

PURIFICATION OF A NORWEGIAN ILMENITE ORE TO PRODUCE SYNTHETIC RUTILE

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ABSTRACT

The study is focused on investigating the production of synthetic rutile of 95% purity or higher from a Norwegian ilmenite ore concentrate. This was to be achieved using a sequential process involving oxidative-reductive roasting at 975°C, followed by magnetic separation to further concentrate the sample and finally leaching with 20% HCl to remove mostly Fe-based impurities leaving behind synthetic rutile. The key process parameters considered were roasting time (1 and 2 hrs), leaching temperature (100, 125 and 145°C), pulp density (15 and 25wt%) and leaching time (3 and 6 hrs). The option of directly leaching the concentrate without pre-treatment was also evaluated. Test work was conducted using samples screened to a size fraction of 105-212 µm. Samples were leached in a 1 L glass autoclave. The reactor was hermetically sealed and thus the resulting pressure was not controlled but was dependent on the process temperature. The product from leaching was calcined and analysed via XRD and SEM to determine the purity of the product. The magnetic separation step was found to be ineffective and discontinued early in the study. Thus far a product with 97% synthetic rutile purity as analysed by SEM has been produced by directly leaching the concentrate at a temperature of 145°C, pulp density of 25wt% and leaching time of 6 hrs.

KEYWORDS

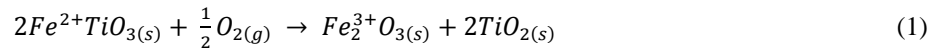
Ilmenite, synthetic rutile, roasting, magnetic separation, HCl leaching.

INTRODUCTION

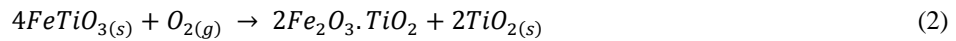
The study investigates the use of a process route comprising oxidative-reductive roasting, followed by magnetic separation and then hydrochloric acid leaching and calcination to produce synthetic rutile from ilmenite concentrate. The grade of synthetic rutile produced should be suitable for chlorination to produce pigment grade TiO₂. Hence the proposed process should produce a product consisting of no less than 95% synthetic rutile. Additionally, the product should have no more than 1.5wt% combined content of CaO and MgO (Zhang et al., 2011) as they tend to form high-boiling-point chloride leading to the malfunctioning of fluidized bed chlorinator (Cardarelli, 2008). Finally the product should have no more than 2.1wt% of Fe₂O₃.

The widely used ways to produce such a product at present include smelting, the Becher process, Benilite process and hydrochloric acid (HCl) leaching (Lasheen, 2005; Naly and Aly, 2009). The HCl process has been selected for this study as it is desired to incorporate it into a larger flowsheet which contains a patented hydrochloric acid regeneration process. It will be applied to a specific ilmenite concentrate and will also incorporate the pre-treatments of oxidative-reductive roasting and magnetic separation similar to the Laporte, Austpac and TSR processes (Guillet, 2015).

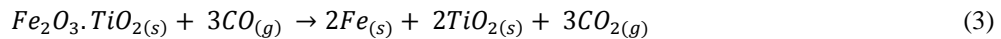
The HCl process produces synthetic rutile by purification of the ilmenite concentrate. Hence the goal is to dissolve as much of the impurities as possible while dissolving as little of the TiO_2 as possible. The major impurity in the concentrate is the Fe. Oxidative-reductive roasting plays a critical role in facilitating the removal of Fe through HCl leaching. Guillet (2015) reports that oxidative roasting in excess of $900^\circ C$ converts Fe from the ferrous to the ferric state forming hematite. The ilmenite is broken down to an iron-doped rutile with a hematite layer on top with most of the Fe migrating to the surface of the particles and in the cleavages as per equation 1 below.



However, Fe in its' ferric state is not amenable to HCl leaching thus it has to be reduced back to ferrous. This is done by reductive roasting in excess of $900^\circ C$ in the absence of oxygen with the use of pet coke as a reducing agent. The hematite undergoes a transformation to magnetite, which is highly magnetic and can be removed by magnetic separation. The more Fe removed prior to leaching the less the burden on this step in terms of temperature and leaching time. However, the transformation is only partial, a complete transformation would require a temperature of $1300^\circ C$ under pressure of neutral atmosphere. Zhang et al. (2011) states that the oxidative roast breaks down the ilmenite to iron oxides namely pseudobrookite and rutile as per equation 2 below.



