

LEACHABILITY OF NITRIDED ILMENITE IN HYDROCHLORIC ACID

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ABSTRACT

Titanium nitride in upgraded nitrided ilmenite (bulk of iron removed) can selectively be chlorinated to produce titanium tetrachloride. Except for iron, most other components present during this low temperature (*ca.* 200 °C) chlorination reaction will not react with chlorine. It is therefore necessary to remove as much iron as possible from the nitrided ilmenite. Hydrochloric acid leaching is a possible process route to remove metallic iron from nitrided ilmenite without excessive dissolution of species like titanium nitride and calcium oxide. Calcium oxide dissolution results in unrecoverable acid consumption. The leachability of nitrided ilmenite in hydrochloric acid was evaluated by determining the dissolution of species like aluminium, calcium, titanium and magnesium in a batch leach reactor for 60 minutes at 90 °C under reflux conditions. The hydrochloric acid concentration (11%, 18% and 25%), initial acid-to-iron mole ratio (2:1, 2.5:1 and 3.3:1), and solid-to-liquid mass ratio (1:8.33 to 1:2.13) were varied. The results indicate that a hydrochloric acid concentration of 25 wt. % supplied in a 2:1 acid-to-iron mole ratio would produce the most favourable upgraded nitrided ilmenite product. The dissolution of iron in this solution reached 97 percent after only 60 minutes. The total dissolution of calcium and titanium species was 0.01 and 0.11 wt. % respectively. Hydrochloric acid can therefore be used as lixiviant to remove metallic iron from nitrided ilmenite.

Key words: titanium nitride, upgraded nitrided ilmenite, hydrochloric acid leaching, metallic iron dissolution

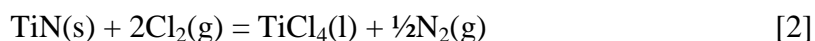
1 Introduction

The Council for Scientific and Industrial Research (CSIR) in South Africa is investigating alternative feedstocks for the production of TiCl₄ via low temperature (*ca.* 200 °C) chlorination of TiN¹. One of the feed materials considered is ilmenite (FeO.TiO₂).

Titanium nitride is obtained from ilmenite by carbothermally reducing it in a nitrogen atmosphere (Reaction 1). Reaction 1 is referred to as the nitriding reaction.



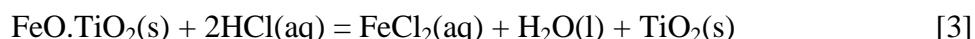
The TiN can then be chlorinated at ~200 °C and ~5 bar (Reaction 2).



Metallic iron chlorinates readily under these conditions². It is therefore required to remove the bulk of the iron from the nitrated ilmenite before chlorinating the TiN. Any components or impurities other than iron will however not react under these conditions. Table I summarizes the chemical composition of a typical nitrated ilmenite sample.

Commercially, HCl acid is used to remove FeO, and any other metal oxides, from thermally treated ilmenite³. The ilmenite is first thermally treated to ensure iron is present as FeO during the leach reaction⁴.

The dissolution reaction for the iron oxide part in ilmenite is illustrated in Reaction 3.



The solid product obtained is known as synthetic rutile or upgraded ilmenite and contains at least 92 percent TiO₂.

Hydrochloric acid leaching is therefore a possible process route to remove iron from nitrated ilmenite. However, the iron in nitrated ilmenite is reduced to Fe during the nitrating reaction. The dissolution reaction of nitrated ilmenite is therefore different from commercial processes in that the HCl acid will react with Fe to produce H₂(g), Reaction 4, instead of reacting with FeO to produce H₂O(l) (Reaction 3).



The purpose of this study was to evaluate if HCl acid can be used as lixiviant to remove Fe from nitrated ilmenite without excessive product (TiN) dissolution and dissolution of components that could lead to unrecoverable acid consumption (*e.g.* CaO forming CaCl₂).

The leachability of Fe, Al, Ca, Mg and Ti from nitrated ilmenite was evaluated by investigating different acid concentrations, initial HCl-to-Fe mole ratios, and solid-to-liquid mass ratios at a fixed period where Fe dissolution is virtually complete.

2 Experimental

2.1 Sample characteristics

Nitrated ilmenite was obtained by nitrating un-roasted Hillendale ilmenite at approximately 1325 °C with 30 percent excess bituminous coal under N₂(g) for 6 hours. The nitrated ilmenite was cooled down under N₂(g) and then magnetically separated from the residual char. Chemical analysis (ICP-OES) was conducted on the nitrated ilmenite sample to determine its composition. Table I presents a composition for the nitrated ilmenite sample obtained.

