

RESEARCH ARTICLE

## Effect of Sulphate Ions on Leaching of Ilmenite with Hydrochloric Acid

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### Abstract

The titanium content in the ilmenite is enriched by removing the iron content present in the ilmenite. The titanium content enriched ilmenite thus obtained is called Synthetic Rutile (SR) or Beneficiated Ilmenite (BI). The iron content in the ilmenite is removed by carbo-thermic reduction followed by leaching with hydrochloric acid. The leach liquor contains ferrous and ferric chloride with small percentage of free acid and fines (powdered BI generated during leaching process). The quality of leaching process is mainly governed by the higher percentage of TiO<sub>2</sub> content (above 93%) in BI, minimum quantity of free acid (less than 1%) and minimum quantity of fines (less than 1%) in the leach liquor. The effect of sulphate (calcium zinc, sodium and potassium) ions on the leaching properties of the ilmenite was studied under laboratory conditions (30% hydrochloric acid, 75°C, one atmospheric pressure and stirring at 500 rpm). The addition of sulphate ions enhance the titanium content in BI and reduced the quantity of free acid and fines generated in leach liquor. Among the different sulphate catalyst tried, the sulphates of divalent metal (calcium and magnesium) shows better performance than sulphate of monovalent metal (sodium and potassium). The maximum leaching was given by the addition of calcium sulphate and the percentage of leaching enhances to 95%, when the leaching medium contains 100 mg of calcium sulphate. The kinetic study shows that the leaching reaction is following first order kinetics.

**Keywords:** Ilmenite, leaching, synthetic rutile, titanium dioxide, calcium sulphate, first order kinetics.

### Introduction

Synthetic Rutile (SR) or Beneficiated Ilmenite (BI) is mainly used for the production of titanium dioxide. Synthetic rutile is mainly produced from the ilmenite through Benalite process. The production process typically involves reduction of ferric content to ferrous oxide and subsequent acid treatment to remove iron, leaving a TiO<sub>2</sub>-rich phase. The quality of SR is mainly based on the percentage of titanium content, the particle size and colour of the material. Usually the SR contains more than 93% of titanium dioxide. The particle size of SR is in the range between US mesh of -10 and +200. The quality of the SR produced can be enhanced by the post and pre treatment of ilmenite during the reduction process. The reducing roasting of titanium concentrate over wide range of operating condition to develop a new technology of processing was reported in the literature (Popov *et al.*, 2011). The modification of leaching process is another technique used to improve the quality of SR. There are several reports available in literature focusing on the modification of ilmenite leaching with hydrochloric acid (Lanyon *et al.*, 1999; Olanipekun, 1999; Ogasawara and De-Araujo, 2000; Baba *et al.*, 2013). The reactivity of ilmenite ore during leaching with hydrochloric acid can be greatly enhanced by reduction in solution using metallic iron (Mahmoud *et al.*, 2004).

The dissolution of ilmenite is enhanced by the addition of little amount of methanol in hydrochloric acid (Habib *et al.*, 2006). The effect of addition of soluble chlorides of ferrous chloride, manganese chloride, magnesium chloride, nickel chloride, calcium chloride and ammonium chloride on the leaching performance and the kinetics of the leaching process with these ions have been reported (Reid and Sinha, 1975). A patent was reported in literature for improving the leaching of ilmenite by addition of gypsum or sulphuric acid (Chen and Huntoon, 1977). The leach liquor contains mainly ferrous and ferric chloride. These leach liquor is subjected to spray roasting to generate hydrochloric acid for recycling and iron oxide. The iron oxide generated can be used as the raw material for the production of pig iron or used as red oxide pigment. The present study deals with effect of addition of calcium sulphate, magnesium sulphate, sodium sulphate and potassium sulphate on the leaching of ilmenite with hydrochloric acid.

### Materials and methods

**Raw material:** The Quilon grade ilmenite (Q Grade) is used as the ore for the study. The Q grade ilmenite contains approx. 60% of titanium dioxide, 25% of Fe<sub>2</sub>O<sub>3</sub> and 10% of FeO with smaller percentage of other metal oxides (silica, alumina, etc.).

The constituents present in the ore are analyzed by Atomic Absorption spectrometer (AA 100) of Perking Elmer and X-ray fluoresce analyzer (XRF) of Bruker. All reagents and chemical used in this study are of AR grade quality.

**Conversion of raw ilmenite to reduced ilmenite:**  
The ilmenite is subjected to carbothermic reduction in air tight cylindrical stainless steel Tube of 50 CC capacity at 900°C for 15 min using petroleum coke as reductant. The ilmenite to petroleum coke was in the ratio of 10: 1. The reduced ilmenite consists of approx. 60% of titanium dioxide, 30% of FeO and 2% of Fe<sub>2</sub>O<sub>3</sub>. The reduction process would not enrich the titanium dioxide content but convert the ferric state of iron to leachable ferrous form. Thus, the kinetics of the leaching process is enhanced due to the reduction of ilmenite. Moreover, the ferrous state is generated by the removal the oxygen the crystal lattice of ilmenite, generating porous surface enhancing the hydrochloric acid attack during leaching.