The resulting pseudobrookite is then mixed with coal and sulphur in a rotary kiln at temperatures in excess of $1200^\circ C$ to reduce it to metallic iron and rutile as per equation 3 below.



In addition, the oxidative-reductive roasting process is known to keep the particle size of the synthetic rutile close to the ilmenite effectively eliminating the problem of production of fines and any difficulties it causes during filtration (Zhang et al., 2011). Oxidative roasting improves the reducibility of ilmenite bringing down the temperature required for this step (Zhang and Ostrovski, 2000). The oxidative-reductive roasting step is also reported to improve the rate and extent of HCl leaching and

renders the TiO₂ fraction of the concentrate less soluble in HCl (Sarker et al., 2006; Walpole and Winter, 2002). In addition to evaluating the effectiveness of this approach on the concentrate, the study also evaluated the effectiveness of the direct leaching of the concentrate without the roasting pre-treatment.

MATERIALS

The concentrate originating from Tellnes ore from Norway was received as finely milled concentrate. The chemical composition is seen in Table 1 from an XRF (X-ray fluorescence) analysis, mineralogy as seen Table 2 from XRD analysis and particle size profile by mass determined by processing sample using vibrating screens and weighing fractions as seen in Table 3.

Table 1: Chemical composition by weight % of sample as determined by XRF

TiO ₂	Fe	SiO ₂	MnO	MgO	CaO	P ₂ O ₅	Cr ₂ O ₃	V ₂ O ₅	S	C	H ₂ O	Al ₂ O ₃
44.00	35.50	3.30	0.30	4.50	0.35	0.02	0.09	0.20	0.06	0.03	3.50	0.70

**Table 2: Mineralogical composition from XRD analysis
on 105-212 µm size fraction**

Minerals	Formula	Weight %
Ilmenite	FeTiO ₃	84.21
Hematite	Fe ₂ O ₃	8.29
Magnetite	Fe ₃ O ₄	2.98
Albite	NaAlSi ₃ O ₈	2.13
Iron (α)	Fe	0.33
Rutile	TiO ₂	2.05
	Total	99.99

Table 3: Particle size distribution profile by mass

>212 µm	212-105 µm	<105 µm
%	%	%
45	50	5

METHODS

All pre-treatment and test procedures were conducted on sample with a size fraction of 105-212 µm which was prepared using vibrating screens. The roasting was conducted on batch samples of 900 g each. The samples were placed in a ceramic dish in a furnace with air extraction from the top and two holes on the front door to facilitate air movement for oxidative roasting. The holes were blocked to facilitate reductive roasting and in addition, pet coke in the ratio of 100 g of pet coke to 1 kg of ilmenite

sample was added for the reductive roast. The pet coke was 98% carbon with size fraction 0-0.2 mm. The roasting temperature was set at 975°C and two routes were explored. The first was a 1 hour oxidative roasting followed by cooling and then 1 hour reductive roast. The second was a 2 hour oxidative roast followed by 2 hour reductive roast. At the end of each process a sub-sample was obtained for XRD analysis.

The samples were then put through magnetic separation using a Jeffrey-Taylor JT103 magnetic separator. The machine consists of a permanent magnet (0.13T) and an electromagnet (1T). These two magnetic separation steps result in the sample being separated into three fractions, namely highly magnetic, weakly magnetic and non-magnetic. The vibration speed of the conveyor belt that delivers the samples to the magnets was set to 80Hz. This setting was previously explored (Guillet, 2015) as being the optimal one to produce a thin slice of sample with grains being sufficiently separated to allow each grain to be exposed to the magnets. The three fractions would then be analysed by XRD and XRF.