Table I: Chemical composition of nitrified ilmenite

Component	Normalized mass %
SiO ₂	3.52
Al ₂ O ₃	1.87
Fe(metal)	45.32
TiO ₂	5.43
TiN	37.87
CaO	0.13
MgO	0.62
K ₂ O	0.03
MnO	1.26
P ₂ O ₅	0.05
V ₂ O ₅	0.28
C(total)	3.38
S(total)	0.21

The results in Table I (average of three samples) were normalized to include the conversion of TiO₂ to TiN. This conversion (~90 percent) was estimated based on mass loss of sample during the nitrifying reaction. This estimation is based on the assumption that all the iron oxide present in the ilmenite sample reduces to Fe during the nitrifying reaction.

Particle size distribution analysis of the nitrified ilmenite sample found its mass mean particle diameter equal to 185 µm.

2.2 Experimental procedure

Acid leaching of nitrified ilmenite was carried out using a 500 ml three-necked glass flask as reactor. The reaction vessel was equipped with two condensers in series and an overhead stirrer fitted with a PTFE-coated shaft and impeller. A temperature controlled heating mantle regulated temperature inside the reaction vessel.

The required mass of nitrified ilmenite sample ($d_{50} = 185 \mu\text{m}$) was first loaded into the reaction vessel. Once the reactor and solids reached a temperature of 90 °C, HCl acid (analytical grade) with the required concentration (11%, 18% or 25%) was added to the reactor at a rate of 10 ml/min from a second heated vessel. The 100 ml HCl acid was thus added over 10 minutes. This was done to prevent excessive foaming caused by H₂(g) evolution. A stirring speed of 100 rpm was applied to keep the slurry suspended during the leaching experiment.

After the required reaction period (60 minutes), the slurry was filtered off and the solid residue thoroughly washed with hot water. The washed solids were then heated in air for 60 minutes at 80 °C. Chemical analysis on both leached solids (ICP-OES) and leach liquor (ICP-AES) were conducted to determine the solids chemical composition and the total Ti, Ca, Mg and Al in the leach liquor.

3 Results and discussion

3.1 The extent of Fe dissolution after 60 minutes

The weight percent Fe dissolved after 60 minutes in 90 °C HCl acid is summarized in Table II. The results are reported for three HCl acid concentrations at three different initial HCl/Fe mole ratios. The weight percent Fe dissolved was calculated from the results for the leached solid's chemical analysis.

Table II: Iron dissolution in hydrochloric acid after 60 minutes

HCl concentration (wt. %)	N _{HCl} / N _{Fe} (mol/mol)	Fe dissolved (wt. %)
11%	2.0	96.8
	2.5	97.2
	3.3	97.7
18%	2.0	96.9
	2.5	97.9
	3.3	97.2
25%	2.0	96.8
	2.5	97.2
	3.3	96.6

The results summarized in Table II indicate that the dissolution of Fe can reach levels of at least 96 percent after 60 minutes in 90 °C HCl acid. The dissolution of Fe is therefore virtually complete after 60 minutes. A leach duration of 60 minutes is therefore assumed sufficient to evaluate the dissolution of other components in HCl acid.

The time required to obtain the same FeO dissolution in Reaction 3 is approximately 3-5 hours⁴⁻⁶. The residence time required for Fe dissolution is therefore significantly less than that of partially reduced iron (*i.e.* iron as FeO).

3.2 Effect of HCl concentration

Figure 1 illustrates the effect of HCl acid concentration on the dissolution of Al, Ti, Ca and Mg. An increase in HCl acid concentration results in an increase of Al and Ti dissolution but a decrease in the dissolution of Ca and Mg. The increase in Ti dissolution with an increase in HCl acid concentration is comparable with previous findings^{5,7}.

