

## Upgrading ilmenite by an oxidation-magnetic separation-pressure leaching process

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An oxidation-magnetic separation-pressure leaching process has been found to be much more effective for upgrading Yunnan ilmenite ores to synthetic rutile. The effects of oxidation, magnetic separation and pressure leaching were examined to optimize the experimental conditions. The optimum conditions were found to be: oxidation: 900°C, 30 min; magnetic separation: excitation intensity 5.0 A, charging current 1.1 A, feeding speed 100 g/min; pressure leaching: 220 g/l HCl solution, 6 h at 135°C, S/L ratios of 1:4 and 0.12 MPa pressure. Under these conditions, synthetic rutile was obtained with 93.7% TiO<sub>2</sub>, 2.31% Fe. The particles are mostly sized above 105 µm and can be used as a feed for chlorination processes.

**Key words:** Oxidation, Leaching, Ilmenite, Synthetic rutile, Hydrochloric acid.

### INTRODUCTION

Nowadays, the methods for commercial production of TiO<sub>2</sub> pigment are the sulfate and chlorination processes. The sulfate process can utilise relatively low grade feedstocks but sulfuric acid consumption and production of large volumes of ferrous sulfate waste are major economic and environmental problems. The chlorination process is of short duration, large capacity, low cost, high grade of products, small environmental pollution and other significant characteristics (Lasheen, 2008; Sun, 2001; Dong, 2012). The chlorination process is superior to the sulfate process as regards economics and generation of less waste materials. However, the chlorination process needs high-grade raw materials. At present, the technology and equipment for production of high quality titania materials are relatively backward, production scale is small, which cannot satisfy the demand for raw materials for the chlorination process. Therefore, in order to develop the chlorination process, it is important to research large-scale production technology of titania materials using abundant low-grade titanium iron ores as raw material in China.

Titania-rich material generally refers to the electric furnace smelting titania slag or synthetic rutile which has not less than 85 mass percent TiO<sub>2</sub>. At present, the methods of manufacturing titania-rich materials include electric furnace smelting (Natziger and Elger, 1987), reducing

corrosion (Becher, 1963; Farrow and Ritchie, 1987), acid leaching (Walpole, 1997) and so on. Because of the simple production process, easy large-scaling of equipment, less "three wastes" and easy recycling, the electric furnace smelting becomes a dominant method, but has a low ability to remove calcium and magnesium. Reducing corrosion method is suitable for high grade titanium iron ore of weathering, which requires high temperature reduction related to technical difficulties. Due to the large amount of "three wastes" and process complexity, the use of the sulphuric acid leaching method has been limited. Owing to the economic and environmental aspects of the hydrochloric acid leaching method meeting the requirements of industrial production, it has been widely used.

Titanium mineral resources of Yunnan province in China are relatively abundant, there are mainly primary titanium magnetite, titanium iron ores and vanadium titanium magnetite. The TiO<sub>2</sub> grade of primary titanium magnetite is low, it is of no development and utilization value; the reserves of vanadium titanium magnetite are small, dominant development in Yunnan is inferior to Panzhihua of China; titanium iron ores with higher grade TiO<sub>2</sub>, easy to exploit and utilize, lower impurity content of CaO and MgO have been proven to be ideal raw materials for smelting high grade titania slag and preparation of synthetic rutile.

Investigations (Mahmoud et al., 2004; Mackey et al., 1974; Lasheen, 2005) have indicated that ilmenite can be upgraded by a combined

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pyrometallurgical – hydrometallurgical process to a product with 90-95 mass percent TiO<sub>2</sub>. Other investigations (Gireesh, 2013; Olanipekun, 1999; Vásquez, 2012) have studied in details the kinetics mechanism of ilmenite by hydrochloric acid leaching.

In this work, a oxidation-magnetic separation-pressure leaching process was investigated to produce synthetic rutile from Yunnan ilmenite with high Mg content. The experimental parameters affecting the grade or size of titanium dioxide and the oxidation process were investigated and optimized.

## EXPERIMENTAL

### Materials

Ilmenite ore utilized in this investigation was acquired from Yunnan province in China. Phase identification of ilmenite ore, oxidized ore and beneficiated ore were carried out using X-ray diffraction (XRD). The main phase in ilmenite ore is ilmenite (FeTiO<sub>3</sub>) and hematite (Fe<sub>2</sub>O<sub>3</sub>). The chemical analyses of the sample and the dominant impurity phases are given in table 1. The particle size distribution of the samples is measured with sieve analyses. All particles passed 630 μm of a Retsch sieve shaker.

