



## The digestion of New Zealand ilmenite by hydrochloric acid



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### ABSTRACT

Ilmenite ( $\text{FeTiO}_3$ ) is an important source of titanium, for which the main application is  $\text{TiO}_2$  pigment. One route to the production of  $\text{TiO}_2$  from ilmenite may be the digestion of both the Fe and Ti components in hydrochloric acid and the subsequent direct hydrolysis of the Ti. The process requires that the Ti be solubilized. A kinetic study is performed of the leaching of New Zealand (Barrytown) placer ilmenite (ground to a  $10\ \mu\text{m}$  median particle diameter) by hydrochloric acid in a stirred reactor. Around 90% extraction of both Fe and Ti is achieved with a 32% w/w HCl concentration, with a 2:1 w/w ratio of HCl to  $\text{FeTiO}_3$  over the temperature range 60 to 90 °C. The shrinking sphere model is a good representation of the kinetics if particle size distribution is accounted for. The reaction rate is estimated to be 4th order in HCl concentration. The temperature rise due to an exothermic reaction is calculated to be c. 41 °C. Undesirable, in situ hydrolysis of Ti during digestion can be limited by control of temperature, reaction time and acid concentration. The data and models presented may facilitate the preliminary design of an industrial process to digest ilmenite to dissolve and retain Ti in solution.

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### 1. Introduction

Extensive deposits of ilmenite occur as placer deposits (beach sands) on the West Coast of the South Island of New Zealand. The size of the resource has been extensively surveyed, with the Barrytown old beach sands deposit near Westport containing approximately 6.9 million tonnes of ilmenite, found at an average concentration of 13.8%. Nearby, at Carters Beach, surveys found 6.5–9.6 million tonnes at 7.6–15% (Christie and Brathwaite, 1998). The source of the ilmenite is the metamorphic rocks of the Southern Alps (Grapes and Watanabe, 1992). Associated with the ilmenite are the potentially valuable accessory minerals gold, monazite and zircon. There have been several attempts in the past to develop the resource, including extensive work in the 1980's on processing technologies (Mann and James, 1989). The Barrytown ilmenite deposit is not currently being exploited but there has been recent commercial interest in developing the resource (Mills, 2013).

Ilmenite supplies about 90% of the world's demand for titanium (Ti) minerals. World Ti resources are estimated to be >2 billion tonnes, with world production of ilmenite at 6.2 million tonnes and rutile ore at 7.0 million tonnes in 2012 (U.S.GeologicalSurvey, 2013). There is a growing demand for  $\text{TiO}_2$  for use as a pigment and for Ti metal for use in alloys. To meet the demand,  $\text{TiO}_2$  pigment production is increasing,

with world production capacity at 6.5 million tonnes in 2012 (U.S.GeologicalSurvey, 2013). Titanium metal sponge production has also grown steadily to 214 thousand tonnes in 2012 (U.S.GeologicalSurvey, 2013) from 51 thousand tonnes in 1997, and is expected to continue to grow with the increasing use of the metal in the aerospace and other industries.

For the production of  $\text{TiO}_2$  via the chloride route (with  $\text{TiCl}_4$  as an intermediate), the dominant feedstock is a high-grade rutile or synthetic rutile feedstock. The upgrading of ilmenite to synthetic rutile containing >85%  $\text{TiO}_2$  is commonly performed with hydrochloric acid to leach out the Fe, usually after an oxidation and reduction step, leaving the Ti (Gireesh et al., 2015; Girgin, 1990; Sinha, 1984; Jackson and Wadsworth, 1976; Jain and Jena, 1977). The reactivity of ilmenite varies with the mineral's source. Most ilmenites are relatively insoluble in HCl and must first undergo an oxidation and a reduction step (Ogasawara and de Araujo, 2000; Wahyuningsih et al., 2013); a few are relatively soluble directly in HCl (Olanipekun, 1999).

