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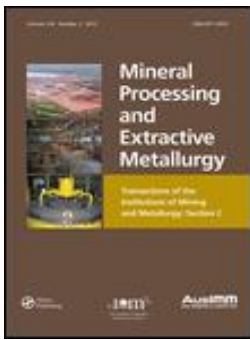
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Production of synthetic rutile from ilmenite via anion-exchange

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ABSTRACT

This investigation identified that ion-exchange chromatography can efficiently remove iron from the leaching of ilmenite by HCl. The strong basic anionic-exchange resin IRA 410 Cl is capable of retaining the negatively charged iron chloro complex from 20% HCl leachate of ilmenite. Oxidative conversion of Fe^{2+} to Fe^{3+} facilitates the iron exchange to the resin, resulting in an iron-free solution of titanium oxychloride (TiOCl_2). This can be directly used to produce synthetic rutile. The procedure is relatively simple and generates little acid waste.

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ion-exchange; ilmenite; TiO_2 ;
acid leaching

Introduction

Titanium dioxide (TiO_2) is one of the most common raw materials used in the chemical manufacturing industries since its commercial availability from 1920s. TiO_2 is used in many products including paint, plastic, paper, sunscreen and photovoltaic devices, etc. (Zhang W et al. 2011; Gazquez et al. 2014; Zhou et al. 2015). Furthermore, the optical and catalytic properties of TiO_2 nano-particles have been subject to many applications in recent years (Jayaweera et al. 2007; Baltrusaitis et al. 2011; Dariani et al. 2016). TiO_2 is also used to produce metallic titanium, which is known for its strength and thermal resistance.


Among many natural titanium-rich minerals, rutile, ilmenite and leucoxene are the most common feedstock in the TiO_2 manufacturing process. Although rutile contains 93–96% TiO_2 , many rutile deposits are becoming depleted through commercial use and demand for the other feedstocks such as ilmenite has gained increasing attention. However, both ilmenite (FeTiO_3) and leucoxene ($\text{Fe}_2\text{O}_3 \cdot n\text{TiO}_2$) contain significant amounts of iron. The TiO_2 content in ilmenite, which may range from 40 to 60%, is extracted and purified by various pyro- and hydrometallurgical methods. Ilmenite provides over 90% of global TiO_2 , which is equivalent to an annual production of 4.5 million tonnes. The two major processes for the manufacture of TiO_2 are the sulphate and chloride processes (Reck & Richards 1999; Van Dyk et al. 2002; McNulty 2007). The chloride process is more dominant when the feedstock is either rutile or synthetic rutile produced from ilmenite due to its cost effectiveness and efficiency in waste management. Generally in the chloride process, rutile or synthetic rutile is treated with chlorine gas and coke at high temperatures to

produce gaseous titanium tetrachloride, carbon oxides, and iron waste (ferrous chloride). The titanium tetrachloride is then fed to a high temperature oxidising reactor to generate TiO_2 . In addition, the feed material must contain less than 0.6% (w/w) magnesium and calcium to prevent clogging due to the formation of chlorides with low melting points. The chloride process requires a feedstock containing a minimum of 70% TiO_2 . This prerequisite creates an intermediate step to increase the TiO_2 content in the feedstock, which involves a thermo reductive conversion with or without acid leaching steps to remove iron, making the process more expensive and environmentally costly.

The majority of research reported recently has focused primarily on improving the existing methodologies, which are mainly about iron removal via precipitation/solvent extraction (Nagasubramanian & Liu 1979; Vasquez & Molina 2008; Filippou & Hudon 2009; Mehdilo & Irannajad 2012). Furthermore, several investigations have been reported that examined the possibility of using anion-exchange resins to remove specific metal impurities selectively through the formation of metal-chloro complexes at different HCl concentrations (Kekesi et al. 2002; Bernardis et al. 2005; Csicsovszki et al. 2005).

