Sulphatisation and sulphidisation for hydrometallurgical extraction of main constituents of a local ilmenite ore

E. M. KHAIRY, M. K. HUSSEIN and K. A. EL-BARAWY

SYNOPSIS

Sulphatisation and sulphidisation experiments were tried on a local ilmenite ore prior to leaching out the main products. Crushed samples of a local ore were analysed and mineralogically examined. They were sulphatised by heating with different proportions of $(NH_4)_2\ SO_4$ at 300°-500°C, or $NaHSO_4$ at 400°-800°C, for different periods up to 9 hours. Optimum conversion with $(NH_4)_2SO_4$ was attained at 400°C, whereby up to 91% of the iron and 95% of the titanium contents of the ore could be leached out with 7N H_2SO_4. Better conversion was acquired with preoxidised samples, whereas complete conversion of iron was obtained with pre-reduced samples. Mixtures of pure Fe_2O_3 and TiO_2 showed lower leachability due to structural differences in the ore. With $NaHSO_4$, almost complete conversion of both iron and titanium was accomplished at 600°C, when stoichimometric proportions were used; lower proportions of $NaHSO_4$ lead to preferential leaching of iron rather than titanium. Separation of TiO_2 from iron was quantitatively achieved through controlled hydrolysis.

Sulphidisation with ZnS revealed complete conversion of iron oxides into 1 : 1 HCl leachable sulphides, at 800°-900°C. Leached out titanium was rather low. It may be stated that sulphidisation decreases in the order $FeO > Fe_2O_3 > TiO_2$. Separation of iron from titanium may be effected through sulphidisation followed by HCl leaching.

ILMENITE ores occur in UAR in large quantities, constituting two main reserves. The first, estimated to be about 10 million tons, occurs at Abu Ghalaga (AG) in the south-eastern desert, and the second comprises one of the chief constituents of beach placers, called black sands (BS), which are deposited on the shores of the Nile delta, especially at Rosetta and El-Arish. According to previous studies[1] AG ilmenite occurs in the form of lenticular, vein-like bodies intimately associated with metagabbro. The chief lens is about 300 m long, 150 m wide and 45 to 100 m thick.

The presence of iron and titanium in solid solution in ilmenite renders their separation by common dressing techniques almost impractical. Application of chemical and metallurgical techniques seems necessary. Several investigators have studied the leachabilities of titanium-bearing materials after sulphatisation or sulphidisation. A common practice frequently utilised with ilmenite ores involves sulphatisation with H_2SO_4 through batch or continuous digestion.[2] The factors influencing the breaking down of the ore, including acid concentration, temperature, particle size of the ore grains and catalysts, have been investigated.[3] Other sulphatising agents were also used, particularly ammonium and sodium sulphates. Patwardhan[4] reported the possibility of extraction of 36-84% of TiO_2 from ilmenite by heating with ammonium-sodium sulphate mixtures at 300°-340°C. Treatment with sodium sulphate at different temperatures up to 1200° in presence of carbon, followed by leaching with H_2SO_4, was found[5] to effect extraction of 79-92% of TiO_2-content of ilmenite and other titanium-bearing minerals. Kamlet[6] used ammonium sulphate at 380°-420°C in a reducing atmosphere, followed by leaching in water or recycled ammonium sulphate solution at 25°-35°. It was reported that about 1·5 the strichiometric amount of $(NH_4)_2\ SO_4$ was required for optimum conversion.

Sulphidisation of ilmenite ores is not as yet well studied. Several investigations were carried out, however, on the preparation and properties of titanium sulphide by sulphidising TiO_2. Muller[7], Bensel[8] and Kleffner[9] obtained the sulphide by heating TiO_2 with metal sulphides and carbon in the arc furnace. Dubrovskaya and others[10] pointed out that the S-content of titanium sulphide increased with rise of sulphidising temperature. At 900° the product obtained was close to TiS and at 1200° to Ti_2S_3; the existence of both phases was substantiated by X-ray analysis.

In the present work Fe_2O_3-TiO_2 mixtures, as well as AG ilmenite, are sulphatised with ammonium sulphate

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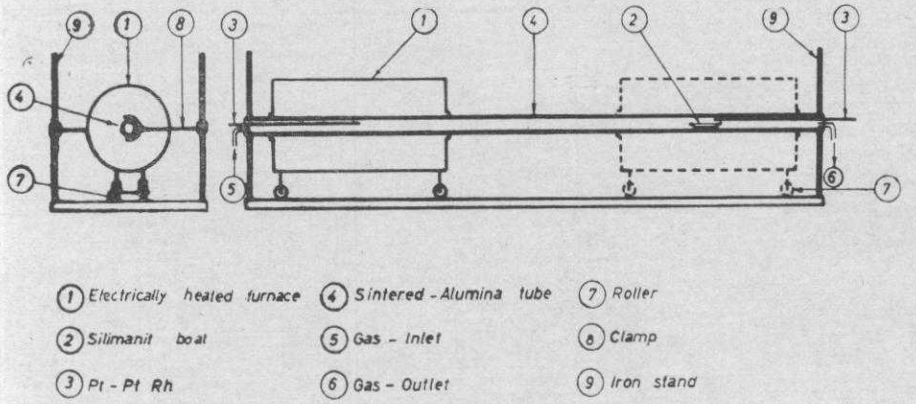
Dr E. M. Khairy, Messrs M. K. Hussein and K. A. El-Barawy, National Research Centre, Cairo.



