

Preparation of Rutile from Ilmenite Concentrate Through Pressure Leaching with Hydrochloric Acid



JUNYI XIANG, SONGLI LIU, XUEWEI LV, and CHENGUANG BAI

Take into account the fact that the natural rutile utilized for the production of titanium dioxide pigment through chloride process is desperately lacking worldwide especially in China, an attempt was exploited for extracting synthetic rutile from Yunnan ilmenite concentrate with hydrochloric acid pressure leaching process. The leaching parameters for one step leaching process were investigated. The results shown that the optimum condition is leaching temperature of 413 K (140 °C), acid concentration of 20 pct HCl, leaching time of 4 hours and liquid/solid mass ratio of 8:1. A two steps leaching process was also suggested to reutilize the leaching liquor which with a high content of HCl. The results showed that the content of HCl decreased from 135 to 75 g/L, total iron increased from 44.5 g/L to about 87.6 g/L, and the liquid/solid mass ratio decreased to 5:1 with a two steps leaching process. The leaching product produced through a two steps leaching process shows a pure golden red with a high content of titanium (92.65 pct TiO₂), a relatively low content of calcium (0.10 pct CaO) and magnesium (0.12 pct MgO), but high content of silicon (5.72 pct SiO₂).

DOI: 10.1007/s11663-016-0885-5

© The Minerals, Metals & Materials Society and ASM International 2016

I. INTRODUCTION

TITANIUM dioxide pigment is widely used in painting, plastic and paper production, and chemical industry.^[1] It is mainly commercially manufactured by two methods, named sulfuric acid process and chloride process. The sulfuric acid process involves the digestion of condensed sulfuric acid with ilmenite concentrate or acid soluble titanium slag, the purification of titanium sulfate solution, the hydrolyzation of hydrous titanium dioxide and the drying and calcination of the precipitate.^[2] This process produces huge quantities of dilute sulfuric acid containing large amounts of ferrous sulfate annually. Compared with the sulfate process, only a small amount of iron chloride is generated as the waste in chloride process.^[3] Chloride process gradually tends to replace sulfate acid process due to both environmental and economic reasons. A relative high grade of rutile is necessary for the chloride process.^[4] However, the producers of chloride pigment have to face a raw material supply problem due to the limited of natural rutile. This makes the upgrading of ilmenite to high titanium intermediates, such as titanium slag, upgrading titanium slag (UGS) and synthetic rutile, to be important. Synthetic rutile is one of the most important substitutes to natural rutile, which consists largely of titanium dioxide and a small amount of iron, calcium,

magnesium and other impurities. Generally speaking, the content of titanium in the synthetic rutile should be higher than 90 pct TiO₂ by weight for high productive efficiency and low chlorine gas consumption. The total content of CaO and MgO should be less than 1 pct by weight as they seriously influence the fluidization process.

There are several commercialized processes, such as Benelite process,^[5] Austpac process,^[6] Murso process^[7] and Becher process,^[8] being used in the manufacture of synthetic rutile from ilmenite concentrate ore. In these processes, Benelite process, Austpac process and Murso process all involve a hydrochloric acid leaching step even though different pretreatment methods and equipment are adopted. Hydrochloric acid is preferred to other acids as its comparatively easier recovery of a number of the useful free acid from its waste solution.^[9]

In the past decades, a considerable number of investigations were focused on upgrading of ilmenite concentrate by leaching with hydrochloric acid as summarized in Table I. The hydrochloric acid leaching of ilmenite concentrate can be divided into two main categories, atmospheric leaching process and pressure leaching process. Most studies were performed in order to obtain optimum leaching conditions. Main factors that affect leaching efficiency are hydrochloric acid concentration, leaching temperature, L/S ratio, leaching time *etc.* Types of ore also have an immediate impact on the selection of pretreatment and leaching parameters.

In our previous study, hydrochloric acid leaching of Yunnan ilmenite with different thermal pretreatments was carried out.^[15] As shown in Table I, the oxidation pretreatment process has the advantage with less proportion of fine products (<4 pct) than reduction pretreatment (~38 pct) and non-pretreatment (~21

JUNYI XIANG, XUEWEI LV, and CHENGUANG BAI are with the School of Materials Science and Engineering, Chongqing University, Chongqing, 400044, China. Contact e-mail: lvxuewei@163.com. SONGLI LIU is with the School of Resources and Environmental Engineering, Panzhihua University, Panzhihua, 617000, China.

Manuscript submitted July 31, 2016.

Article published online December 29, 2016.

Table I. Summary of Previous Works on Upgrading Ilmenite Using Hydrochloric Acid Leaching