In the present investigation, we have used an anion-exchange resin to remove iron from an HCl ilmenite leachate. The procedure is simpler than that used by previous researchers and produces a solution of TiOCl_2 which can be used to manufacture synthetic rutile. The success of this approach relies on the efficient binding of the negatively charged chloro complex of iron to the anionic exchanger IRA 410 Cl.

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Table 1. Chemical composition of ilmenite.

Compound	TiO ₂	FeO	Total iron as Fe	SiO ₂	P ₂ O ₅	ZrO ₂	V ₂ O ₅	Al ₂ O ₃	Cr ₂ O ₃
wt-%	53.66	17.48	30.04	1.54	0.03	0.83	0.20	0.65	0.07

Experimental

Materials

The ilmenite beach sand samples used in this investigation were obtained from Lanka Mineral Sands Ltd, Sri Lanka. The chemical composition of the bulk sample is given in Table 1 (Arachchi et al. 2016). The raw ilmenite sample was ground to an average particle size of $100 \pm 25 \mu\text{m}$, as determined using scanning electron microscopy. An industrial grade anion-exchanger, AMBERLITE™ IRA 410 Cl, obtained from S D Fine-Chem Ltd. (product of Rohm & Haas) was used as the column material in the ion-exchange process. The spherical shape resin beads had a harmonic mean diameter of 0.75 mm. The total exchange capacity of the resin is $\geq 1.25 \text{ eq/L Cl}^-$ form.

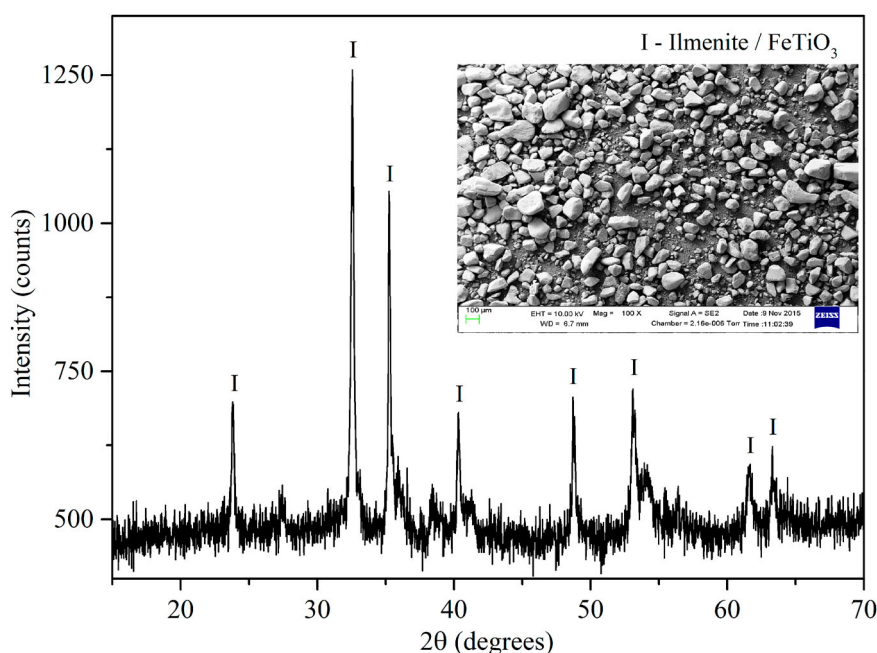
Sample analysis

X-ray diffraction (XRD) analysis and scanning electron microscope (SEM) imaging were carried out using a Rigaku Ultima-IV X-ray diffractometer and ZEISS Sigma scanning electron microscope, respectively. X-ray fluorescence analysis was carried out using a Thermo Scientific Niton XL3t GOLDD+ analyzer. The XRD pattern of the ilmenite (Figure 1) shows the major phase in the ilmenite sample as FeTiO₃ (JCPDS No: 01-070-6246). The SEM image of ground ilmenite shows the ilmenite had dense texture and smooth appearance. Total iron concentration in the

leach solutions was determined using a Thermo Scientific iCE 3000 Series atomic absorption spectrometer (AAS). Total titanium in the acid leached solution was determined using a PerkinElmer Lambda 35 UV-vis spectrophotometer, through colorimetric peroxide method (Mostafa et al. 2013).