1 *Furnace for heating sample ZnS mixtures in N_2 atmosphere*

or sodium bisulphate under a variety of conditions, followed by leaching with 7N H_2SO_4 ; Sulphidisation is also performed using ZnS, followed by leaching with 1 : 1 HCl. The products obtained are subjected to chemical and X-ray analyses and separation techniques of iron and titanium ore tried.

Materials and experimental technique

Titanium oxide, TiO_2, with a minimum purity of 98%, as well as chemically pure ammonium sulphate, sodium bisulphate and zinc sulphide were used. The ilmenite ore, Abu Ghalaga (AG), was provided in big lumps by the General Ilmenite Co., Egypt. A 10 kg sample was crushed to a size of about 10 mm and a representative sample was taken by quartering. This sample was then ground in a ball mill to appropriate grain size, followed by sieve analysis. Chemical analysis of the chief constituents yielded 39·2% for total iron, 18·9%Fe^{2+} and 20·3% Fe^{3+}, 41·15% for titanium, and 3·1% for silica. This corresponds to 27% TiO_2 combined with FeO in the form of $FeTiO_3$ and the remainder is either combined with Fe_2O_3 as pseudobrookite or forms a solid solution with ilmenite. Spectroscopic investigation revealed the presence of Al, Ca, Mn, V, Co, Ni, Cd, Mg and Zr as trace elements.

X-ray diffraction gave lines of maximum intensity corresponding to ilmenite, with less intense lines of hematite ; no lines for pseudobrookite were detected. Mineralogical investigation showed that the mineral is chiefly composed of a granular mosaic of ilmenite grains (70–75% of the ore) in the form of anhedral to subhedral crystals of diameter ranging from 0·8 to 0·2 mm. The interlocking grains are sometimes separated by quartz or silicate gangue and they often enclose exsolution bodies of hematite. The ilmenite-hematite exsolution intergrowth may represent the progressive unmixing of two solid solutions which are ferriferous ilmenite and titaniferous hematite. Electron-probe microanalysis revealed the presence of a main titaniferous structure composed of both titanium and iron oxides in varying compositions. The grains contain pure iron oxide, silica or iron sulphide as inclusions. Some grains of pure iron oxide were detected. The ore was found to exhibit feeble magnetic properties ; the magnetic fraction amounted to about 4%.

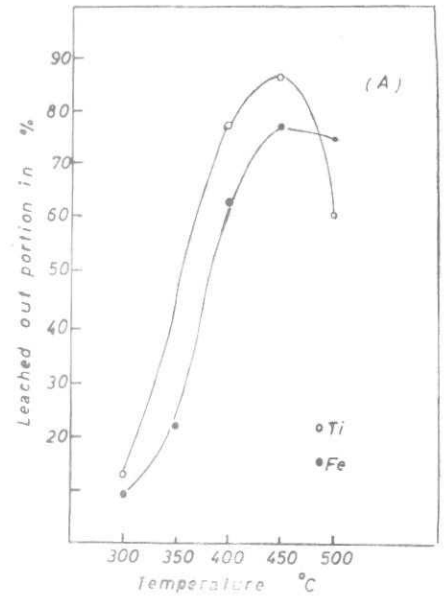
Sulphatisation was performed by mixing the sample with different proportions of ammonium sulphate or sodium bisulphate. The mixture placed in a covered crucible was heated in a previously calibrated automatically-controlled electric muffle furnace of the Heraeus type. The reaction products were leached out with $7NH_2SO_4$ and the dissolved iron and titanium determined by chemical analysis.

Sulphidisation was carried out with zinc sulphide. The sample was heated in a tube furnace provided with rolls which move smoothly on rails (Fig. 1). In the middle of the hot zone of the furnace a calibrated Pt/Pt-Rd thermocouple was inserted in a special socket. A gas-tight silica tube was placed inside the furnace so that the furnace may be moved freely along it ; the sample was placed in a silimanite boat right below the hot junction of the thermocouple. The reaction tube was closed from both ends and oxygen-free nitrogen gas was passed through inlet and outlet tubes at an adjusted flow rate. The furnace located at the other end of the reaction tube was heated up, and after a certain period sufficient to expel air and reach the requisite temperature, it was displaced so that the boat and charge lie in its hot zone. At the end of the experiment, the furnace was returned to its original position and the charge allowed to cool. After attaining room temperature, the boat was withdrawn, the reaction products leached out with 1 : 1 HCl and the dissolved proportions analysed.

Results and discussion

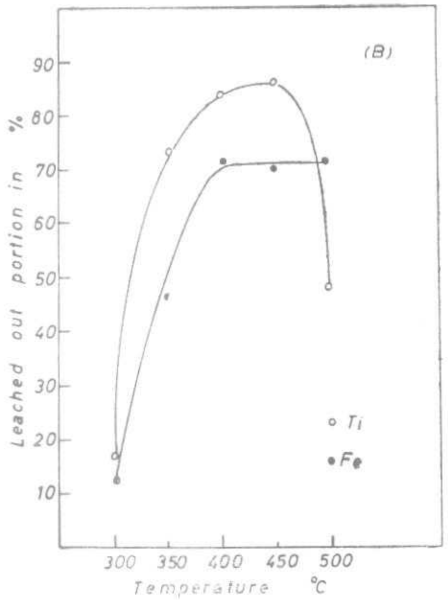
Sulphatisation with ammonium sulphate

Three mixtures with the following iron oxide/titanium oxide ratios were used : 25–75 (A) 50–50 (B) and 75–25 (C). These proportions were mixed with $(NH_4)_2SO_4$ in the ratio of 1 g oxides mixture/5g $(NH_4)_2SO_4$ and then heated for 3 hours at 300°–500°. The results showing the leached out iron and titanium