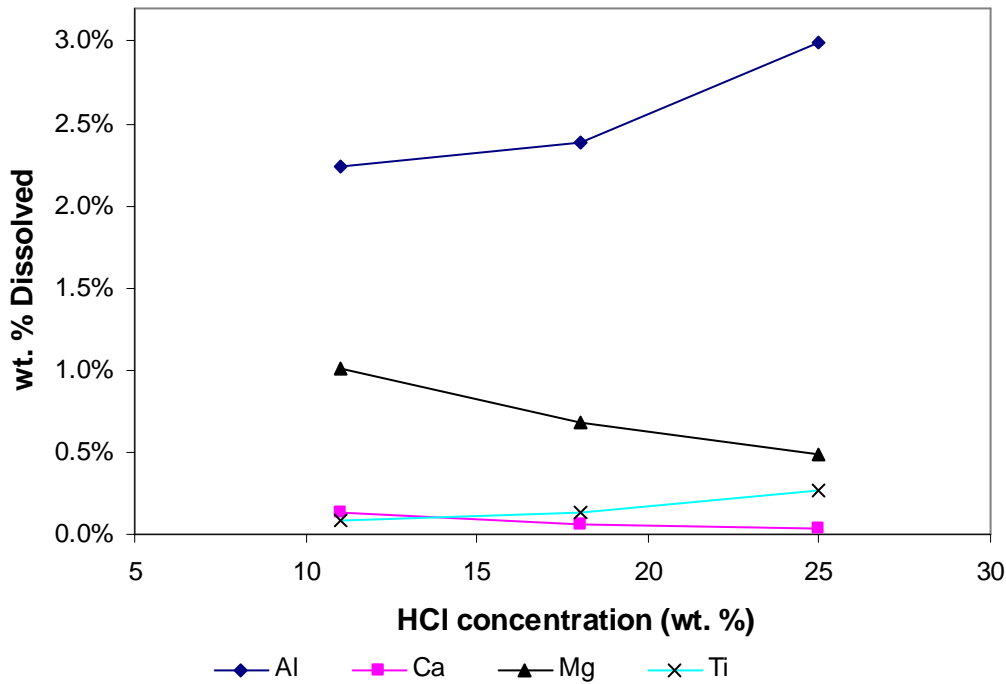


Figure 1: Effect of hydrochloric acid concentration on dissolution
 (90 °C, $d_{50} = 185 \mu\text{m}$, 100 rpm, 2.5 mol HCl/mol Fe)

The dissolution of components illustrated in Figure 1 is relatively low. These components will therefore still be present in the upgraded nitrated ilmenite. This is acceptable for the low temperature chlorination process as these species will not react with Cl_2 (as discussed in Section 1). The dissolution of these species (excluding Ti), and other impurities, is almost complete in existing FeO-leach practices^{4,6}.

3.3 Effect of initial HCl/Fe mol ratio

Table III summarizes the results obtained from the evaluation of different HCl acid-to-iron mole ratios on the dissolution of Al, Ti, Ca and Mg in 25 wt. % HCl acid. The weight percent dissolved is based on the results of the leach liquor analysis.

Table III: The effect of initial HCl/Fe mol ratios on dissolution in 25% HCl

Excess acid (mol %)		0	20	40
$N_{\text{HCl}} / N_{\text{Fe}}$ (mol/mol)		2.0	2.5	3.3
wt. % dissolved	Al	2.14	2.99	3.57
	Ca	0.01	0.03	0.05
	Mg	0.17	0.49	0.84
	Ti	0.11	0.27	0.44

The tendency for Ti dissolution to increase with an increase in the acid-to-iron mole ratio, as reported in Table III, is similar to findings from previous work⁷⁻⁹. The extent of Ti dissolution is however significantly less due to the high acid-to-ilmenite ratios evaluated in these previous works. For example, after 8 hours in a 105°C 6M HCl acid solution, van Dyk *et al.*⁸ found that 45 percent Ti dissolved in a 60:1 acid-to-ilmenite ratio, and approximately 5 percent in a 4:1 acid-to-ilmenite ratio.

The dissolution of all species given in Table III significantly increased with an increase in acid-to-iron mole ratio. The dissolution of Al increased with 67 percent when increasing the acid-to-iron ratio from the stoichiometric level of 2:1 to that of 3.3:1. The dissolution of Ti, Ca and Mg increased significantly more, with increases of at least 4 times more. The dissolution of these species is therefore dependant on the amount of excess (or free) acid available for reaction. The optimum mol ratio of acid-to-iron would be at levels equal to or very close to the stoichiometric ratio.

3.4 Effect of solid-to-liquid mass ratio

Figures 2 and 3 illustrate the effect of solid-to-liquid mass ratio on the dissolution of Ca and Ti respectively. Magnesium presents the same dissolution profile as illustrated in Figure 2, and Al the same dissolution profile as illustrated in Figure 3.