Acid leaching of ilmenite and anion-exchange separation

A pair of columns used in the leaching/anion-exchange process was mounted as shown in Figure 2(b). Two glass columns having an inner diameter of 2.5 cm and length of 45 cm were used. Both columns were connected in a closed-loop and the first column was packed with 5.0 g of ilmenite and the second with 50 cm³ of IRA 410 Cl resin swelled with 20% HCl. A volume of 300 mL of 20% HCl was run through the two columns continuously. The ilmenite leachate resulting from the first column was used as the feed-stock to the second column which removed iron from the leachate. The effluent of the second column was fed back in to the first column to complete a single iteration in the loop. The entire volume of 300 mL of test solution was run through the column system at a flow rate of 150 mL h^{-1} . A sample size of 2.0 mL was taken periodically from the effluent for AAS and colorimetric analysis. In order to assess the effects of both leaching and ion-exchange process, a control experiment was performed with a single column

**Figure 1.** XRD pattern of raw ilmenite. Inserted: SEM image.

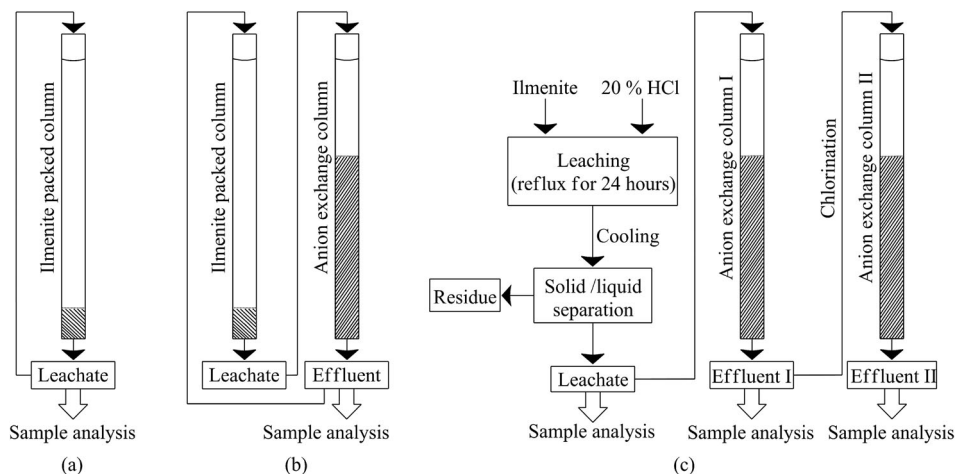


Figure 2. Experimental set-up (a) control experiment, (b) anion-exchange experiment, and (c) batch experiment.

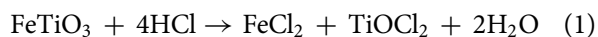
(Figure 2(a)) to mimic the leaching of ions from the ilmenite sample with a volume of 300 mL of 20% HCl. The leachate of the control experiment was also measured in parallel with the anion-exchange system.

Experiments were also performed under reflux conditions (~381 K). The experimental set-up is shown in Figure 2(c). An ilmenite sample of 5.0 g was leached using 300 mL of 20% HCl under reflux for 24 h. The filtrate was cooled to 303 K before being fed into the first column filled with 50 mL of IRA 410 Cl resin. The effluent of the first column was purged with chlorine gas and then used as the feedstock for the second column, which was identical to the first column. Two millilitres of samples were pipetted out from the acid leachate, first column (effluent I), and the second column (effluent II) for AAS and colorimetric analysis. In all the experiments, the flow rate was maintained at 150 mL h⁻¹.