The digestion of ilmenite by HCl may be investigated with the view to producing a pigment-grade  $\text{TiO}_2$  directly from the Ti- and Fe-containing digestion solution. Since the Ti needs to be in a soluble form, and its subsequent hydrolysis must occur in a controlled fashion (i.e. no significant hydrolysis can have occurred already), the conditions required for digestion are different from those normally.

Various factors affecting ilmenite digestion in HCl have been studied (Duncan and Metson, 1982a; Sasikumar et al., 2004; Sarker et al., 2006; Sasikumar et al., 2007; Janssen and Putnis, 2011). Where acid concentrations are too low, or temperatures too high, the already-hydrolyzed Ti can accumulate and block the pores that should be formed during digestion, thereby preventing further leaching and inhibiting digestion.

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More specifically, leaching occurs selectively, leaving a lattice structure of undigested material (Duncan and Metson, 1982b).

Here, we describe the reactivity of New Zealand-sourced ilmenite in concentrated HCl under conditions that might be suitable for industrial production of TiO<sub>2</sub>, and the data are used to model the digestion process.

## 2. Experimental section

### 2.1. Ilmenite

Ilmenite concentrate from Barrytown, Westland, New Zealand was supplied by Rio Tinto Pty Ltd. The composition of the ilmenite was determined using borate fusion and X-ray fluorescence spectrometry by Spectrachem Analytical Services, Lower Hutt, New Zealand. The ilmenite was then ground in small batches (35 g for 2 min) in a 150-mm disc mill (Tema, UK) for the digestion experiments. A Malvern Mastersizer 3000 (Malvern Instruments, UK) was used to measure particle size of the ground ilmenite.

### 2.2. Digestion procedure

The ground ilmenite was digested in 32% w/w HCl (8.8 mol kg<sup>-1</sup> HCl or 10.3 M HCl at 20 °C) at temperatures of 60, 80, 85 and 90 °C. The ratio of acid to ilmenite was 2 to 1, calculated as kg 100% HCl to kg ilmenite in ore by analysis, the latter calculated as equivalent ilmenite based on Fe<sub>2</sub>O<sub>3</sub> being treated as FeO and taking (mol Ti + mol Fe)/2. This amounts to 8.50 mol HCl to 1 mol “FeTiO<sub>3</sub>”, bearing in mind that the Ti-to-Fe ratio in the ilmenite is not 1:1.

Digestion of ground ilmenite in hot HCl took place in a 3 L round-bottom glass flask, fitted with a reflux condenser, and with a Teflon paddle stirrer on a glass shaft. The HCl was preheated in the flask on a heating element before ilmenite addition. The element was also used in the 90 °C experiment to provide rapid initial heating after ilmenite addition since the boiling point of 32% w/w HCl is 84 °C.

Samples of liquor were collected at timed intervals and rapidly filtered through glass fiber paper while still hot. The Ti and Fe contents were analyzed by reduction with Al metal followed by quantitative oxidation by titration with cerium sulfate solution using the indicators methyl blue (for Ti) and N-phenylanthranilic acid (for Fe). The results are presented as percentage dissolution, based on the total Ti and Fe contents of the added ilmenite and the Ti and Fe contents of the solution adjusted for solution mass increases due to dissolution and removed sample volumes.

## 3. Results and discussion

### 3.1. Ilmenite composition

The elemental composition of the Barrytown ilmenite, including inclusions, is shown in Table 1. It has been shown previously that the ilmenite phase contains most of a sample's Ti, Fe and Mn (Duncan and Metson, 1982b). The inclusions consist mainly of silicate minerals such as quartz and feldspars, and these are the repository of most of the oxides listed in Table 1 and are resistant to dissolution in HCl. In addition, apatite is present as inclusions and is soluble in HCl (Duncan and Metson, 1982b).

### 3.2. Particle size distribution

Being from a placer deposit, the mined ilmenite had a narrow size distribution, centered of around 150–250 μm (Fig. 1a). Grinding resulted in the particle size distribution shown in Fig. 1b, with D50 = 10.0 μm, D10 = 1.3 μm and D90 = 76 μm.