Leaching tests were conducted in a Buchiglasuster Ecoclave glass autoclave that had been retrofitted to handle high temperature and high pressure HCl conditions. The 1 L reactor had a working volume of 800 mL. The slurry was agitated using an overhead Teflon stirrer and the desired temperature was achieved using a heating circulator with heating oil. The reactor was airtight and hence pressurized by the vaporisation of the solution. The samples, pre-treated by roasting and magnetic separation, were prepared using a spinning riffler microscale. The sample was added to the reactor through an opening at the top using a funnel followed by the 20% HCl solution. The HCl solution was prepared by diluting 35% analytical reagent grade HCl with deionised water. The slurry was agitated at a rate of 550 rpm and heated to the desired temperature. The leaching time was counted from the time that the desired temperature was attained. The time it took to reach the desired temperature was noted and during the leaching course a sample of solution was obtained for analysis. Further samples were obtained and filtered during the rest of the test for analysis via inductively coupled plasma atomic emission spectroscopy (ICP-AES). The elements of interest were Ti and Fe. At the end of the leaching test the reactor was cooled using the circulator by setting it to cooling. The cooling typically lasted for an hour at the end of which another solution sample was taken. When the slurry temperature was at 40°C, the reactor was emptied from the bottom using the drainage port and valve. The slurry was allowed to stand for a few minutes with the solid material quickly settling to the bottom and through a transparent container showing two distinct phases. The supernatant was poured out carefully for vacuum filtration and the remaining solid was washed with deionised water. This mixture was allowed to sit allowing the solids to quickly settle to the bottom and the supernatant liquid is poured out. The remaining solids are placed in a drying dish along with the filtered material and dried overnight in an oven at 65°C. This method was preferred to recovering the solids via vacuum filtration alone as it proved difficult to lift the heavy material in the filter paper without tearing. The sample was then calcined at 985°C for 90 minutes and then analysed using XRD and SEM to determine the amount of rutile in the product and the impurities present.

The leaching experiments evaluated the influence of the following parameters: temperature (100, 125 and 145°C) and resulting pressures (1, 1.4 and 2.4 bar overpressure respectively), leaching time (3 and 6 hours) and pulp density (15 and 25wt%).

RESULTS AND DISCUSSION

The most conclusive results from the leaching tests on samples that were pre-treated with roasting and directly leached without roasting can be seen in Table 4. The amount of Ti and Fe leached in each test was determined by the amounts leached in solution (ICP-AES) and by material balance using the weights of samples before and after the test and the chemistry of the elements in the samples. The low amounts of Ti leached showed that almost negligible amounts of TiO₂ were lost in each test. In all cases, a small amount of Ti initially leached out but then precipitated and then completely stopped leaching as expected from the literature (Guillet, 2015). Under the current process conditions of 20% HCl and temperature range 100-145°C, TiOCl₂ complex is formed which hydrolyses to synthetic rutile and regenerates HCl as per equations 4 and 5:

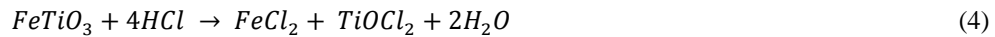


Table 4: Leaching Tests Conducted and Resulting Rutile Product

Test No.	Roasting Time* (hrs)	Petcoke Added (wt%)	Leaching Temp. (°C)	Leaching Time (hrs)	Pulp Density (wt%)	Rutile in Product (%)	Ti Leached (%)	Fe Leached (%)
1	1	10	100	6	25	47.89	0.53	61.03
2	1	10	145	6	25	84.55	0.05	86.40
3	2	10	100	6	25	45.35	0.34	57.79
4	2	10	145	6	25	79.33	0.05	81.07
5	0	0	145	6	25	97.43	0.04	95.09
6	0	0	145	3	25	87.85	0.03	92.48
7	0	0	125	6	25	92.23	0.06	94.46
8	0	0	100	6	25	53.05	0.83	67.60
9	0	0	100	6	15	92.00	0.95	94.76

*Roasting time for each step, oxidative and reductive roasting.

The time it took for the Ti to precipitate and stop leaching varied with temperature. For the tests conducted at 145°C this happened after the first hour (Figure 1) and for the one at 125°C it took 2 hours for the Ti to precipitate and stop leaching out. In the case of the tests conducted at 100°C the Ti slowly

precipitated until almost the end of the experiment (Figure 2). Closer examination of the Fe-Ti leach curves of all tests did not reveal any clear pattern or relation between the leaching of the two metals.