Results and discussion

Leaching of titanium and iron from ilmenite

The leaching of the ilmenite occurred according to the following chemical equations (Olanipekun 1999; Jaya-weera et al. 2011):



The parameters that affect the rate of leaching are particle size, temperature, acid concentration, stirring, and acid to ilmenite molar ratio (Van Dyk et al. 2002). In this investigation, the acid concentration and acid-to-ilmenite molar ratio were selected based on the results of previous investigations (Mahmoud et al. 2004; El-Hazek et al. 2007; Zhang L et al. 2011). Leaching and ion-exchange purification were carried out at 303 K as a continuous process (Figure 2(b)), whereas leaching under refluxing condition was

performed at 381 K and the subsequent ion-exchange purification processes were carried out at 303 K, as a batch experiment (Figure 2(c)).

The iron in ilmenite exists in both ferrous and ferric forms. Previous leaching kinetic studies (Van Dyk et al. 2002) have suggested at high acid-to-ilmenite mole ratios both iron and titanium leach into solution. At low ratios, dissolution of iron becomes the main process. Dissolved iron in HCl solution exists as iron chloro complexes with two possible oxidation states of +2 and +3. Kekesi et al. (2002) extensively studied the removal of iron by anion-exchange in HCl solution and reported that in 6 M HCl solutions, Fe(III) chloro complex exhibits a higher anion-exchange distribution value than the Fe(II) chloro complex. Our studies also confirm that the retention affinity of Fe(III) is higher in the acid leachate than that of Fe(II). Therefore, oxidation of Fe(II) to Fe(III) by chlorine gas facilitates the removal of iron from the ilmenite acid leachate.

The oxidation state of Ti remains as +4 during the entire leaching and anion-exchange steps. Titanium, which has a lower diffusion coefficient, migrates across the solid-liquid interface at a slower rate and dissolves in 20% HCl solution. It has been reported (Van Dyk et al. 2002) that polymerised products of TiOCl₂ may cover the pores of the ilmenite particle leading to a decline in the leaching rate. When TiOCl₂ content in the leachate reaches a critical concentration, hydrolysis occurs to produce rutile (TiO₂), as indicated by Equation (2).

The experimental set-up in this investigation was designed to remove iron from the acid leachate of ilmenite in a continuous manner. The control experiments were carried out only to assess the leaching effects of ions without the ion-exchange process. The concentration of iron in the leach solution as a function of time, for both control and leachate passing through the ion-exchange column, is shown in Figure 3(a,b), respectively. The concentration of iron in the leachate increased with leaching time in the control experiment

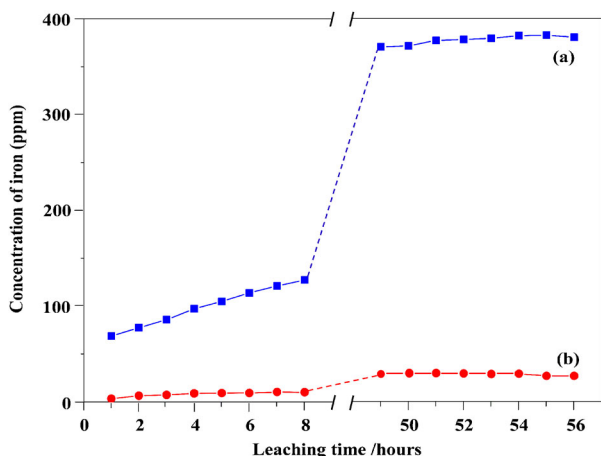


Figure 3. Total iron concentration measured with time at 303 K, (a) control experiment: acid leaching only, (b) acid leaching followed by anion-exchange.

(Figure 3(a)). After 56 h of leaching time, the total iron concentration in the anion-exchange experiment and the control experiment was 27 and 380 ppm, respectively. The concentration difference of total iron between the two experiments is 353 ppm due to the anion-exchange process. This is about 93% reduction of total iron.