**Table 1.** Chemical composition of ilmenite ore.

Constituent	TiO <sub>2</sub>	FeO	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SiO <sub>2</sub>
Content (wt.%)	46.10	31.18	15.38	0.58	2.64	3.90

### Oxidation procedures

The oxidation tests were performed in a laboratory muffle furnace. The furnace was heated to a predetermined temperature before the samples were introduced. An alumina crucible was used in the experiment. The oxidation roasting was conducted in the crucible open to air. The oxidation temperature was varied from 650°C to 950°C. The oxidation time was 10-50 min. Titrimetric analysis was used to determined the percentage of ferric dioxide, ferrous dioxide and titanium dioxide.

### Magnetic separation procedures

The oxidized ores were magnetically separated by a laboratory magnetic separator. Excitation intensity, charging current and feeding speed were controlled to meet 2 mass percent tailings, 1.5 mass percent SiO<sub>2</sub> of the magnetic concentrate.

### Pressure-leaching and calcining procedures

The leaching process was performed in a 2L zirconium high-pressure reaction kettle. A mechanical stirrer with teflon coating was used to

mix the acid and ilmenite ore. A water condenser was used to reduce the losses of water and hydrochloric acid vapour. The reaction kettle was heated by an electrothermal furnace. In all cases, 150 g of ilmenite ore was introduced into the reaction kettle, and mixed with 10-30 wt% hydrochloric acid solution. Then the solution was heated from room temperature to the boiling temperature (about 100-145°C) in 20-50 minutes. The leaching process was carried out at 0.05-0.3MPa pressure, 100-500 rpm rotating speed and 4-9 h leaching time. When leaching was finished, the mother liquor and solid materials were discharged, the residues through settling separation filter were washed until no iron ions and hydrochloric acid were detected. The synthetic rutile is obtained by calcining of the separated material. The contents of titanium dioxide, ferric dioxide and ferrous dioxide were analyzed by titrimetric analysis. The particle size distribution of the samples was measured with sieve analyses. The synthetic rutile products are divided into rude rutile (> 0.074 mm) and fine rutile (< 0.074 mm), finesse rate was calculated by Eq.(1).

$$\text{Finesse rate(\%)} = \frac{\text{Weight of fine rutile}}{\text{Weight of total rutile}} \times 100\% , \quad (1)$$

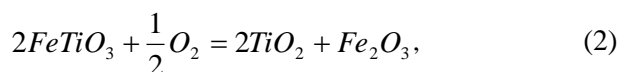
## RESULTS AND DISCUSSION

### Effect of oxidation

The effects of oxidation temperature, oxidation time on the TiO<sub>2</sub> grade and recovery of titania-rich material were studied. When the ilmenite ore was oxidized for 30 min at 900°C, Fe<sub>2</sub>TiO<sub>5</sub> and TiO<sub>2</sub> (rutile) were formed, but a little amount of FeTiO<sub>3</sub> phase remained. The effect of FeO in the oxidized ilmenite-ore on the TiO<sub>2</sub> grade and finesse rate is shown in table 2. Under the experimental conditions, the higher FeO in the oxidation ore, the lower was Fe in the product and the higher was the TiO<sub>2</sub> grade in the product. With the increase of FeO content in the oxidized ore, the finesse rate also increased. "The leaching rate of ferric iron was obviously lower than that of ferrous iron" and "the ferric iron leaching rate is within 40% ~ 50%, and that of ferrous iron can be as high as 99%" (Wang et al., 2011). Therefore, the lower ferric iron oxide in the ore, the better is the leaching rate. But to reduce the finesse rate and to control the degree of oxidation, FeO content in the oxidized ore between 25% - 28% was more appropriate. Fig.1. shows the effect of oxidation temperature on FeO content in the oxidized ore. From the results it could be concluded that at oxidation temperature of 900°C,

and residence time of 30 min, it ensured FeO content in the oxidized ore by 25%.

The oxidation also influenced the reduction of the fine materials. The oxidation reaction of ilmenite ore is written as Eq.(2).



When leaching with hydrochloric acid, both iron and titanium in the ilmenite ore will be dissolved in both untreated and oxidized ilmenite. However, the rutile in oxidized ilmenite is less soluble in hydrochloric acid. The dissolved titanium will hydrate on the surface of the ilmenite and in the solution. Nevertheless, the formation of rutile in oxidized ilmenite can decrease the free energy of hydrate on the surface of the ilmenite. As crystal nucleus, rutile microcrystalline is better than ilmenite. That is to say, the hydrate occurs on the surface of oxidized ilmenite easier than on untreated ilmenite. Moreover, it will lower down the amount of homogeneous nucleation in the solution and the titanium dioxide hydrate finesse under 74  $\mu\text{m}$ .

