgical Society of AIME, Vol. 218, December 1960, pp. 994-1003.

7. Hussein, M.K. and El-Tawil, S.E., "Solid State Reduction of Egyptian Black Sand Ilmenite with Hydrogen, "Indian Journal of Technology, Vol. 5, March, 1967, pp.97-100.

8. Ostberg, G., "Solid State Reduction of Ilmenite," Jernkontorets Annaler, Vol. 144, January, 1960, pp. 46-75.

9. Volk, W. and Statler, H.H., "Hydrogen Reduction of Ilmenite Ores in a Fluid Bed," Journal of Metals, Vol. 22, January, 1970, pp.50-53.