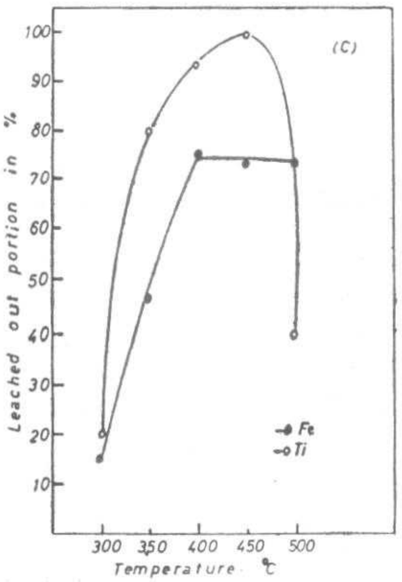


2a *Leachability of sulphatised Fe_2O_3–TiO_2 oxide mixture (25 : 75%) in 7N–H_2SO_4*

proportions in $7NH_2SO_4$ are graphically represented in Fig. 2, related each to the original respective oxide in the sample. In mixture (A), the leached out iron and titanium increase appreciably with rise of temperature, especially between 350° and 400°C. The optimum recoveries achieved at 450° amount to ~78% of the iron and 86% of titanium. At 500°C, the leached out iron decreases slightly, whereas, titanium decreases markedly. Mixtures B and C exhibit somewhat different behaviours. The leached out iron proportions increase markedly with rise of temperature from 350° to 400°C and remain nearly constant at higher temperatures ; about 72 and 75% respectively, of the iron is leached out. Optimum titanium conversions are acquired at 450°, amounting to ~86 and 99·8%, respectively for the two mixtures. One may attribute the increase in the leached out iron in the mixtures to the progressive formation of the double sulphates $(NH_4)_3 Fe (SO_4)_3$ and $(NH_4) Fe (SO_4)_2$ as shown by the reaction : $Fe_2O_3+6\ (NH_4)_2\ SO_4 \rightarrow 2\ NH_4\ Fe\ (SO_4)_2 .\ (NH_4)_2\ SO_4+6\ NH_3+3H_2O$



2b *Leachability of sulphatised Fe_2O_3–TiO_2 mixture (50 : 50%) in 7N–H_2SO_4*



2c *Leachability of sulphatised Fe_2O_3–TiO_2 mixture (75 : 25%) in 7N–H_2SO_4*

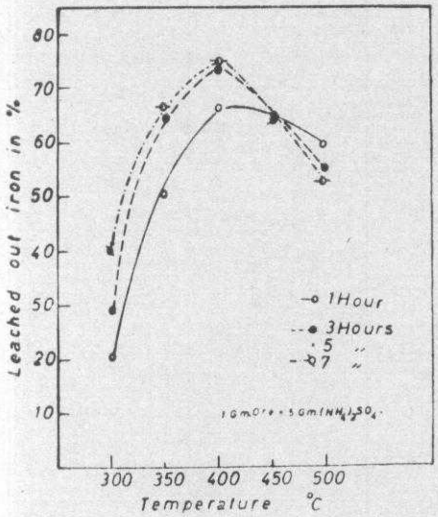
X-ray patterns obtained for reaction products reveal the presence of $(NH_4)_3$ Fe $(SO_4)_3$ at 350°, and (NH_4) Fe $(SO_4)_2$ at 400°. At 500°, the main products are $FeSO_4$ and $Fe_2\ (SO_4)_3$.

Titanium oxide reacts with $(NH_4)_2\ SO_4$ to an extent increasing with rise of temperature, with the formation of the soluble sulphate. The reaction may take place up to 450° presumably according to equation (1), while it proceeds at higher temperatures according to equation (2) due to decomposition of the double sulphate.

$$TiO_2+3\ (NH_4)_2\ SO_4 \rightarrow Ti\ (SO_4)_2 .\ (NH_4)_2\ SO_4+4NH_3+2H_2O \tag{1}$$

$$TiO_2+2SO_3 \rightarrow Ti\ (SO_4)_2 \tag{2}$$

It seems that the affinity of titanium oxide to react with $(NH_4)_2\ SO_4$ is somewhat higher than that



3a *Leachability of iron in A. G. ilmenite sulphatised with* $(NH_4)_2SO_4$ *in* $7N\text{-}H_2SO_4$

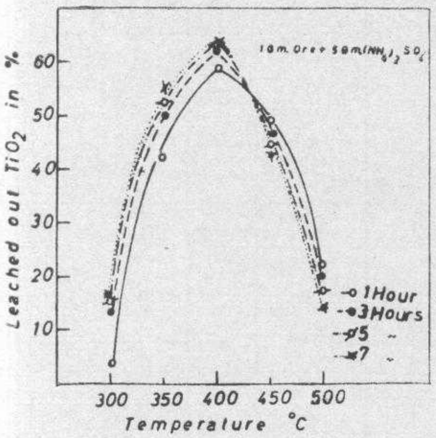
of iron oxide. However, the leached out iron in the mixture is considerably higher than if pure iron oxide is treated under similar conditions. This may be ascribed to probable indirect sulphatisation of iron oxide through the formed titanium sulphate, taking place according to :

$$3Ti\ (SO_4)_2 + 2Fe_2O_3 + 2(NH_4)_2\ SO_7 \rightarrow 2Fe_2\ (SO_4)_3\ (NH_4)_2\ SO_4 + 3TiO_2$$