**Table 1**  
Ilmenite composition.

Oxide	Weight (%)
TiO <sub>2</sub>	47.1
FeO	37.5
Fe <sub>2</sub> O <sub>3</sub>	3.0
SiO <sub>2</sub>	5.2
Al <sub>2</sub> O <sub>3</sub>	2.3
MnO	1.7
MgO	0.2
CaO	1.1
Na <sub>2</sub> O	0.3
K <sub>2</sub> O	0.3
P <sub>2</sub> O <sub>5</sub>	0.2
V <sub>2</sub> O <sub>5</sub>	0.1

### 3.3. Digestion profiles

Slightly more Fe was digested than Ti (Fig. 2), reflecting the fact that the ilmenite does not have a stoichiometric ratio of Fe and Ti (i.e. the elemental analysis does not correspond with FeTiO<sub>3</sub> but rather to Fe<sub>0.97</sub>Ti<sub>1.03</sub>O<sub>3</sub>), and that the slight excess of Ti may be present as the more insoluble rutile structure.

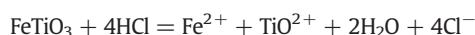
The ultimate decreases in proportion of Ti digested at 85 °C and 90 °C were due to the hydrolysis and precipitation of titanium hydroxide, TiO(OH)<sub>2</sub>. It is essential that this phenomenon be avoided if the digestion liquor is to be used for subsequent hydrolysis to TiO<sub>2</sub> for several reasons. The TiO(OH)<sub>2</sub> precipitate may block the pores or partially coat the dissolving ilmenite, thereby inhibiting further digestion. More importantly, it is likely to become associated with gangue, such as fine silicates, introducing impurities in the TiO<sub>2</sub>. Also this uncontrolled nucleation of TiO<sub>2</sub> reduces the degree of control possible over the final form of any TiO<sub>2</sub> pigment produced.

Digestion of over 80% of Ti, without hydrolysis, was achieved (concentration of about 81 g kg<sup>-1</sup>, expressed as weight of TiO<sub>2</sub>, as is the normal convention) and Fe digestion reached 84% (a concentration of 80 g kg<sup>-1</sup> as FeO). Had ilmenite particles of a narrower size distribution been used, such that none of the larger, slower-to-digest particles had been present, the percentages of digestion would have been higher. One trial (data not shown), using more finely ground ilmenite and less acid (therefore with an acid-to-ilmenite ratio of 1.44:1 w/w, yielded over 90% digestion of both Ti and Fe, which therefore lead to higher concentrations of Ti and Fe in solution (up to 87 g kg<sup>-1</sup> TiO<sub>2</sub>).

Complete digestion of the Ti component will not be possible, in part because some Ti is present as rutile inclusions (Duncan and Metson, 1982b), and rutile is not soluble in HCl.

### 3.4. Acid concentration

The digestion proceeds according the stoichiometric reaction:



with 4 mol HCl for each mol of ilmenite. The reaction does not proceed to Ti<sup>4+</sup> ions in solution because Ti, under these conditions, is the TiO<sup>2+</sup> complex, most likely as TiOCl<sup>4-</sup> (Cservenyak et al., 1996; Kelsall and Robbins, 1990; Sole, 1999). This reaction has been carried out here in a way that might have direct relevance to an industrial process, without a huge excess of HCl. Therefore the concentration of HCl declines significantly with reaction.

The 2:1 w/w ratio of HCl:TiO<sub>2</sub> used here represents 8.3 mol of HCl for each mole of FeTiO<sub>3</sub>, which is an excess of 4.3 mol of HCl per mol of FeTiO<sub>3</sub>. The calculated approximate HCl concentrations are shown in Fig. 3, with HCl concentration changing from 32% w/w initially to around 15% w/w when digestion peaked. If the digested Ti is hydrolyzed during the reaction (an undesirable situation if subsequent direct pigment

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