Origin of Ilmenite Ore	Chemical Composition, (Wt. Pct)	Methods	Leaching Conditions	Synthetic Rutile, (Wt. Pct)	References
Eastern Australia	/	Reduction-two step pressure leaching (Benilite process)	19 pct HCl, 416 K (143°C), L/S = 1.4 to 1.6, 4 hours	TiO ₂ 94.14, TFe 1.41, TiO ₂ recovery 98.3, Fines 1.7	10
Westport in New Zealand	TiO ₂ 50.4, FeO 34.1, Fe ₂ O ₃ 12.1, CaO 0.04, MgO 0.67, SiO ₂ 0.76	Oxidation-magnetic separation-leaching (Austpac process)	25 pct HCl, 383 K (110°C), L/S = 1.4 to 1.6, 4 hours	TiO ₂ 97.3, Fe ₂ O ₃ 1.08, CaO 0.01, MgO 0.02, SiO ₂ 0.79	6
NA	TiO ₂ 52.9, FeO 30.8, Fe ₂ O ₃ 11.9, MgO 0.54	Oxidation-reduction-leaching (Murso process)	20 pct HCl, 383 K (110°C), L/S = 2.4, 3-4 hours	TiO ₂ 96.6, Fe ₂ O ₃ 0.5, MgO 0.15, -75 μm 4-5	7
Abu Ghalaga	TiO ₂ 41.10, FeO 24.40, Fe ₂ O ₃ 28.60, CaO 0.15, MgO 0.64, SiO ₂ 2.43	Reductive leaching (addition iron powder during leaching)	20 pct HCl, 383 K (110°C), L/S = 7.3, 5 hours	TiO ₂ 89.45, Fe ₂ O ₃ 0.77, CaO 0.01, MgO 0.04, SiO ₂ 5.80	11
Bangladesh	TiO ₂ 39.5, FeO 24.2, Fe ₂ O ₃ 33.0	Oxidation-reduction -leaching	15 pct HCl, 348 K (75°C), L/S = 100, 2 hours	TiO ₂ 90.8, TFe 5.6	12
Tellnes in Norway	TiO ₂ 51.38, FeO 40.38, Fe ₂ O ₃ 6.50, MgO 3.25	①Direct leaching ②Oxidation-leaching	20 pct HCl, 433 K (160°C), L/S = 4, 10 hours	① TiO ₂ 94.72, Fe ₂ O ₃ 1.44, SiO ₂ 0.44 ② TiO ₂ 84.47, Fe ₂ O ₃ 4.18, SiO ₂ 0.28	13
Panzhuhua in Chia	TiO ₂ 47.25, FeO 34.21, Fe ₂ O ₃ 5.56, CaO 1.08, MgO 6.23, SiO ₂ 2.75	Mechanical activation-leaching	20 pct HCl, 373 K (100°C), L/S = 5.5:1, ≥6 hours	TiO ₂ 92, Fe ₂ O ₃ 2.1, CaO + MgO 0.28	14
Yunnan in China	TiO ₂ 45.92, FeO 31.67, Fe ₂ O ₃ 17.15, CaO 0.15, MgO 1.21, SiO ₂ 2.84	①Direct leaching ②Oxidation-leaching ③Reduction-leaching	26 pct HCl, 381 K (108°C), L/S = 10:1, ≥7 hours	① TiO ₂ 83.98, -75 μm 26 pct ② TiO ₂ 92.36, -75 μm 4 pct ③ TiO ₂ 92.76, -75 μm 42 pct	15

Table II. Summary of Materials Information

Samples	Chemical Composition (Pct)						Particle Size Distribution (Pct)			
	TiO ₂	Fe ₂ O ₃	FeO	CaO	MgO	SiO ₂	-47 μm	47-74 μm	74-150 μm	150-425 μm
Untreated	45.92	17.15	31.67	0.15	1.21	2.84	0.30	3.00	28.70	68.00
Oxidized	45.55	41.44	7.83	0.15	1.20	2.83	0.15	2.80	26.42	70.63

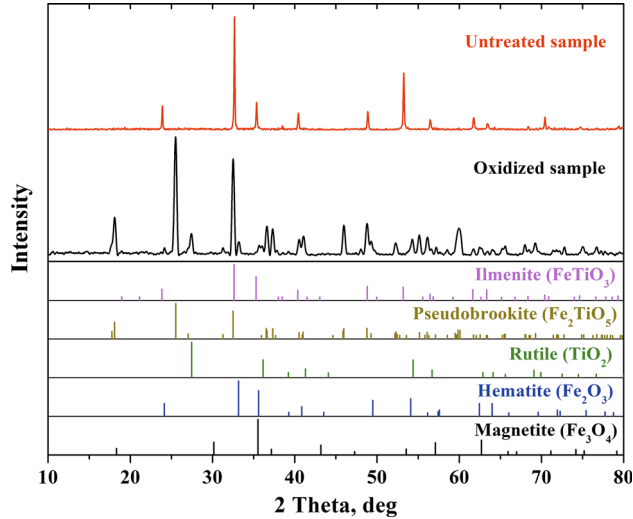


Fig. 1—Comparison of XRD patterns of untreated and oxidized samples with the standard diffraction spectrums.

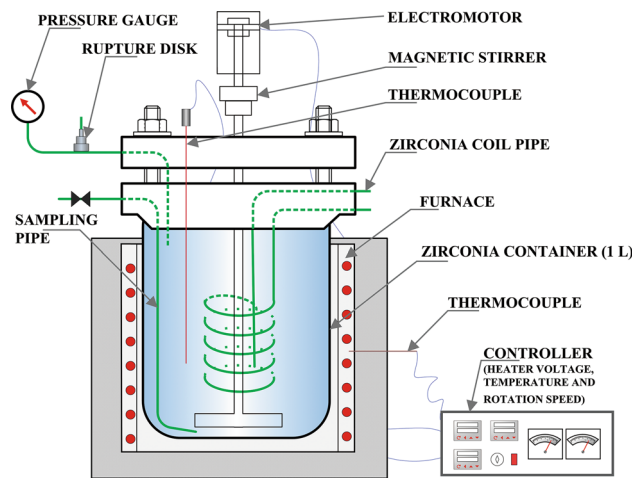


Fig. 2—Schematic figure of the leaching apparatus.

pct). The leaching efficiency of impurities can be significantly enhanced by increasing the leaching temperature. However, ultrahigh leaching temperature is not suitable for atmospheric leaching process as the low boiling point of hydrochloric acid solution and emission of volatile hydrogen chloride. Therefore, oxidation roasting of Yunnan ilmenite concentrate, followed by hydrochloric acid leaching in an autoclave was applied in this study. The effect of process parameters, such as