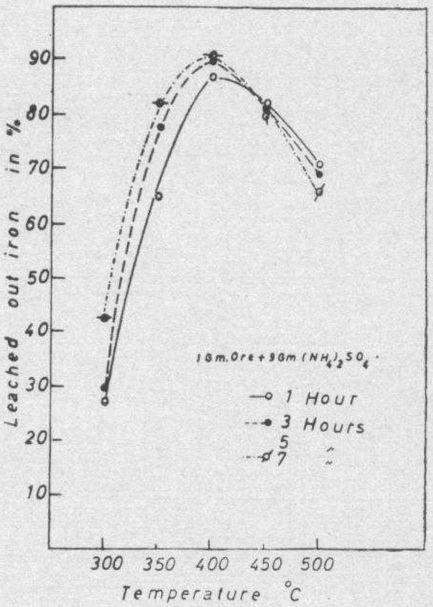
$$3TiO_2 + 6(NH_4)_2\ SO_4 \rightarrow 3Ti\ (SO_4)_2 + 12NH_3 + 6H_2O$$

Or

$$Ti\ (SO_4)_2 + 3(NH_4)_2\ SO_4 + Fe_2O_3 \rightarrow Ti\ (SO_4)_2 + FeSO_4 + 6NH_3 + 3H_2O$$



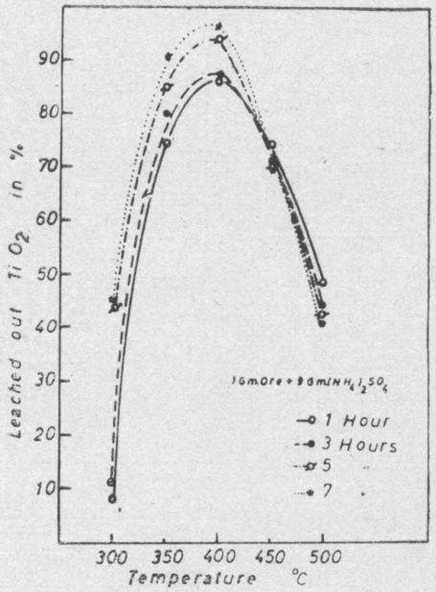
3b *Leachability of* TiO_2 *in A. G. ilmenite sulphatised with* $(NH_4)_2SO_4$ *in* $7N\text{-}H_2SO_4$



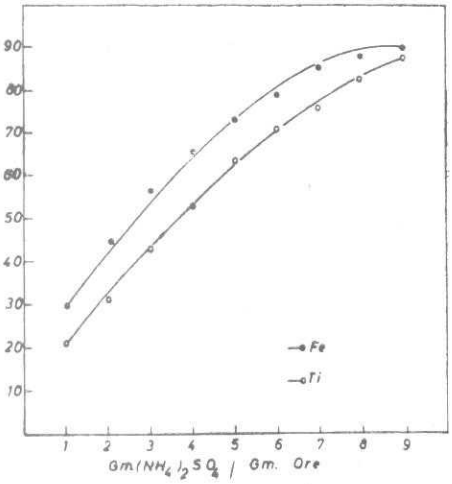
4a *Leachability of iron in A. G. ilmenite sulphatised with* $(NH_4)_2SO_4$ *in* $7N\text{-}H_2SO_4$

Behaviour of Abu-Ghalaga ilmenite

The effect of changing the temperature as well as the reaction period on the extent of conversion of the ilmenite constituents upon sulphatisation is studied with three mixtures containing 5, 7 and 9g $(NH_4)_2SO_4$/g ore. Three mixtures were heated for different

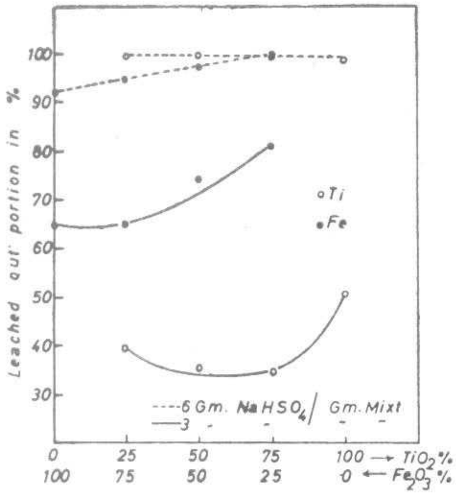


4b *Leachability of titanium in A. G. ilmenite sulphatised with* $(NH_4)_2\ SO_4$ *in* $7N\text{-}H_2SO_4$



5 *Leached out iron and titanium in A. G. ilmenite sulphatised at 400° with different proportions of* $(NH_4)_2 SO_4$

periods up to 7 hours and at various temperatures up to 500°. The results obtained showing the extent of conversion of iron and titanium oxides into soluble products are represented in Figs. 3 and 4. It is apparent that the soluble iron proportions increase invariably with rise of temperature up to 400°, above which leachability decreases markedly. Meanwhile, changing the heating duration exerts also noticeable effects in increasing the leached out proportion up to 400°. Optimum conversion corresponds to 75, 86 and 91% of the iron content of the ore in the three mixtures, respectively. The maximum conversion acquired with titanium at 400° amounts to 64, 77 and 96% of the total titanium content in the ore for the same mixtures.