Titanium concentrations for both control experiment and leachate which passed through the anion-exchange resin were also measured and are shown in Figure 4(a,b), respectively. The leaching of titanium is less efficient as it is thermodynamically unfavourable in comparison to the leaching of iron in HCl as also reported by Tsuchida et al. (1982). In control and anion-exchange experiments, the titanium concentration in the effluent increased with leaching time. However, the results show a slightly lower concentrations of titanium in the effluent when the leachate was passed through the anion-exchange resin (Figure 4(b)). This suggests that there is a loss of titanium in the anion-exchange process, probably as a result of

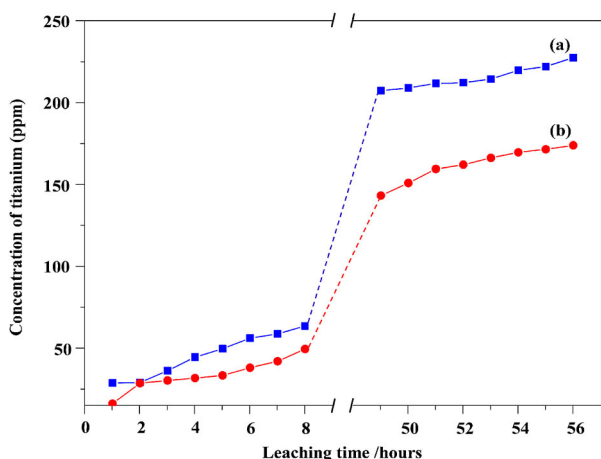
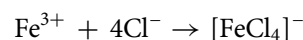


Figure 4. Total titanium concentration measured with time at 303 K, (a) control experiment: acid leaching only, (b) acid leaching followed by anion-exchange.

re-precipitation of a small fraction of TiOCl_2 . However, the difference in exchange capacity of iron and titanium in the anion-exchange column is sufficiently large for the application of this technique for the removal of iron from ilmenite in 20% HCl solution.

Experiments were also performed to examine the reusability and practicality of the resin by passing acid leachate through the anion-exchange column and subsequent elution with 0.6% HCl solution to remove trapped iron. Results of four cycles clearly indicated that anion-exchange capacity did not change with number of cycles (see Supplementary data).

The function of the anion-exchange resin is to retain negatively charged species. HCl is ideal for complexation, having the capability to form anionic complexes of many hydrated metal ions, including Fe^{3+} in highly acidic medium (Kekesi & Isshiki 1994). Fe^{3+} exists in the form of $[\text{FeCl}_4]^-$ in concentrated HCl solutions as shown by the following equation:



The presence of Fe^{3+} in the form of $[\text{FeCl}_4]^-$ allows the anion-exchange resin to retain iron from the ilmenite leachate. This explains the reduction of total iron concentration in the effluent samples after the anion-exchange process (Figure 3(b)) with respect to the total iron in the control experiment (Figure 3(a)). However, the ferrous form of iron has a low equilibrium distribution coefficient in HCl solutions $>6 \text{ mol dm}^{-3}$ compared with the ferric state (Kekesi et al. 2002). Hence, iron removal from an acidic leachate of ilmenite through anion-exchange is limited by the Fe^{2+} content in the ilmenite leachate. Therefore, an oxidative conversion of ferrous to ferric should facilitate the iron removal process in ilmenite through anion-exchange chromatography.