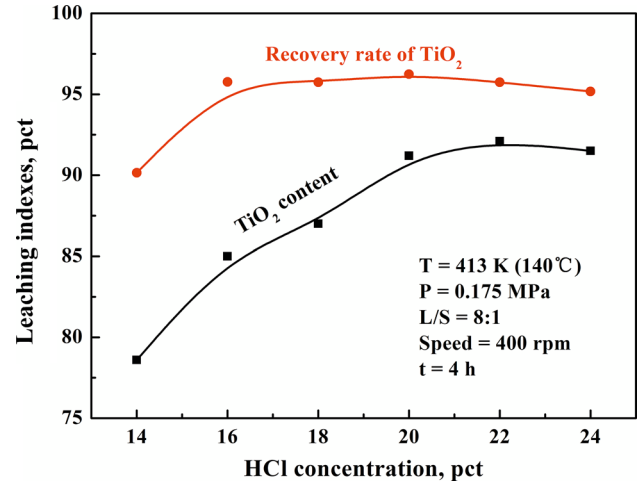


Fig. 3—Effect of hydrochloric acid concentration on the TiO₂ content in the leaching product and corresponding recovery rate.

hydrochloric acid concentration, L/S mass ratio, leaching time, and the reutilization of leaching liquor on leaching behavior were studied for the purpose of improving the economy of the process.

II. EXPERIMENTAL

A. Materials

Ilmenite concentrate for this study were taken from the mining area in Yunnan province, southwest China. The samples was firstly dried at 373 K (100°C) for 24 hours, then roasted in a laboratory open muffle furnace. The roasting was conducted at temperature of 1173 K (900°C) and lasting 1 hour. The chemical composition and particle size distribution the samples were summarized in Table II. The untreated sample contains 45.92 pct TiO₂, 17.15 pct Fe₂O₃, 31.67 pct FeO, 1.21 pct MgO and 2.84 pct SiO₂. After oxidation roasting, large portion of ferrous iron was oxidized to ferric iron, with a content of 41.44 pct F₂O₃ in the roasted sample. As shown in Figure 1, the major crystalline phases transform from ilmenite (FeTiO₃) into pseudobrookite (Fe₂TiO₅), rutile (TiO₂) and hematite (Fe₂O₃).

B. Pressure Acid Leaching

The oxidized sample was leached in hydrochloric acid at certain temperature, L/S ratio and time. As shown in Figure 2, the leaching experiments were performed at an

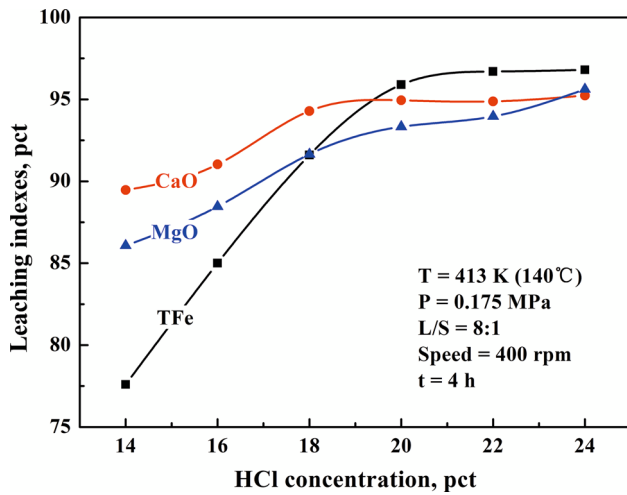


Fig. 4—Effect of hydrochloric acid concentration on the leaching rate of Fe, CaO and MgO.

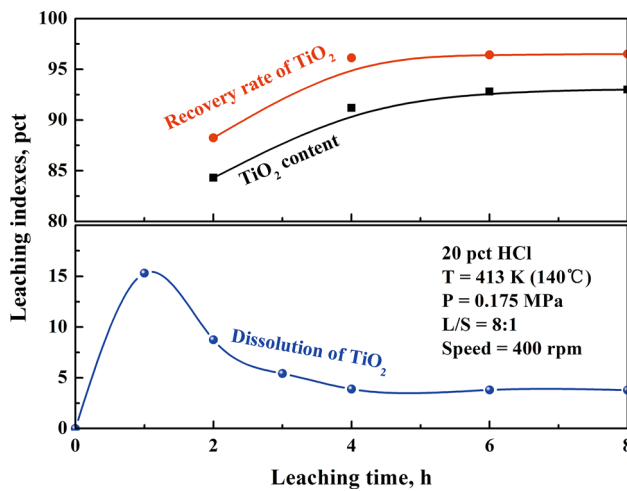


Fig. 5—Effect of leaching time on the dissolution of TiO₂, the TiO₂ content in the leaching product and corresponding recovery rate.

autoclave equipped with a zirconia container and stirring paddle. One immersion thermocouple was used to monitor the temperature of the leaching solution. An integrated controller was used to maintain the desired heater voltage, reaction temperature and stirring speed. A zirconia coil pipe was used to cool off the solution by pumping cooling water.

For each leaching test, the oxidized sample and solution were charged into the reactor and the mixture was well mixed with mechanical stirring with a speed of 400 rpm. The mixture was heated to 413 K (140°C) as soon as possible. After a specific leaching time, the slurry was cooled to below 323 K (50°C). Then the slurry was filtered using a Buckner funnel equipped with a glass filter. The leaching residue was dried at 373 K (100°C) for 5 hours followed by roasted at 1173 K (900°C) for 1 hour to achieve the phase transformation of titanium dioxide. Both filter liquor and product were analyzed to determine the contents of titanium dioxide, iron, calcium oxide and magnesium oxide.