6 *Leachability of* Fe_2O_3–TiO_2 *mixtures sulphatised at 600° with* $NaHSO_4$ *in* $7N$-H_2SO_4

The effect of changing the ammonium sulphate proportion upon the sulphatisation extent can be elucidated by the results obtained with finely-crushed samples of A. G. ilmenite ore intimately mixed with ammonium sulphate in ratios ranging from 1 to 9 g $(NH_4)_2\ SO_4$/g ore. The mixtures were heated for 3 hours at 400° and the products were leached out with $7NH_2\ SO_4$. The results are shown in Fig. 5. It can be seen that the conversion of iron and titanium oxides increases appreciably with increase of the ammonium sulphate proportion in the the mixture. It may be noted that the relative leached out proportions are somewhat higher for iron than for titanium.

In order to elucidate the above views, two experiments were performed with pre-reduced and pre-oxidised samples of A. G. ilmenite ore. Reduction was effected by hydrogen under conditions causing the reduction of ferric oxide to the ferrous state. Oxidation was performed by heating in oxygen atmosphere at 800°, bringing about the transformation of ferrous oxide to the ferric state. Besides, it is expected that the rather complicated solid solution structures in the ore may be partially or completely destroyed according to :

$$FeO.\ TiO_2 \rightarrow FeO + TiO_2$$
$$Fe_2O_3.\ TiO_2 \rightarrow Fe_2O_3 + TiO_2$$

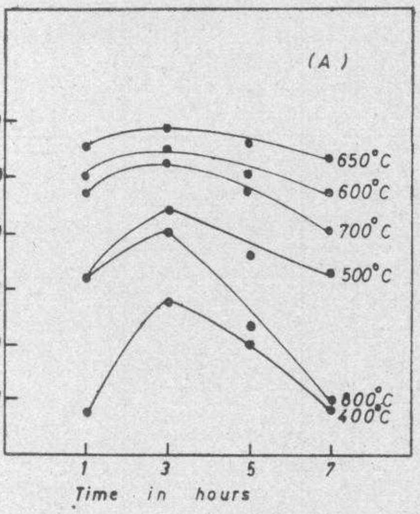
Treated samples were mixed with $(NH_4)_2\ SO_4$ in the ratio 1 : 5 and these mixtures were heated for 3 hours at 400°. The results indicate the conversion values shown in Table I. For comparison, the corresponding values achieved with the pure oxides and their mixtures are also given.

TABLE I Leachability of iron and titanium oxides sulphatised with $(NH_4)_2SO_4$**, in** $7N$-H_2SO_4**.**

		Mixture		Ore		Pre-oxidised		Pre-reduced	
Pure TiO_2	Pure Fe_2O_3	Ti	Fe	Ti	Fe	Ti	Fe	Ti	Fe
87%	29·8%	84%	72%	62%	73%	76%	93%	72%	100%

It can be seen that both treatments improve the conversion extents of iron and titanium oxides present in the ore. Ferrous oxide seems to be somewhat more active than ferric oxide. The slight increase of iron recovery acquired with the pre-reduced samples compared to the pre-oxidised ones, may be attributed as well to the porous nature of the pre-reduced ore, as to the presence of a little metallic iron in the pre-reduced charge, which may accelerate the interaction.

The fact that the soluble titanium proportions in the ore are lower than the corresponding value achieved when pure titanium oxide was sulphatised, advocates the view that the part of titanium oxide still kept in



7a *Leached out iron in A. G. ilmenite sulphatised with $NaHSO_4$ in $7N\text{-}H_2SO_4$*

solid solution with iron oxide is less reactive than free titanium oxide.

Sulphatisation with sodium bisulphate

Behaviour of mixtures of iron and titanium oxides

Three mixtures containing iron oxide/titanium oxide weight ratios 75 : 25, 50 : 50, and 25 : 75 were used. Sulphatisation with $NaHSO_4$ in the ratio of 1 mixture : 6 bisuphate, was performed. This ratio corresponds nearly to the stoichiometric ratio necessary for the conversion of both iron and titanium oxides into soluble forms. In order to elucidate the sulphatisation mechanism, a second series of experiments was conducted at about half the stoichiometric ratio of bisulphate. The oxides-sodium bisulphate mixtures were heated for 3 hours at 600°, and then leached with 7N H_2SO_4. The results obtained indicate that at the stoichiometric $NaHSO_4$ proportion, the leachabilities of iron and titanium oxides increase considerably with their respective proportions in the oxide mixture. Nearly complete conversion of iron oxide and titanium oxide into soluble forms could be accomplished (Fig. 6). The leached out proportions obtained with the mixture containing the lower proportion of $NaHSO_4$ are markedly lower than the above values. The reactions may be outlined as follows :

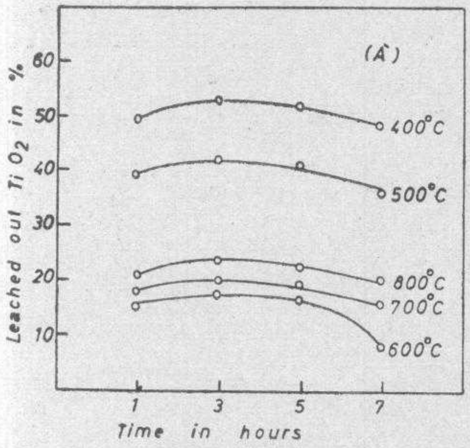
$$
\begin{aligned}
4Fe_2O_3 + 8Na_2S_2O_7 &\rightarrow 4FeSO_4 + 2Fe_2(SO_4)_3 \\
&\quad + 6Na_2SO_4 + 2Na_2O + O_2 \\
TiO_2 + 2Na_2S_2O_7 &\rightarrow Ti\,(SO_4)_2 + 2Na_2SO_4
\end{aligned}
$$

It may be noted that the presence of iron oxide influences the interaction of titanium oxide and $NaHSO_4$ inasmuch as the former reacts more readily with the bisulphate, causing a decrease in the relative conversion of TiO_2, as compared with the proportions obtained in absence of iron oxide. This effect is more pronounced in the mixture containing the lower proportion of $NaHSO_4$.