Production of rutile, titanium oxychloride, and iron oxide

Based on these results, a process was proposed and tested for the production of rutile, titanium oxychloride and iron oxide (Figure 2(c)). The experimental flowsheet is shown in Figure 5. The leaching was carried out under refluxing conditions with 20% HCl and after 24 h the solid residue was separated. The residue was washed with distilled water to remove HCl and other soluble matter. The solid fraction was dried at 383 K and XRD analysis was performed (Figure 6) which confirmed the formation of rutile- TiO_2 (JCPDS No: 00-021-1276). The leachate, after being cooled to room temperature, was fed to the anion-exchange column. The effluent was chlorinated by passing chlorine gas to oxidise the remaining Fe^{2+} to Fe^{3+} and fed in to another anion-exchange column. In all these experiments, the HCl concentration did not

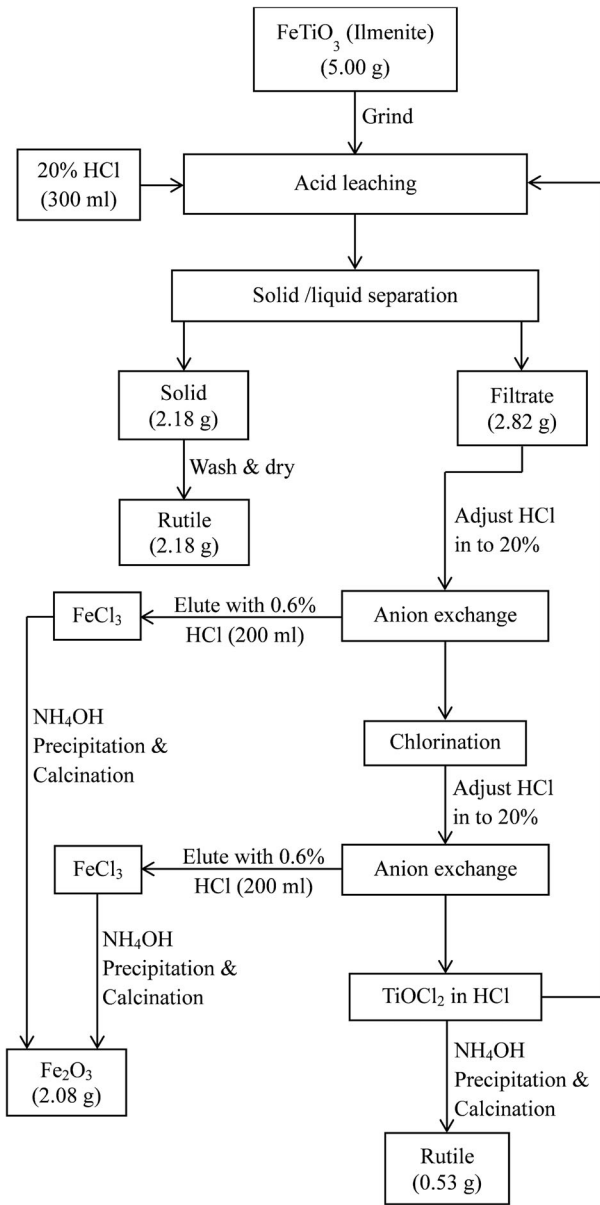


Figure 5. Laboratory flowsheet for the proposed process.

change significantly during the leaching period. The adsorbed iron in columns I and II were eluted with 0.6% HCl and collected separately and labelled as

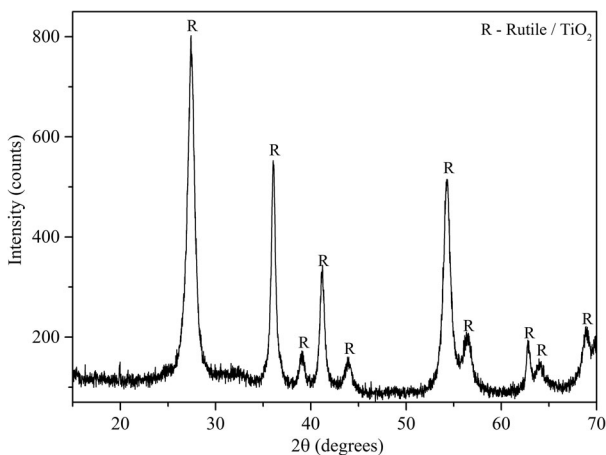


Figure 6. XRD pattern of solid residue dried at 383 K.