**Leaching process:** The leaching of reduced ilmenite is performed in 500 mL round bottom flask with ground joint at the top. About 10 g of ilmenite is taken in the RB flask 100 mL of 30% hydrochloric acid were introduced in to the system. The RB flask is attached with a water condenser to condense the hydrochloric acid vapour generated in the RB flask during the leaching process, usually carried out at higher temperatures. A magnet with teflon coating was introduced in to the RB Flask for mixing the acid and ilmenite. The RB flask is placed in a rota-mantle for providing temperature and agitation. The leaching process was carried out at 75°C, normal atmospheric pressure, 500 rpm rotating speed and 8 h leaching time. Different amount of catalyst (sulphates of calcium, magnesium, sodium and potassium) were introduced in to the RB flask and the leaching efficiency is calculated based on the amount of iron removed from the reduced ilmenite. The iron present in the ilmenite was analyzed by using AAS techniques. The leaching efficiency is calculated as:

$$\text{Leaching efficiency (\%)} = \frac{\text{Amount of FeO removed} \times 100}{\text{Amount of FeO present in reduced ilmenite}}$$

### Results and discussion

Figure 1 shows the leaching efficiency of ilmenite in hydrochloric acid with varying amount of catalyst, (10 mg to 100 mg). Addition of all the catalyst (CaSO<sub>4</sub>, MgSO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub> and K<sub>2</sub>SO<sub>4</sub>) improves the leaching process. As the amount of catalyst increased, leaching process also enhances. The leaching efficiency above 75 mg of catalyst addition was marginal and hence, 100 mg of catalyst can be taken as the optimum value. Among the catalyst tried, the maximum leaching efficacy was given by CaSO<sub>4</sub>. The leaching efficiency by using the catalyst are in the order CaSO<sub>4</sub> > MgSO<sub>4</sub> > Na<sub>2</sub>SO<sub>4</sub> > K<sub>2</sub>SO<sub>4</sub>.

Fig. 1. Leaching efficiency of ilmenite with 30% HCl with catalyst concentration varies from 0 to 100 mg (ilmenite-10 g, 30% HCl-100 mL, striing speed-500 rpm, temperature 75°C, duration of leaching 480 min).

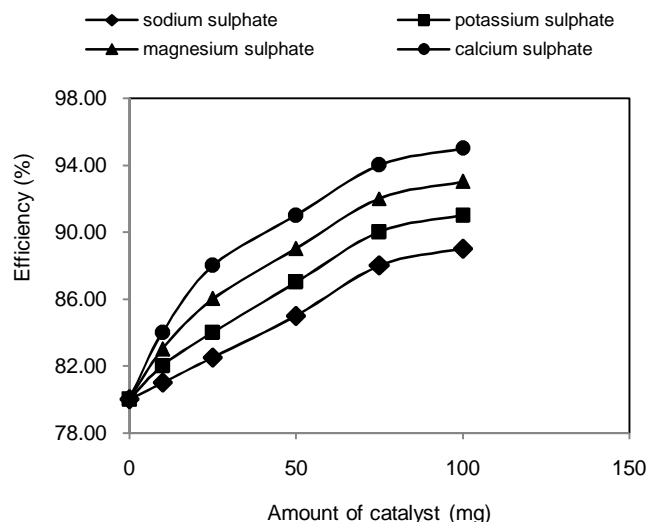
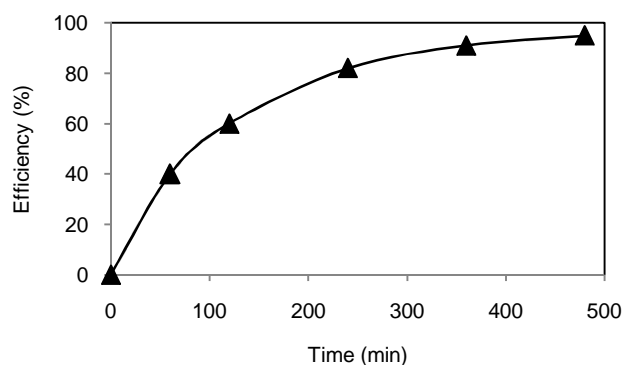


Fig. 2. Variation of leaching efficiency with time for ilmenite (10 g) leaching with 30% HCl (100 mL) and 100 mg of calcium sulphate.



Sulphates of divalent metal (Ca and Mg) are more effective than the sulphates of monovalent metal (Na and K). The leaching efficiency increased to a value of 95%, when the leaching medium contains 100 mg of CaSO<sub>4</sub>. The variation of leaching efficiency with time for 100 mg of calcium sulphate is given in Fig. 2. The leaching efficiency improves with increase in leaching time. The improvement of leaching efficiency with increase in time is due to more contact time between the solid (ilmenite) and liquid (HCl) mixture. The improvement of leaching efficiency above 400 min of leaching time was marginal and hence, leaching time above 480 min was not carried out. More leaching time will generate more fines and affect the quantity of BI produced (BI loss as fines along with spent acid) and also affect the quality of leach liquor.