C. Characterization

For the chemical analysis of the solid samples, a weighed sample of finely ground sample was melted with sodium peroxide and then leached. The titanium and iron contents were determined by reduction–oxidation titration.^[16] Ferric iron was calculated by difference between total and ferrous iron contents. In order to check the titration results, some samples were analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES) by a ICAP 6000 series instrument (Thermo Fisher Scientific, Waltham, MA). The concentration of calcium, magnesium and silicon in the solution were also analyzed using ICP-OES.

The particle size of the samples were analyzed by dry sieving method. The mineralogical composition of the samples were identified by X-ray powder diffraction (XRD) and performed using a Rigaku D/max 2500 diffractometer (Japan) with Cu K α radiation ($\lambda = 0.154$ nm, 40 kV, 150 mA) at scanning rate of 0.3°/seconds. Optical images of the samples were acquired from a Zeiss optical microscopes. A field emission scanning electron microscopy (JSM-7800 FEG SEM, JEOL) with energy dispersive analysis (EDS, Oxford) was used to determine the morphology of the leaching product and distribution of elements therein.

III. RESULTS

A. Leaching

1. Acid concentration

Figure 3 gives the effect of hydrochloric acid concentration on the content of titanium dioxide in the synthetic rutile and recovery rate. As shown in this figure, the titanium dioxide content in the product significantly increased with the increase of acid concentration and the maximum value was achieved between 20 pct and 24 pct hydrochloric acid concentration. However, the recovery rate of titanium dioxide firstly increased to a maximum of about 96 pct, then slightly decreased with increasing acid concentration. As can be seen from Figure 4, after 4 hours leaching, the dissolution of Fe increased rapidly with the increase of acid concentration, and then continued to increase slightly. The dissolution of CaO and MgO also increased with the acid concentration and more than 85 pct were dissolved in solution.

2. Leaching time

Figure 5 gives the effect of leaching time on the content of TiO₂ in leaching product and recovery rate. Leaching time has a significant influence on the content of TiO₂ in the leaching product and recovery rate. The content of TiO₂ started to increase in the first 4 hours, then continued slightly increasing with extended leaching time, reached a maximum of about 92.8 pct after 6 hours leaching. The recovery rate of TiO₂ also increased rapidly initially (2 to 4 hours) then almost kept the content. The fraction of TiO₂ dissolved directly increased to about 15 pct in the first hour of leaching, and then dramatically decreased to about 3 pct after

4 hours. The variation of the dissolved TiO_2 is consistent with the recovery rate results.

3. L/S ratio

The effect of L/S ratio on the content of TiO_2 in the leaching product and corresponding recovery rate was investigated in wide L/S mass ratio range of 5 to 13. As shown in Figure 6, the content of TiO_2 in the leaching product increased with increasing L/S ratio, reached a maximum value then decreased with further increasing L/S mass ratio. However, the recovery rate of TiO_2 slightly decreased with the increase of L/S ratio.

B. Reutilization of the Leaching Filtrate

From all of the research above, the optimum conditions for leaching are 20 pct of hydrochloric acid concentration, 8:1 of L/S mass ratio and 4 to 6 hours of leaching time. After 4 hours of leaching, the chemical analysis of the filter liquor was performed to show the changes in the solution composition. The chemical analysis of the leach liquor before and after leaching was shown in Table III (one step). The total dissolved iron was enriched in the filter liquor reached to about 44.5 g/L. About 2.3 g/L dissolved TiO_2 stayed in the liquor. However, the hydrochloric acid concentration in the filter liquor still very high, about 135 g/L HCl.

Fully use of the hydrochloric acid in the filter liquor is very important due to both environmental and

economic reasons. One way for dealing the filter liquor is to recycle hydrochloric acid through an acid regeneration process. Another way is reused for leaching in which can make the full use of free acid. A two steps leaching process is a great way for using this filter liquor, as shown in Figure 7. The leachant for the first step leaching of any batch is a mixed solution constituted from the leach liquor of the second leaching of a previous batch plus the necessary amount of fresh commercial grade hydrochloric acid. The second step leaching employs fresh commercial grade hydrochloric acid. After a twice leaching, the filter liquor generated from step one then be used for acid regeneration.

Therefore, a two steps leaching process was performed in this study to make the full use of the hydrochloric acid. Both of leaching steps proceed under a pressure of 0.175 MPa, temperature of 413 K (140°C), L/S mass ratio of 5:1, stirring speed of 400 rpm and 4 hours. The leach liquor in the one step leaching is used in the first step leaching. 20 pct of fresh hydrochloric acid was employed in the second step leaching. As shown in Table III, the HCl concentration of the leach liquor decreased from 135 g/L to about 75 g/L HCl after the first step leaching. The concentration of iron enriched to about 87 g/L, whereas the concentration of TiO_2 decreased from 2.3 to 2.0 g/L. After second step leaching, the hydrochloric acid concentration decreased to about 140 g/L HCl makes it possible to reuse this acid in the first step leaching.

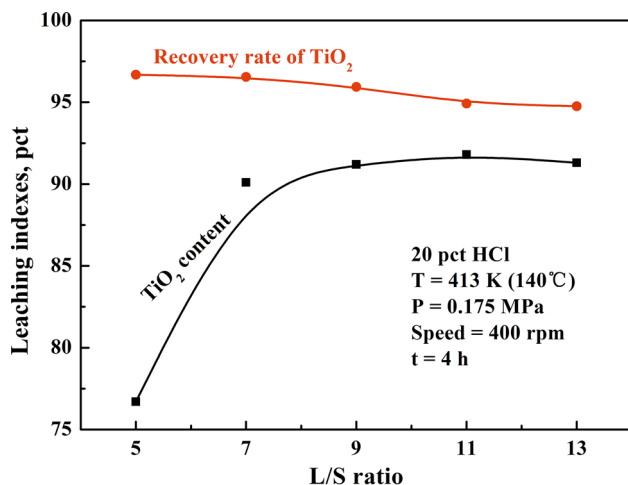


Fig. 6—Effect of L/S mass ratio on the TiO_2 content in the leaching product and corresponding recovery rate.