The magnetic separation process did not produce a highly magnetic fraction only a weakly magnetic and a non-magnetic fraction. Possibly there was not a significant enough amount of magnetite or it was deeply intertwined with other non-magnetic minerals. The magnetic separation step was therefore discontinued early in the test program.

Table 4 shows that roasting samples prior to leaching actually did not produce the desired purity of synthetic rutile as seen from the results of tests 1-4. Analysis by XRD shows that the result of the oxidative roast resulted in the change of ilmenite to mostly pseudobrookite while the reductive roast had no further impact. The analysis also revealed significant amounts of unreacted petcoke in the samples after reductive roasting. It is hypothesized that because the roasting was done in a stationary vessel unlike a rotary kiln which facilitates mixing, the expected reaction of reductive roast did not occur. Without sufficient mixing, some of the petcoke was left un-reacted. Further, the inability to completely eliminate oxygen from the furnace during the reductive roast and the use of an open dish were also contributing factors. Equation 3 shows that gaseous CO reacts with pseudobrookite to break it down. In the open dish used, the gas would have just escaped. The roasting was repeated with the reductive roast being conducted in a porcelain crucible with a lid. However, the resulting material had simply been reduced back to ilmenite and when leached produced similar results.

By comparison, Table 4 also shows that direct leaching of the concentrate yielded a successful result at temperature of 145°C (Test 5). With the remaining 2.57% of the material being composed of a number trace silicate and Fe minerals, it is likely that the limits for Fe, Ca and Mg impurities have not been exceeded. XRF Analysis could not determine this accurately hence other methods such as digestion and ICP analysis have to be evaluated. Although below specification for this specific project, Test 7 was conducted under identical conditions with the exception of temperature being at 125°C and Test 9 conducted at 100°C and pulp density 15wt% also produced positive results with a rutile purity of 92.23% and 92.00% respectively. Figure 1 shows the Fe and Ti leach curves for Test 5. At the 1 hour mark the targeted temperature of 145°C had been reached. At this point the Ti had precipitated after having initially leached out to a small extent and 60% of the Fe has been leached before further leaching occurred. SEM analysis showed that the sample from Test 5 was mostly rutile with silicate and iron oxides as trace minerals (Figure 3 (b)). The analysis also showed that all the rutile grains were porous (Figure 3(a)). This is possibly due to the leached Fe leaving behind unoccupied spaces. Figure 4 (a and b) from Tests 6 and 7 respectively show optical microscope images of grains that have undergone incomplete ilmenite to rutile conversion. The grain with a large ilmenite centre in Figure 4 (b) suggests that the Fe leached out in a consistent manner under which the Fe leached out starting from the surface inwards. However, the grain in Figure 4 (a) shows some ilmenite close to the surface of the grain and scattered around the grain while the centre and bulk have been completely converted to rutile.