elute I and elute II, respectively. The eluted solutions from columns I and II were precipitated with NH_4OH . The precipitates were washed with distilled water several times and dried on a hot plate. The dried samples (iron oxide from the elute) were calcined at 773 K for 6 h and their XRD pattern (Figure 7) confirms the formation of Fe_2O_3 (hematite) (JCPDS No: 01-072-0469). In the previous studies, several reduction procedures have been followed before acid leaching for reducing the iron in ilmenite samples to enhance acid dissolution (Mahmoud et al. 2004). In the present study, the iron reduction step is not required as the iron separation is highly efficient with the +3 oxidation state. The total iron and titanium content in the acid leachate was determined using Equation (3) (Zhang L et al. 2011) and the calculated percentages are given in Table 2.

$$\eta = \frac{c_i \times V \times 10^{-3}}{w_i \times m_i} \times 100\% \quad (3)$$

The total iron and titanium content in the residue after acid leaching, rutile and iron oxide were calculated using the following equation:

$$\eta = \frac{w_f \times m_f}{w_i \times m_i} \times 100\% \quad (4)$$

In Equations (3) and (4), η (wt.%) stands for iron or titanium content, c_i (g L^{-1}) for iron or titanium concentration, V (mL) for the volume of the leaching solution, w_i (wt-%) for the iron or titanium content in ilmenite beach sand, m_i (g) for the mass of the ilmenite beach sand sample, w_f (wt-%) for the iron or titanium content of the prepared solid samples, and m_f (g) for the mass of the prepared solid samples.

The effluent from the second anion-exchange column was also analysed for its total iron and titanium content. Table 2 clearly indicates that the solution has a fairly low iron content (<0.06%). XRF analysis of the solid sample obtained from the effluent indicates the presence of trace amounts of other metals, such as Mn, V and Ca. The effluent containing TiOCl_2 could be used in many applications. The production of rutile from TiOCl_2 has also attracted much attention. Such applications are production of mesoporous titania and inorganic polymer materials based on TiOCl_2 . The effluent enriched with TiOCl_2 was neutralised with NH_4OH resulting in the formation of a colloidal suspension of $\text{TiO}(\text{OH})_2$, which was subsequently separated and dried on a hot plate then calcined at 1173 K for 6 h to increase the crystallinity and produce rutile. The XRD pattern of the sample shown in Figure 8 confirms the formation of rutile (JCPDS No: 00-021-1276). Inserted in Figure 8 is the EDX scan for the rutile which indicates the absence of iron.