Fig. 3. Plot of  $\ln(a/a-x)$  vs time for leaching ilmenite (10 g) with 30% HCl (100 mL) with 100 mg of  $\text{CaSO}_4$  ('a' is the initial concentration of FeO in ilmenite and 'x' is the amount of FeO converted to  $\text{FeCl}_2$ ).

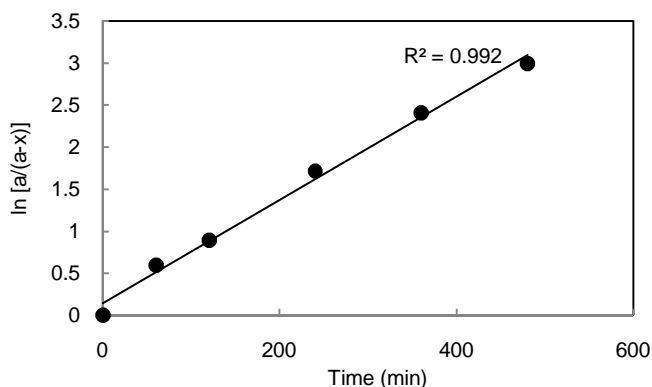


Figure 3 shows the kinetics of the leaching reaction with calcium sulphate as catalyst. The chemical reaction follows a first order kinetics. The rate of the reaction was found to be  $6.15 \times 10^{-3} \text{ min}^{-1}$  when the leaching medium contains 100 mg of calcium sulphate. The sulphate ions act as a catalyst, lower the energy gap of the chemical reaction and enhancing the leaching efficiency. The quality of leach liquor (with 100 mg of catalysts and without catalyst) is given in Table 1. The ferrous chloride content in the leach liquor is enhanced with the presence of catalysts. The percentage of ferrous chloride content is almost same with different catalyst used. The ferric chloride content in the leach liquor increased in catalytic leaching. The highest percentage of ferric chloride was noticed in leach liquor by using calcium sulphate as catalyst. The order of amount of ferric chloride with catalyst follows the same trend as that of leaching efficiency ( $\text{CaSO}_4 > \text{MgSO}_4 > \text{Na}_2\text{SO}_4 > \text{K}_2\text{SO}_4$ ). This catalyst enhanced the leaching by removing the ferric content in ilmenite. The free acid content and fines generation follows the reverse trend of ferric chloride removal.

A patent was reported in literature for improving the leaching of ilmenite by addition of gypsum or sulphuric acid (Chen and Huntoon, 1977). The present study reveals that the sulphates of calcium, sodium, potassium and magnesium can act as catalyst for the leaching process of ilmenite with hydrochloric acid. The rate constant for the leaching process increases with increase in sulphate ion concentration and obeying first order kinetics. Among the different sulphate ions tried, maximum leaching efficiency (95%) was given by adding calcium sulphate in the leaching process. The optimum amounts of catalyst were found to be 100 mg for 10 g of ilmenite. Moreover, the addition of catalyst improves the quality of spent acid (higher percentage of ferrous and ferric chloride and lower percentage of free acid and fines) for acid regeneration process.

Table 1. Quality of leach liquor produced by the leaching of ilmenite (10 g) with 30% HCl (100 mL) and 100 mg of catalyst.

Catalyst (100 mg)	$\text{FeCl}_2$ (%)	$\text{FeCl}_3$ (%)	Free acid (%)	Fines (%)
Nil	26	0.1	2.5	2.0
$\text{Na}_2\text{SO}_4$	29.2	0.2	2.0	1.5
$\text{K}_2\text{SO}_4$	29.3	0.2	1.8	1.3
$\text{MgSO}_4$	30	0.5	1.2	1.0
$\text{CaSO}_4$	30	0.7	1.0	1.0

### Conclusion

1. Addition of sulphates ( $\text{CaSO}_4$ ,  $\text{MgSO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ ) improves the leaching performance of ilmenite with hydrochloric acid.
2. Among the different sulphate ions tried, maximum leaching efficiency (95%) was given by adding calcium sulphate in the leaching process.
3. As the amount of catalysts increases, the iron removal also increases. The amount of iron removal from ilmenite above 75 mg of catalyst inclusion in leaching medium was found to be negligible and 100 mg of catalyst (for 10 g of ilmenite) can be considered as the optimum concentration. The catalyst decreases the energy gap of the chemical reaction thereby enhancing the leaching performance and decreases the free acid contents and fines generation in the spent acid.
4. The ilmenite leaching with hydrochloric acid follows 1<sup>st</sup> order chemical reaction. The rate constant value for leaching reaction using  $\text{CaSO}_4$  as catalyst was found to be  $6.15 \times 10^{-3} \text{ min}^{-1}$ .

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