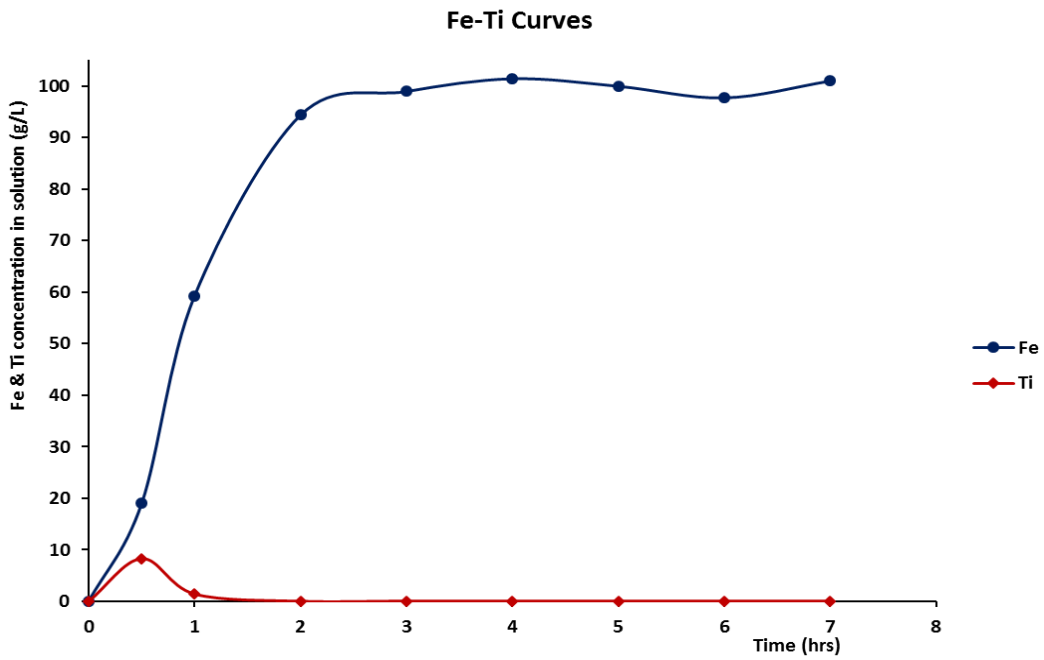


Figure 1: Leach curves for Fe and Ti for test at 145°C, 25 wt%, for 6 hrs with 20% HCl directly on concentrate without roasting.

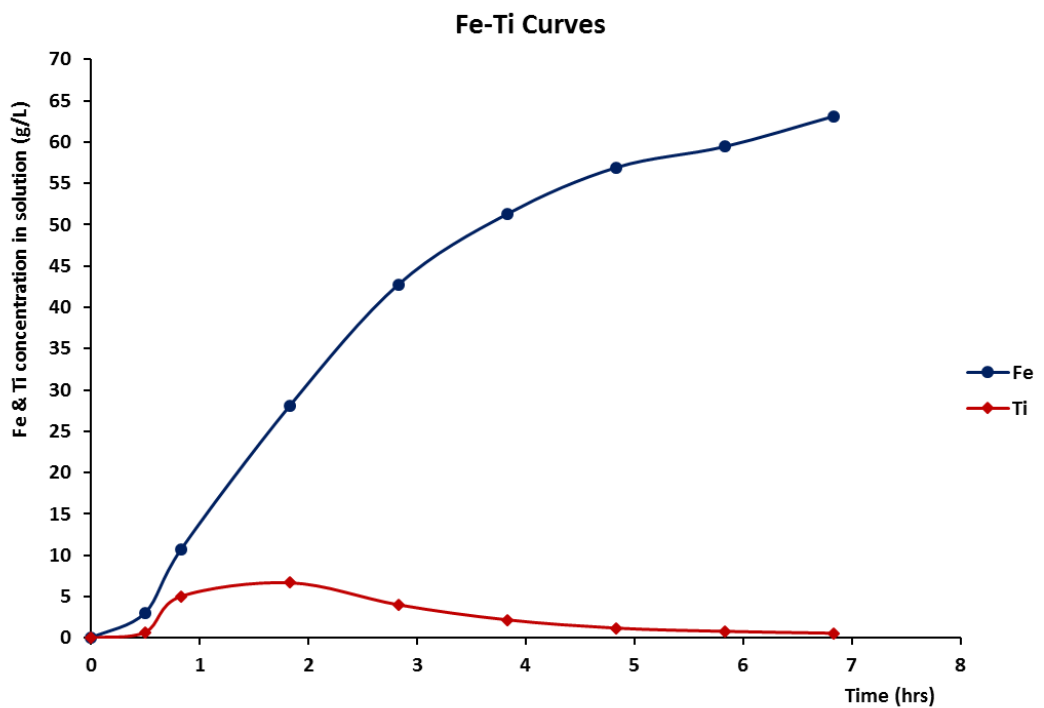


Figure 2: Leach curves for Fe and Ti for test at 100°C, 15 wt%, for 6 hrs with 20% HCl directly on concentrate without roasting.