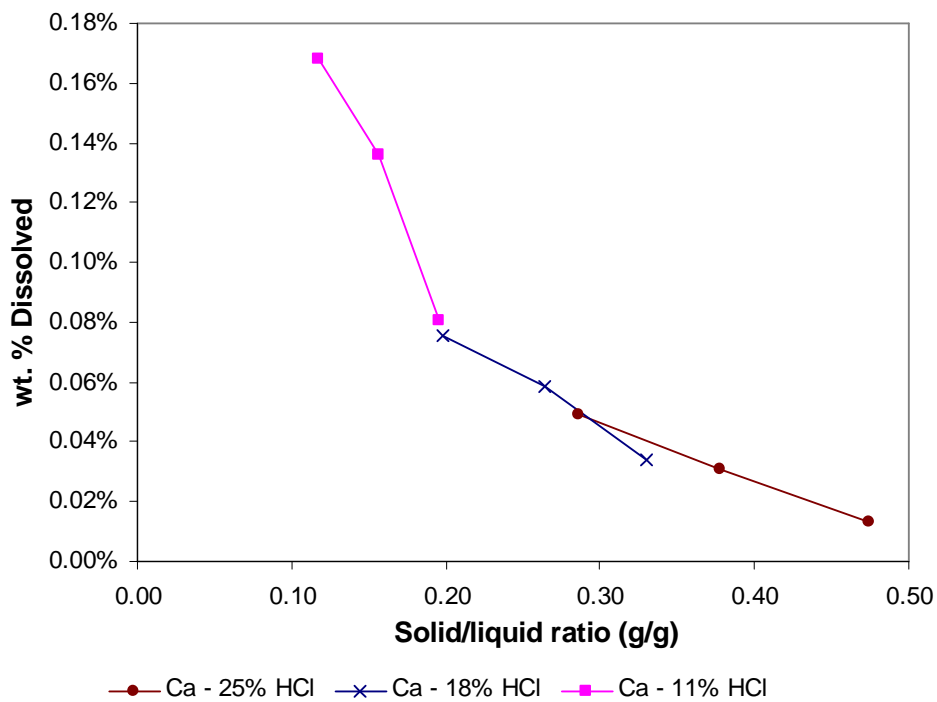


Figure 2: Effect of solid/liquid mass ratio on calcium dissolution
(90 °C, d_{50} = 185 μ m, 100 rpm)

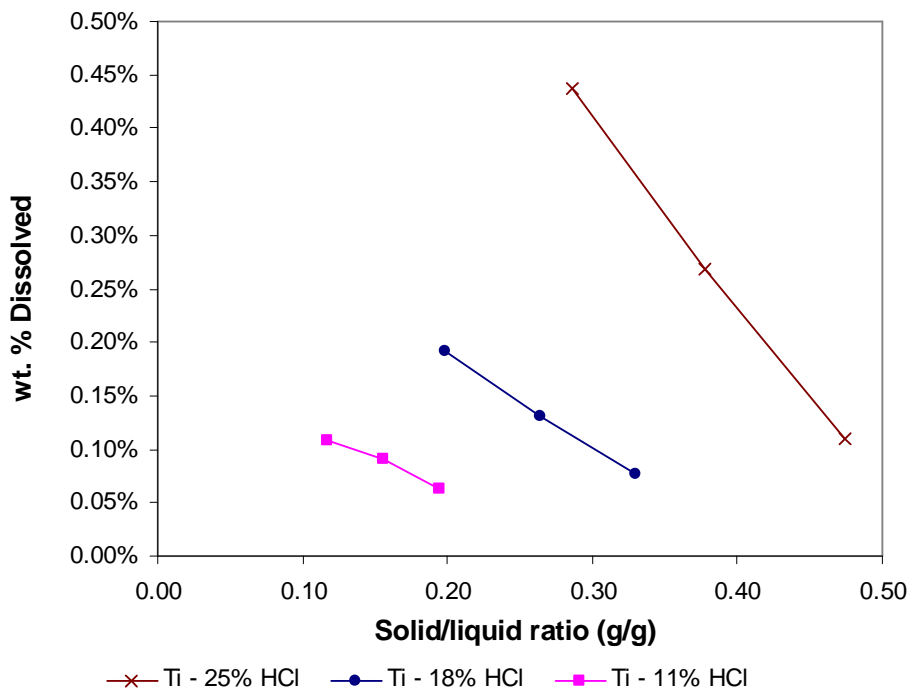


Figure 3: Effect of solid/liquid mass ratio on titanium dissolution
(90 °C, $d_{50} = 185 \mu\text{m}$, 100 rpm)

The results illustrated in Figure 2 indicate that the dissolution of Ca (and Mg) is significantly more favourable at lower solid-liquid mass ratios than at higher ratios. This suggests that the dissolution of Ca and Mg is dependent on the solid-liquid mass ratio of the reaction solution.