C. Leaching Products

As shown in Table III, for one step leach process, the leaching product consists of a titanium content of 91.20 pct TiO_2 by weight, and an iron content of 0.28 pct TFe by weight. After a two steps leaching process, the titanium content in the leaching product upgraded from 75.32 pct to 92.65 pct TiO_2 by weight, and the iron content decreased from 7.91 pct to 0.29 pct TFe by weight. The total amount of CaO and MgO in all of the products is less than 0.5 pct by weight. It should be noted that silicon is enriched in the leaching product with a content of about 5.6 pct SiO_2 by weight due to its acid resistance.

As shown in Figure 8, the optical micrographs clearly show that a small portion of unreacted ilmenite still remained in the leaching residue prepared from the first step leaching, while the leaching residue prepared from second step leaching shows pure golden red without obvious black unreacted ilmenite.

Table III. The Chemical Analysis of the Leaching Liquor and Leaching Products

Method	Leaching Parameters			Before Leaching (g/L)			After Leaching (g/L)			Leaching Product (pct)				
	L/S	T, K (°C)	T (h)	HCl	TFe	TiO_2	HCl	TFe	TiO_2	TiO_2	TFe	CaO	MgO	SiO_2
One step	8:1	413 (140)	4	220	0	0	135	44.5	2.3	91.20	0.28	0.12	0.15	5.63
1st step	5:1	413 (140)	4	135	44.5	2.3	75	87.6	2.0	75.32	7.91	0.18	0.24	4.69
2nd step	5:1	413 (140)	4	220	0	0	140	34.6	1.9	92.65	0.29	0.10	0.12	5.72

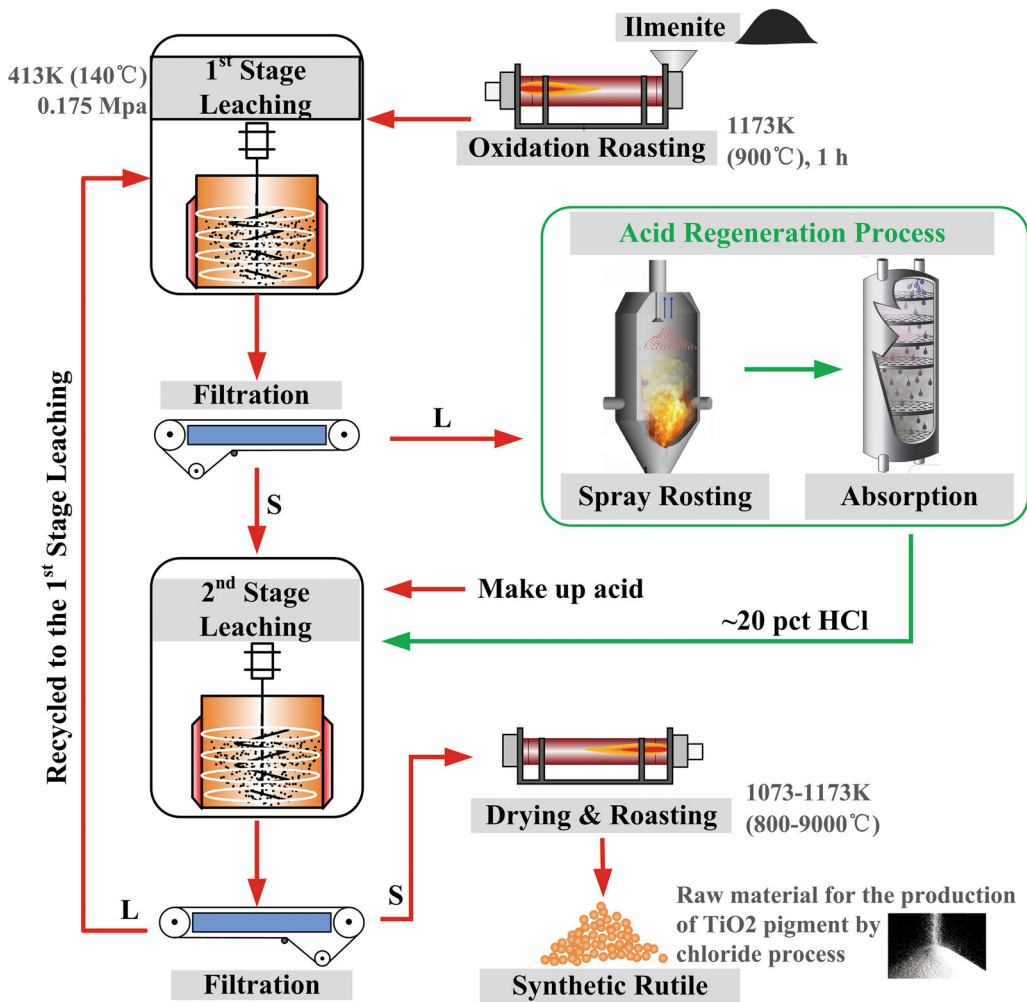


Fig. 7—Flowchart of the synthetic rutile production based on two steps leaching.