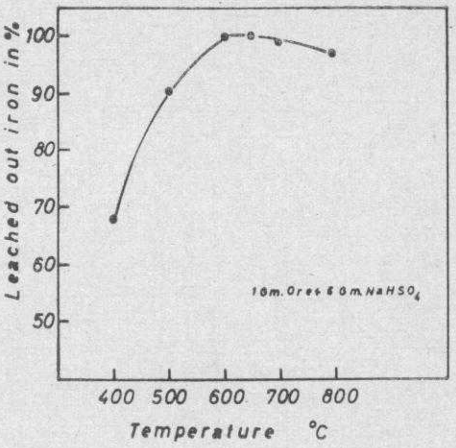
Behaviour of A. G. ilmenite

Finely-crushed samples of the ore were mixed with sodium bisulphate in the ratio 1 : 3, the mixtures heated for various periods up to 7 hours, at different temperatures up to 800°, and then leached out. The results obtained are represented in Figs. 7 and 8.

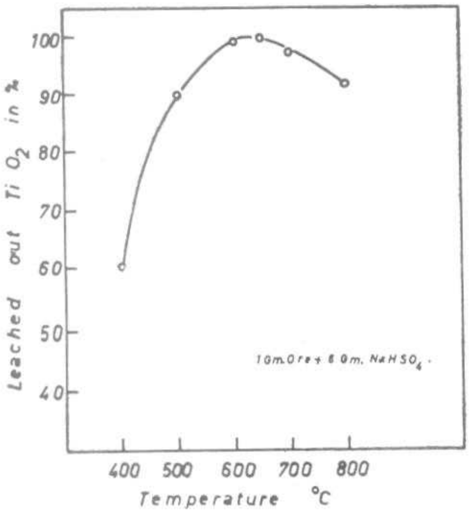
It may be seen from Fig. 7 that the soluble iron proportions increase gradually with rise of temperature up to 650°, whereupon iron is completely leached out ; at higher temperatures the soluble iron proportions decrease. At all the temperatures applied, increasing



7b *Leached out titanium in A. G. ilmenite sulphatised with $NaHSO_4$ in $7N\text{-}H_2SO_4$*



8a *Leached out iron in A. G. ilmenite sulphatised with $NaHSO_4$ in $7N\text{-}H_2SO_4$*



8b *Leached out titanium in A. G. ilmenite sulphatised with NaHSO$_4$ in 7N-H$_2$SO$_4$*

the heating duration up to 3 hours has a marked effect on increasing the amount of leachable iron compounds, whereas longer periods cause decreased leachability. The reaction taking place up to 650°C may be represented by:

$$FeO\ Fe_2O_3\ (\text{in ilmenite}) + 4Na_2S_2O_7 = FeSO_4 + Fe_2(SO_4)_3 + 4Na_2SO_4$$

At higher temperatures, both types of iron sulphate are decomposed into less soluble oxides.

It should be pointed out that the behaviour of iron oxides in the ore upon sulphatisation resembles to a great extent to that of pure iron oxide under the same experimental conditions. However, at the optimum conditions, the extent of conversion of iron oxides in the ore is somewhat higher (95%) than that achieved with the iron oxide-titanium oxide mixture. The difference in behaviour between the ore and the mixture is plausibly attributed to structural differences of iron oxides in the ore, both ferrous and ferric states being present.

Considering the results achieved with a higher sodium bisulphate ratio, i.e., 6 g/g ore, Fig. 8, shows that the leached out iron and titanium proportions increase gradually with rise of temperature until the optimum condition is acquired at 600°C—650°C. Under these conditions, both iron and titanium oxides are almost entirely brought into solution. Above 650°C and up to 800°C, the leachabilities decrease slightly. It is apparent that for the complete conversion of iron and titanium oxides into soluble sulphates, the sodium bisulphate ratio should be $\geqq$ the respective stoichiometric ratio.

It appears of interest to carry out two additional experiments, with pre-oxidised, and pre-reduced ore respectively. For pre-oxidation, samples of the ore were heated in oxygen atmosphere at 800°C. Under these conditions it has been shown that ferrous oxide in the ore is almost completely converted into the ferric state.[11] Reduction of a rather large sample of the ore is carried out with hydrogen gas, under conditions shown to convert ferric into ferrous oxide. The pre-oxidised and pre-reduced samples were mixed with NaHSO$_4$ in the ratio 1 : 3 and the process was carried out for 3 hours at 600°C. The results obtained are recorded in Table II.