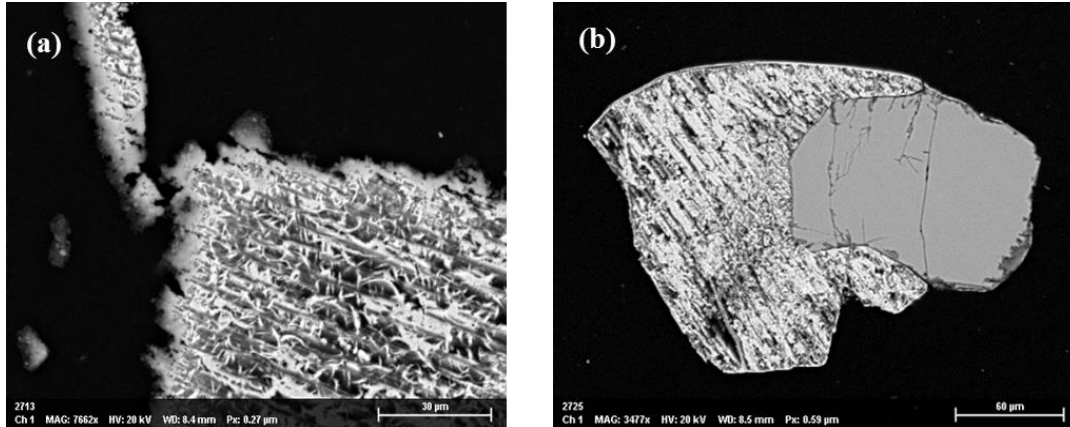


Figure 3: SEM scans of residual grains from Test 5; 145°C, 25 wt%, for 6 hrs with 20% HCl directly on concentrate without roasting.

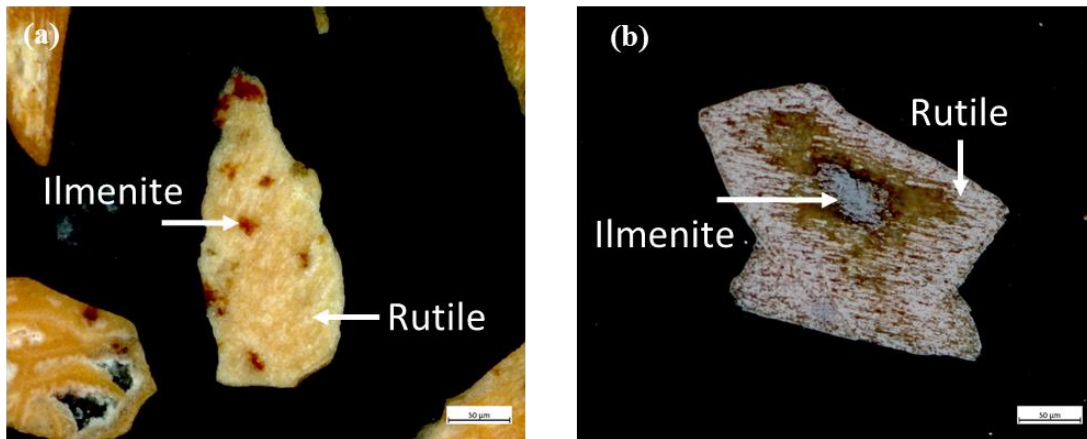


Figure 4: Optical Microscope images of residual grains from Test 6 (a) and Test 7 (b)

CONCLUSION

The approach of direct leaching of the tested ilmenite concentrate without pre-treatment has produced promising results to be investigated at larger scale. The most superior product of 97.43% rutile is achieved at a leaching temperature of 145°C, pulp density of 25wt% and leaching time of 6 hrs. Tests conducted at 125°C, pulp density 25wt% and 6 hrs and 100°C, pulp density 15wt% and 6 hrs, also produced positive results with a rutile purity of 92.23% and 92.00% respectively, which may still find successful application. Contrary to other studies which show the formation of a product layer on the rutile grains, the particles in this study at all tested temperatures of 100, 125 and 145°C did not show any such layer around the grains. The rutile particles were all porous and there seemed to be no relation between the Fe leaching and the Ti leaching and precipitation effects and eventual halting in Ti leaching. Further work in this project will focus on understanding the leaching mechanisms of Fe and Ti for this material under the current process conditions.

ACKNOWLEDGMENT

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