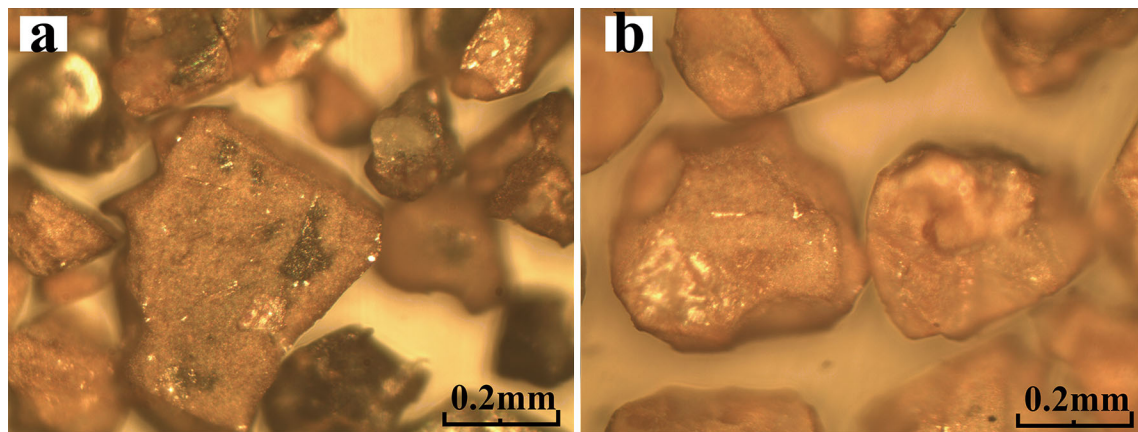


Fig. 8—Optical micrographs of the leaching products after roasting (a) first step leaching product (b) second step leaching product.

Figure 9 shows the SEM image of the second step leaching product after roasting with corresponding EDS maps of O, Ti, Si, Fe, Ca and Mg. The leaching product presented a well particle size with about 200 μm in

diameter. The dominant elements in the surface of the product are O, Ti and Si. The XRD results also reveal that the rutile (TiO_2) and quartz (SiO_2) in the leaching product is the dominant phase, as shown in Figure 10.

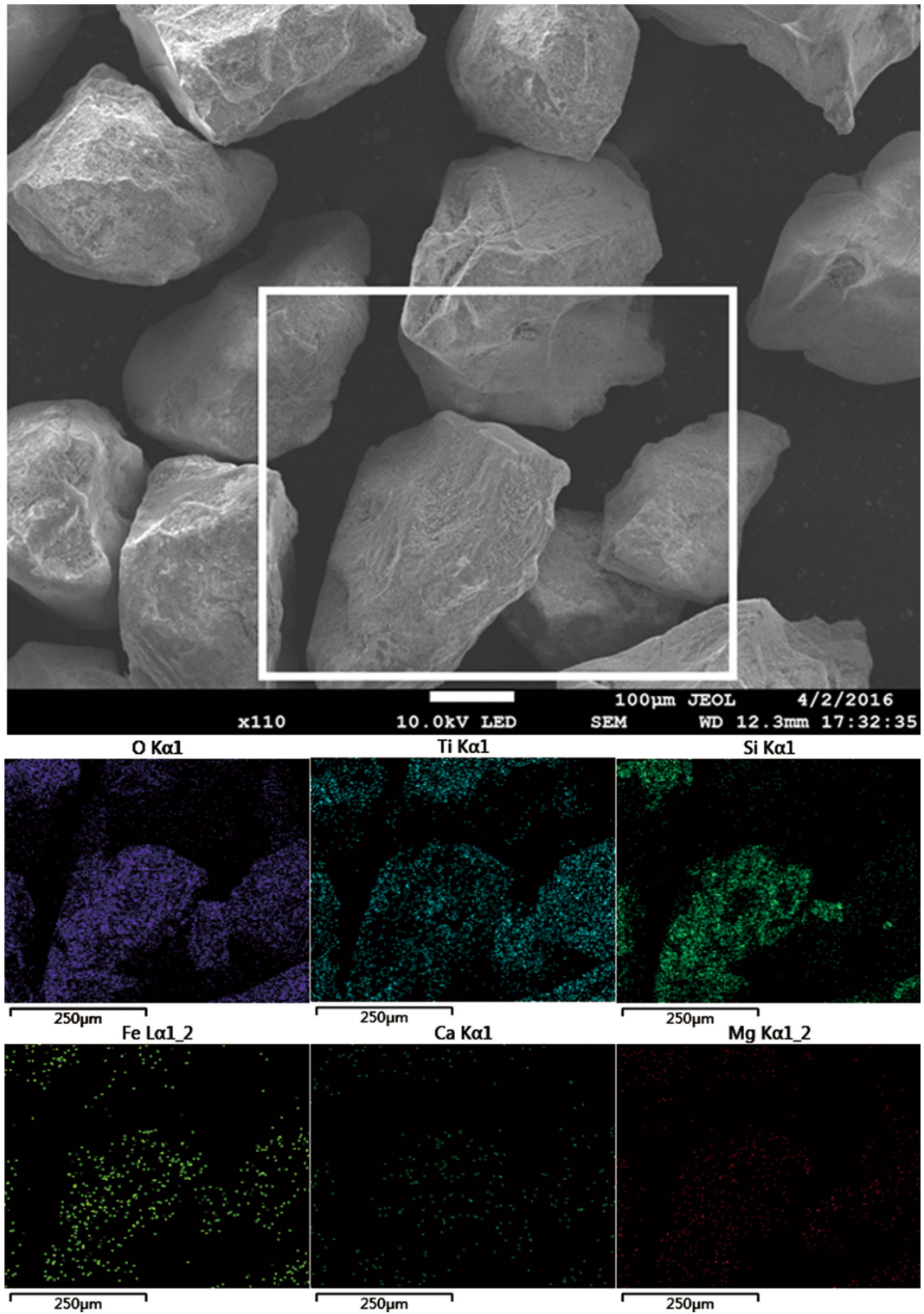


Fig. 9—SEM image of the second step leaching product after roasting with corresponding EDS maps of O, Ti, Fe, Si, Ca and Mg.