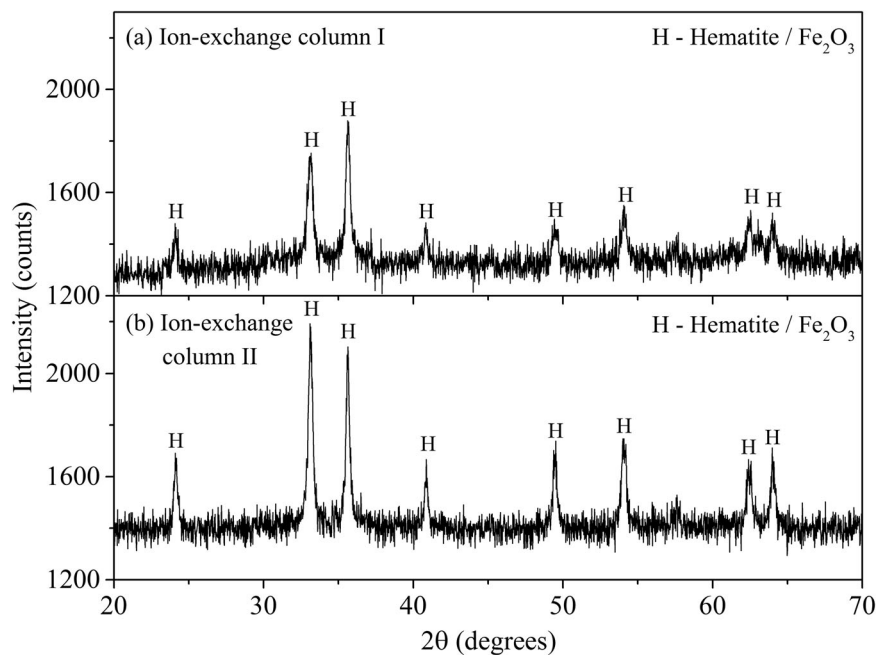


Figure 7. XRD pattern of prepared iron oxide, (a) from anion-exchange column I, (b) from anion-exchange column II.

Table 2. Iron and titanium distribution during batch experiment with respect to the feedstock.

Sample	Total iron %	Total titanium %
Residue	3.69*	79.89*
Leachate	97.26 [#]	20.01 ^Δ
Effluent I	51.60 [#]	18.20 ^Δ
Effluent II	0.06 [#]	17.50 ^Δ
Rutile from the effluent II	0.06*	15.76*
Elute I + Elute II	97.21 [#]	0.88 ^Δ
Iron oxide from the elute I and II	97.17*	0.62*

Notes: * Determined by XRF.

[#] Determined by AAS.

^Δ Determined by colorimetry.

Conclusions

The present work has shown that leaching of ilmenite in 20% HCl produces two forms of titanium-bearing products, namely, rutile (TiO_2), which remains in the solid phase, and TiOCl_2 which leaches out to the aqueous phase. Separation of the leached iron in the solution by ion-exchange was over 99% efficient after oxidising the leached Fe^{2+} to Fe^{3+} . Furthermore, regeneration of the resin bed with dilute HCl facilitated the production of Fe_2O_3 . Hydrolysis of the TiOCl_2 followed by calcination produced a high-grade pigment feedstock form of TiO_2 .

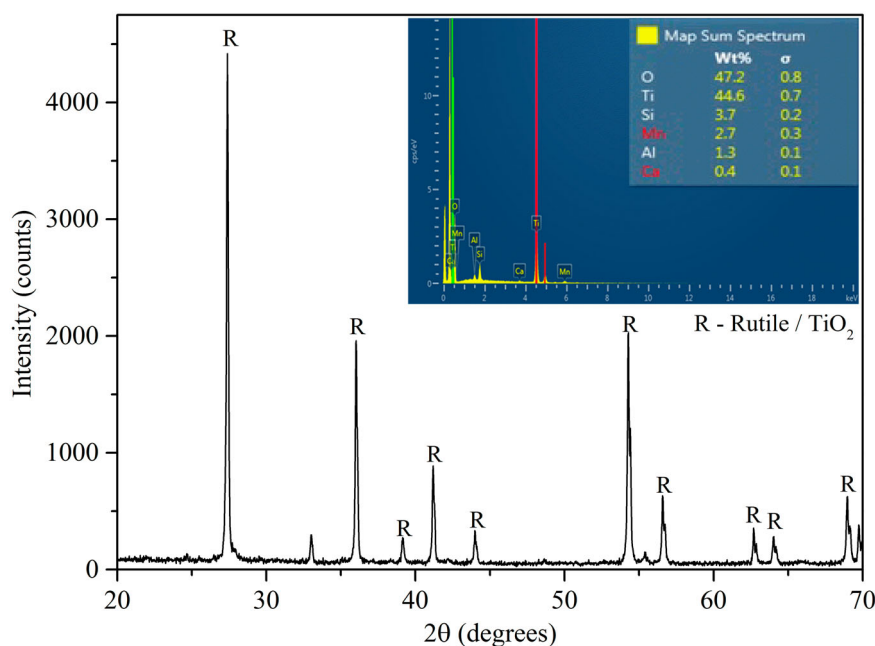


Figure 8. XRD pattern of rutile prepared from TiOCl_2 solution. Inserted: EDX scan.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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