TABLE II **Leachability of iron and titanium oxides sulphatised with NaHSO$_4$ in 7N-H$_2$SO$_4$**

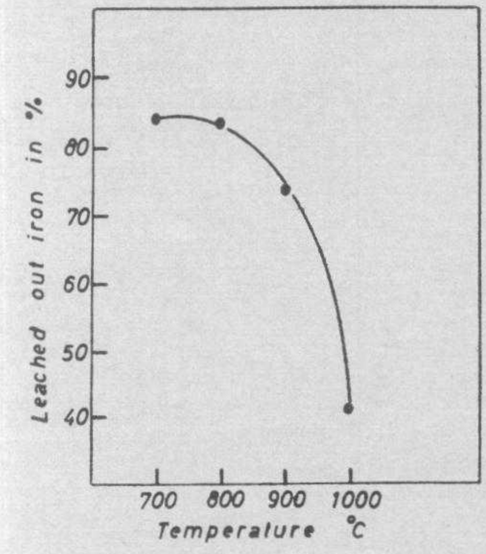
Material	Leached-out iron proportion
Ferric oxide + TiO$_2$ (1 : 1)	75%
Pre-oxidised ore	78%
Pre-reduced ore	98%
Untreated ore	95%

It is clear that under the prevailing conditions, sulphatisation takes place more readily if iron is present in the ferrous rather than in the ferric state. The effect of such pre-treatment is however much less pronounced at the higher NaHSO$_4$ ratio (1 ore : 6 NaHSO$_4$), whereby complete conversion of the iron oxides into soluble sulphates takes place.

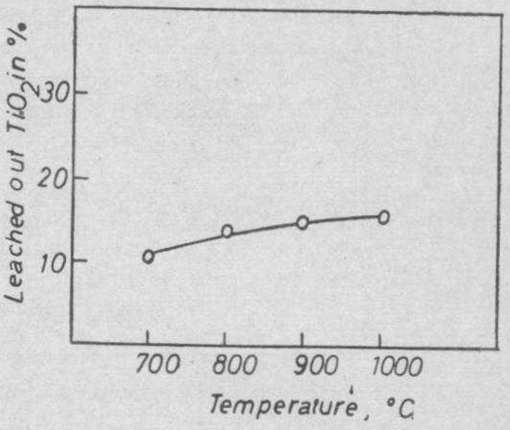
Regarding the behaviour of titanium present in the ore, it can be seen [Fig. (7b)] that the leachability amounts to about 50% after heating at 400°C, but decreases pronouncedly with rise of temperature up to 600°C. At higher temperatures, a slight increase of the soluble titanium compounds takes place. The increase of the reaction duration from 1 to 3 hours causes a slight increase in the leached out titanium proportions. At still longer periods, one can differentiate between two modes of behaviour. Thus, at 400°C and 800°C, the soluble proportions achieved remain more or less the same, while at the intermediate temperature range, pronounced decrease of the leached out proportions occurs.

The above results may be explained in view of the different affinities of iron and titanium oxides towards sulphatisation. Up to 400°C, Ti(SO$_4$)$_2$ is probably formed according to reaction iron oxide reacts most probably to an approximately similar extent with sodium bisulphate. At higher temperatures up to about 600°C, iron is more readily sulphatised with subsequent decrease of the leached out titanium proportions. Above 600°C, ferrous as well as ferric sulphates starts to decompose thermally yielding the less soluble oxide, and hence the lower tendency for sulphatisation of titanium may then occur.

It should be noted that the leached out titanium proportion achieved with the ore after heating for 3 hours at 600°C (18%) is lower than the corresponding value obtained with Fe$_2$O$_3$: TiO$_2$ mixture in the ratio 1 : 1 (35%). This can be also correlated with the structural differences of iron oxide in the ore.



9a *Leached out iron in Fe_2O_3–TiO_2 mixture sulphidised with ZnS in 1 : 1 HCl*



9b *Leached out titanium in Fe_2O_3–TiO_2 mixture sulphidised with ZnS in 1 : 1 HCl*

Separation of iron from titanium in the leaching medium

In the previous study it was possible under specified conditions to convert both iron and titanium oxides present in ilmenite into soluble products. The problem of separating iron from titanium in such leaching medium was investigated by El Kalliny[12], applying the ion-exchange technique. In other investigations[13], the separation was effected by hydrolysis techniques, which seem to be more convenient for industrial application. We adopted this technique by treating the sulphate solution containing both iron and titanium with sodium carbonate, the pH of the solution being controlled at 6·5. Orthophosphoric acid 10%, was then added until the pH of the solution acquired a value of 2·5. By such treatment titanium was precipitated, washed with 10% sulphuric acid, dried and heated at 900°C to obtain titanium oxide free from iron. Quantitative recovery of titanium oxide was thus made possible.

Sulphidisation with ZnS

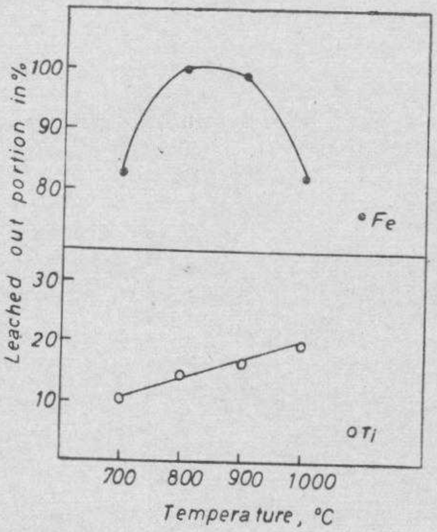
Behaviour of mixtures of iron and titanium oxides

Pure fine iron oxide is thoroughly mixed with titanium oxide in the ratio 1 : 2 and sulphidisation is performed with ZnS added in the ratio of about 2g/g mixture. The process is carried out in pure nitrogen atmosphere and extends for 3 hours at 700°C. The products are leached out in 1:1 HCl. The results are represented in Fig. 9.