IV. DISCUSSION

Yunnan ilmenite concentrate was a light weathered ilmenite ore with 31.67 pct FeO and 17.15 pct Fe_2O_3 by weight. After roasting in the air, large amounts of ilmenite

phase shifted to pseudobrookite (Fe_2TiO_5) with a decreasing FeO content to 7.83 pct by weight (as shown in Table II and Figure 1). Ilmenite and pseudobrookite will react with hydrochloric acid as the following chemical reactions:

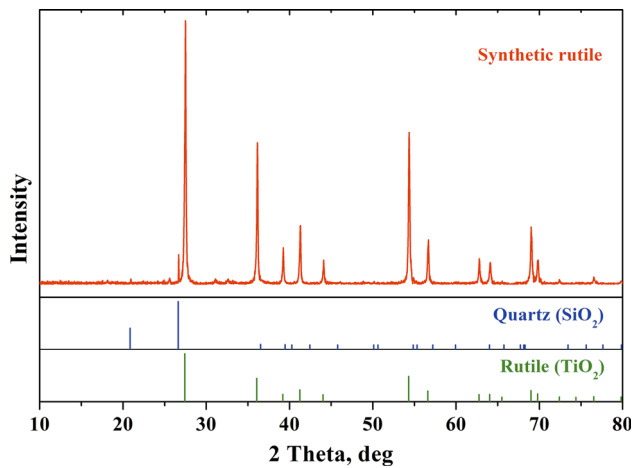
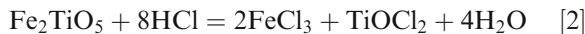
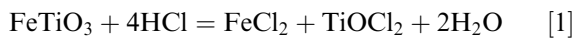
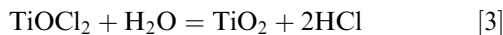


Fig. 10—XRD pattern of the synthetic rutile made by a two steps leaching process with the standard diffraction spectrums.



However, different with the dissolution of iron, the dissolved TiO_2 will hydrolysis and precipitation from the solution follow the reaction:



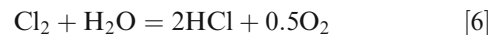
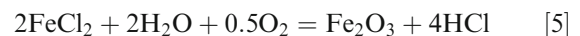
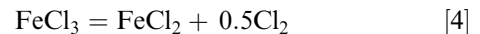
The dissolution of TiO_2 without hydrolysis is a direct loss of titanium for the manufacture of synthetic rutile. So make clear the leaching mechanism of TiO_2 is particular important. The leaching behavior of TiO_2 was significantly influenced by the L/S mass ratio, hydrochloric acid concentration, leaching temperature and the types of ore. L/S ratio is the first and most critical event that significantly influences the dissolution of TiO_2 . Generally, the dissolution of titanium will increase with the increasing acid concentration and the extent of time when using an extremely high L/S mass ratio. The dissolution behavior of TiO_2 in 35.4 to 36.3 pct,^[17] 23 to 30.3 pct,^[9] 1.8 to 26 pct,^[18] and 0.17 to 3.6 pct^[19] hydrochloric acid have been investigated. Among those studies, the dissolution of titanium directly increased with the increase of leaching temperature and the extent of time. A very large portion of titanium dissolved in the solution and the polymerization reaction does not happen. It has been reported that the polymerization of titanium will occur when the concentration of $[\text{Ti(IV)}] > 10^{-3} \text{ M}$ and $[\text{H(I)}] > 0.5 \text{ M}$.^[20] However, even the Ti(IV) concentration in the leach solution exceeds the value of 10^{-3} M , polymerization never occur in some investigations^[9,17] maybe due to the low leach temperature.

Temperature is another critical event that significantly influences the polymerization of the dissolved TiO_2 . Higher temperatures not only increase the dissolution of TiO_2 , but also accelerate the polymerization especially at lower L/S ratio. When temperature is higher than 373 K (100°C), especially at boiling point, such as those used by Rafael Vásquez^[21] and C. Sasikumar,^[22] the content

of Ti dissolved in solution directly increased to a peak value then dramatically decreased to stable value as the precipitate of TiOCl_2 . As shown in Figure 5, the content of TiO_2 in the leaching product increased with the extent of leaching time as the removal of impurities and the precipitation of $\text{TiO}_2 \cdot \text{H}_2\text{O}$. The precipitation of $\text{TiO}_2 \cdot \text{H}_2\text{O}$ completed after 4 hours of leaching, and the recovery rate of TiO_2 increased to a stable value at the same time. The dissolution rates of iron and titanium were increased with the increasing acid concentration (Figure 4) and L/S ratio (Figure 6) in this study. The polymerization of the dissolved Ti becomes little difficult in the solution with a high acid concentration. For this reason, the recovery rate of TiO_2 decreased when using high concentration of acid and L/S ratio.

Compared with atmosphere pressure leaching process,^[15] pressure leaching process decreased the maximum fraction of TiO_2 dissolved in solution from 18 pct to 15 pct during leaching, and also decreased the minimum fraction of TiO_2 lost in solution from 5 pct to 3 pct after the end of leaching (Figure 5). However, the L/S mass ratio still as high as 8:1 when utilizing one step leaching process.

High L/S mass ratio and acid concentration were necessary to enhance the dissolution of impurities and improve the leaching efficiency, while generated more waste acid which comprising mainly water, iron chlorides and some free hydrochloric acid. Recovery of hydrochloric acid from waste leach liquor is known as “spray-roasted” process, in which hydrochloride gas generated as the decomposition of iron chlorides and the volatilization of free hydrochloric acid then is absorbed in water to form hydrochloric acid solution with 17 to 20 pct HCl. The regeneration reaction of the hydrochloric acid can be written as:^[5]



Too much water and low concentration of iron chlorides will consume more fuel during roasting, and the concentration of hydrochloric acid will be reduced by the vapor. The leach liquor is not directly used commercially for spray roasting, such as Benilite process and “Enhanced Acid Regeneration” (EARS) process. It is usually concentrated through evaporating a large portion of water before spray roasting process. In this way, the two steps leaching process in this study has a great significance for spray roasting process as the increase of total iron concentration. In addition, the concentration of the dissolved titanium dioxide in the leach liquor decreased slightly as the polymerization (as shown in Table III). Therefore, it makes sense to use a multistep leaching process to enhance the leaching efficiency as well as make the most use of the free acid.