The dissolution of Ti and Al seems to not be strongly dependent on the solid-liquid mass ratio in Figure 3. The results do however suggest that the acid-to-iron mol ratio has a dominant effect on the dissolution of Ti and Al.

3.5 Optimum HCl leach conditions

The optimum HCl leach conditions would be where the HCl acid can dissolve virtually all of the Fe from the nitrated ilmenite but with little dissolution of other species, especially Ca (unrecoverable acid consumption) and Ti (part of product). The HCl acid with highest concentration conforming to the above considerations would be the selected acid concentration.

The findings from this study indicates that a 25 wt. % HCl acid with a 2:1 acid-to-Fe mole ratio at 90 °C would produce upgraded nitrated ilmenite closest to the required conditions as described above.

The normalised composition for a nitrated ilmenite sample leached with 25 wt. % HCl acid for 60 minutes (*ca* 90 °C) is given in Table IV for an acid-to-Fe mole ratio of 2:1.

Table IV: Chemical composition of leached nitrated ilmenite

Component	Normalized mass %
SiO ₂	6.06
Al ₂ O ₃	3.56
Fe(metal)	2.15
TiO ₂	10.00
TiN	69.90
CaO	0.12
MgO	1.29
K ₂ O	0.07
MnO	1.10
P ₂ O ₅	0.03
V ₂ O ₅	0.56
C(total)	5.16
S(total)	0.27

The limited dissolution of CaO, as illustrated in Table IV, will lead to reduced acid consumption compared to that of FeO-leach units where most of the CaO is dissolved⁴. Acid losses can be attributed to dissolved CaCl₂⁶.

Low temperature chlorination of the product summarized in Table IV will result in 0.051 mole unwanted Cl₂ consumption for each mole TiCl₄ produced. Only Fe will react to produce unwanted FeCl₃¹. This translates to a 97.8 percent yield (moles reactant required to produce desired product (TiCl₄) divided by moles reactant (Cl₂) fed) for Cl₂ supplied to the low temperature chlorination reactor. The remaining solids will leave the reactor as inert material. These inert materials can be treated and partially recycled back to the nitrating unit to recover some of the un-reacted TiO₂.

The TiO₂ and FeO content in slag used for the high-temperature chlorination process are typically 85 and 12 wt. % respectively¹⁰. If only FeO contributed to unwanted Cl₂ consumption (FeCl₂ produced), a 92.7 percent yield for Cl₂ supplied can be obtained in the chlorination reactor. Chlorine losses more than three times higher can therefore be expected in the conventional chloride process compared to the low temperature chlorination process.

4 Conclusions

The results obtained from this study indicate that HCl acid can be successfully used as lixiviant to remove Fe from nitrated ilmenite.

The following is a summary of findings from this study:

- Metallic iron dissolution from nitrated ilmenite reached levels of at least 96 percent after 60 minutes in 90 °C HCl acid. This is applicable for all HCl acid concentrations (11%, 18% and 25%) evaluated in this study.

- An increase in HCl acid concentration results in an increase of Ti and Al dissolution, and a slight decrease in Ca and Mg dissolution.
- The dissolution of all four species (Al, Ca, Mg, and Ti) increased with an increase in excess acid available for reaction. The excess acid available for reaction (or acid-to-iron mole ratio) had the largest effect on the dissolution of Al and Ti.
- The dissolution of Ca and Mg reduced for an increase in the initial solid-to-liquid mass ratio, but the dissolution of Al and Ti was not strongly dependant on the solid-to-liquid mass ratio. The solid-to-liquid mass ratio of the reaction solution had the largest effect on the dissolution of Ca and Mg.

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I graduated with a B.Eng Chemical engineering degree at the North-West University - Potchefstroom Campus in 2008. In 2009 the CSIR awarded me a bursary to complete an M.Eng degree. At the end of 2009 I completed the B.Eng (Hons) Chemical engineering degree with specialisation in plant design at the University of Pretoria. Starting from January 2010 I was employed as a full time employee of the CSIR. I am however still busy with the M.Eng Chemical engineering degree, and will be finished by the end of 2010. My main focus at the CSIR is to evaluate different feed materials for production of titanium tetrachloride.