The leached out iron proportions increase with rise of temperature up to 700°C, thereby ~85% of the total iron present is leached out, which value remains more or less constant up to 800°C. Above 800°C the leached out proportions decrease regularly at first and more sharply afterwards ; about 40% of the iron is present in a leachable form at 1000°C. It may be admitted that about 20% of Fe_2O_3 is leachable by direct action of 1 : 1 HCl. Sulphidisation proceeds probably according to the following mechanism :

$$9Fe_2O_3 + ZnS = 6Fe_3O_4 + ZnO + SO_2$$
$$2Fe_3O_4 + ZnS = 6FeO + Zn + SO_2$$
$$FeO + ZnS = FeS + ZnO$$
$$\text{or } FeO + ZnS = FeS + Zn + \tfrac{1}{2}O_2$$

The decrease of leachability above 800°C may be attributed as well to the formation of purrhotite structure, $Fe_{1-x}S$[14] as to increased evaporation of ZnS. The leachability of titanium increases slightly with rise of temperature from 700°C to 800°C and remains constant



10 *Leached out iron and titanium in A. G. ilmenite sulphidised with ZnS in 1 : 1 HCl* irrespective of further increase of temperature. Under these conditions, 15% only of the titanium content can be leached out. Apparently this value is much lower than the corresponding one obtained when pure titanium oxide is used (42%). This can be taken to indicate the greater tendency of iron oxide to be sulphidised than titanium oxide thus hindering the rapid reaction of the latter. Sulphidisation of TiO_2 proceeds probably according to :

$$\begin{array}{lll} TiO_2 + ZnS & = & TiS + ZnO + \tfrac{1}{2}O_2 \\ TiO_2 + 2ZnS & = & TiS + 2ZnO + S \\ 2TiO_2 + 3ZnS & = & Ti_2S_3 + 3ZnO + \tfrac{1}{2}O_2 \\ 5TiO_2 + 8ZnS & = & Ti_2S_3 + Ti_3S_4 + 8ZnO + SO_2 \\ TiO_2 + 2ZnS & = & TiS_2 + 2ZnO \end{array}$$

X-ray analysis of the reaction products at 900°C reveals the presence of TiS and Ti_3S_4. The latter may be also formed according to :

$$3\ Ti_2S_3 = 2Ti_3S_4 + S$$

Behaviour of Abu-Ghalaga ilmenite

A. G. ilmenite is sulphidised under the same conditions utilised with oxide mixtures. A sample of the ore having appropriate grain size is mixed with zinc sulphide in the ratio 3·5 g ZnS/g ore. The experiments are carried out in pure nitrogen atmosphere for 1 hour at different temperatures up to 1000°C.

Fig. 10 shows that the leachability of iron proportions increase with rise of temperature reaching almost complete conversion at 800°-900°C. Above 900°C the leached out proportion decreases reaching 82% at 1000°C. It is noteworthy that the values acquired along the temperature range 400° to 1000°C are higher than those obtained with pure iron oxide or its simple mixture with titanium oxide. This may be attributed to the readiness of conversion of lower iron oxide into sulphide,

The curve representing the behaviour of titanium shows that the leached out proportions are rather low. About 20% of the titanium content can be leached out at 1000°C. These results are comparable with those obtained with the mixture, but much lower than the corresponding values obtained with pure titanium oxide.

Apparently, one can adopt the conditions at which complete conversion of iron oxide and minimum conversion of titanium oxide into soluble sulphide, for separation of both constituents from each other, iron from the leached out products and titanium in the residue.

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Discussions

Mr **Sunil Dey** (Chemical and Metallurgical Design Co., New Delhi) : As stated by Dr Khairy, during sulphatisation about 80-90% of both Ti and Fe are converted to soluble sulphate. Similarly, during sulphidisation about 20% of Ti and 100% Fe are converted to leachable sulphide in hydrochloric acid. I think that sulphatisation and sulphidisation should be preferential to titanium and not to Fe as shown in the paper, considering the economics of the process.

Mr **R. N. Misra** (NML) : The work of Prof. Khairy and his colleagues is of interest to us because we are also working on Indian ilmenites. The ore referred to by the authors contain Cr and V. Has the reaction of Cr and V been studied ?

From the economic point of view, is the process studied comparable to other processes like Sorel process, chlorination or reduction and iron aqueous oxidation ?

It was surprising to note that solubility of Fe and Ti decreases after an increasing trend for 3 hours. What could be the reason ?

Prof. Dr **E. M. Khairy** (Author) : In reply to the first question regarding the economics of the process I have to mention that our investigations are still at the laboratory stage. The results obtained revealed the possibility of separating titanium from the leaching liquor containing iron, through controlled hydrolysis at pH 6·5. Studies are being conducted for an economic hydro-metallurgical extraction of the main constituents of ilmenite ores by applying the process on pilot plant scale.

In reply to Mr Misra, I may state that the Abu Ghalaga ore used in this investigation contains traces of chromium. In our previous studies on chlorination, chromium was mentioned with regard to one grade of another ilmenite ore present in black sands. No special attention was therefore paid to chromium in this investigation. Vanadium and its separation are being studied separately in our laboratory.

The process presented in this paper is one of the processes investigated for the utilisation of Egyptian ilmenite ores. The process is based on solid state reduction followed by leaching, preferential chlorination, smelting and chlorination of the slags produced, etc. We are now trying to evaluate all these processes economically. The effect of time above 3 hours on lowering leachability of pre-sulphidised ore is probably due to interactions between FeS and TiS (or $Ti_2 S_3$), indirect sulphidisation of titanium oxide through iron sulphide. This leads to decreasing conversion into soluble products. At the same time and due to application of relatively high temperatures, thermal decomposition of reaction products or of sulphidising agent takes place. Apparently the latter process becomes more pronounced as the reaction period is increased. This problem needs further study.