Since the high content of acid insoluble of silicon dioxide within the raw ilmenite concentrate, it results a

content of SiO₂ as high as 5.5 pct by weight in the synthetic rutile product (Table III). This also hinders the further upgrading of synthetic rutile only through acid leaching process. The silicon can be effectively separated from the leaching product to enter into the solution by pressure leaching with alkali, after which the content of titanium can be upgraded to about 95 pct TiO₂ by weight. Maybe there is no need to remove the silicon dioxide as it will not affect the fluidizing chlorination process. Furthermore, adding an alkali leaching process will increase the consumption, and brings the problem of alkali treating wastewater.

V. CONCLUSIONS

Hydrochloric acid pressure leaching process was used to deal with Yunnan ilmenite concentrate in the present investigation and the following conclusions can be drawn:

- (1) The most suitable leaching conditions for one step leaching process are found to be: a hydrochloric acid of 20 pct, a L/S mass ratio of 8:1, a leaching temperature of 413 K (140°C), a leaching time of 4 hours.
- (2) The leaching liquor was reutilized in a two steps leaching process, after which, the content of hydrochloric acid was decreased from 135 g/L to about 75 g/L HCl in the first step leaching, the content of total iron enriched to about 80 g/L. The two step leaching process significantly low down the L/S mass ratio and the leaching liquor is more suitable for spray roasting process.
- (3) The synthetic rutile produced through a two steps leaching process shows a pure golden red with a high content of titanium (92.65 pct TiO₂), a relatively low content calcium (0.10 pct CaO) and magnesium (0.12 pct MgO), and a high content of silicon (5.72 pct SiO₂). This product can be improved by purification to minimize the silicon content. This product could be a good raw material for the production of TiO₂ pigment by fluidizing chlorination process.

ACKNOWLEDGMENTS

The authors would like to thank the Natural Science Foundation of China (Grant No. 51404047) and Basic and Frontier Research Program of Chongqing (Grant No. cstc2014jcyjA50011) for funding this work.

REFERENCES

1. J.H. Braun, A. Baidins, and R.E. Marganski: *Prog. Org. Coat.*, 1992, vol. 20, pp. 105–38.
2. K.K. Sahu, T.C. Alex, D. Mishra, and A. Agrawal: *Waste Manage. Res.*, 2006, vol. 24, pp. 74–79.
3. T.S. Mackey: *Ind. Eng. Chem. Prod. Res. Dev.*, 1974, vol. 13, pp. 9–18.
4. W.S. Zhang, Z.W. Zhu, and C.Y. Cheng: *Hydrometallurgy*, 2011, vol. 108, pp. 177–88.
5. J. Chen: (Google Patents: 1974).
6. E.A. Walpole and J.D. Winter: in *Chloride Metallurgy 2002-International Conference on the Practice and Theory of Chloride/Metal Interaction* (Citeseer: 2002).
7. H.N. Sinha: *TMS PAPER NO A 72-32, 1972*, AIME, New York, 1972. 14 pp.
8. J.B. Farrow, I.M. Ritchie, and P. Mangano: *Hydrometallurgy*, 1987, vol. 18, pp. 21–38.
9. E. Olanipekun: *Hydrometallurgy*, 1999, vol. 53, pp. 1–10.
10. J.H. Chen and L.W. Huntoon: (Google Patents: 1977).
11. M.H.H. Mahmoud, A.A.I. Afifi, and I.A. Ibrahim: *Hydrometallurgy*, 2004, vol. 73, pp. 99–109.
12. M.K. Sarker, A.K.M.B. Rashid, and A.S.W. Kurny: *Int. J. Miner. Process.*, 2006, vol. 80, pp. 223–28.
13. A. Janssen and A. Putnis: *Hydrometallurgy*, 2011, vol. 109, pp. 194–201.
14. C. Li, B. Liang, and Hai.Yu. Wang: *Hydrometallurgy*, 2008, vol. 91, pp. 121–29.
15. S.L. Liu and J.Y. Xiang: *Metall. Mater. Trans. B-Proc. Metall. Mater. Proc. Sci.*, 2016, vol. 47, pp. 1334–39.
16. J. Barksdale: *Soil Sci.* 1950, vol. 70.
17. H. Tsuchida, E. Narita, H. Takeuchi, M. Adachi, and T. Okabe: *Bull. Chem. Soc. Jpn.*, 1982, vol. 55, pp. 1934–1938.
18. A.A. Baba, F.A. Adekola, E.E. Toye, and R.B. Bale: *J. Miner. Mater. Charact. Eng.* 2009, vol. 8, p. 787.
19. M. Imahashi and N. Takamatsu: *Bull. Chem. Soc. Jpn.*, 1976, vol. 49, pp. 1549–53.
20. B. Nabivanets and L.N. Kudritskaya: *Russian J. Inorg. Chem.* 1967, vol. 12, p. 616.
21. R. Vásquez and A. Molina: *Miner. Eng.*, 2012, vol. 39, pp. 99–105.
22. C. Sasikumar, D.S. Rao, S. Srikanth, N.K. Mukhopadhyay, and S.P. Mehrotra: *Hydrometallurgy*, 2007, vol. 88, pp. 154–69.