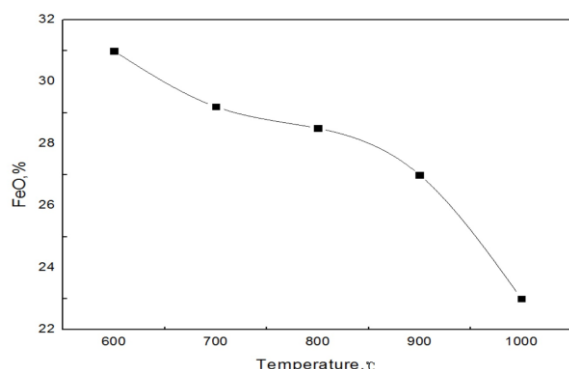


Fig. 1. The effect of oxidation temperature on FeO content in the oxidized ore.

Figs. 2 and 3 show the effect of oxidation on the finesse of rutile. Obviously, the finesse rate of oxidized products is smaller than that of un-oxidized products.

#### Effect of magnetic separation

Several magnetic separation experiments were performed with excitation intensity 3.0-9.0A, charging current 0.7-1.5A and feeding speed 50-300 g/min. From the results plotted in table 3, it is evident that the  $TiO_2$  content of the concentrate increased through magnetic separation but the  $SiO_2$  content decreased. The magnetic separation test achieved the purpose of silicon-reduction and titanium-increase. The optimum conditions of magnetic separation were excitation intensity 5.0A, charging current 1.1A and feeding speed 100g/min.

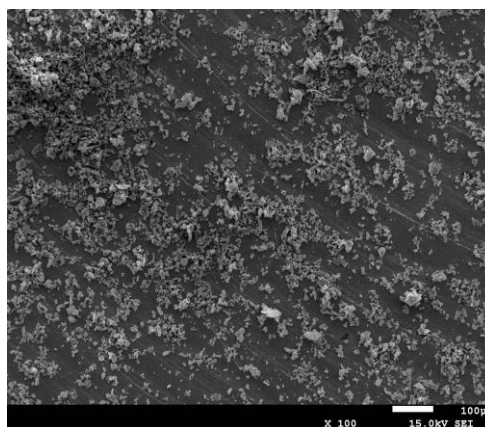


Fig. 2. SEM of rutile (unoxidized).

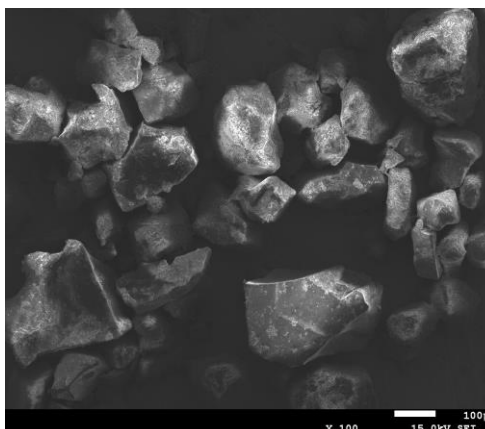


Fig. 3. SEM of rutile (oxidized).

#### Effect of hydrochloric acid concentration

The effect of hydrochloric acid concentration was studied in the range from 200 to 240 g/l at 6 h leaching time, S/L ratios of 1:4, 0.12 MPa pressure and 135°C. The results shown in Fig.4 indicate that with the increase in hydrochloric acid concentration, the grade of the products increases. For getting a grade of 92% or more of artificial rutile product, the concentration of hydrochloric acid should be 220 g/l or higher.

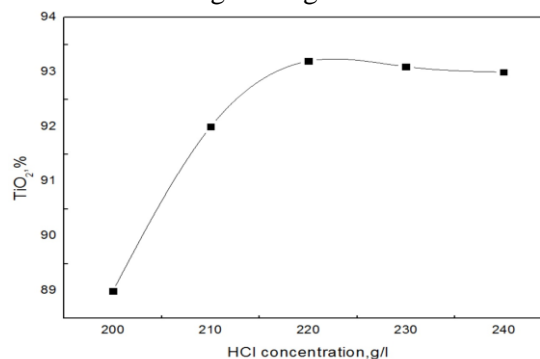


Fig. 4. The effect of HCl concentration on  $TiO_2$  content in the rutile product.

**Table 2.** The effect of FeO in oxidized ilmenite ore on leaching.

Frequence /time	FeO of oxidized ore /%	Finesse rate /%	Fe of product/%	TiO <sub>2</sub> of product /%
10	<u>23.10~23.90</u>	<u>10.06~12.87</u>	<u>3.62~3.93</u>	<u>87.52~89.13</u>
	23.30	11.90	3.81	88.58
10	<u>25.20~25.93</u>	<u>12.94~15.06</u>	<u>2.52~2.86</u>	<u>89.21~91.27</u>
	25.61	13.37	2.72	90.87
10	<u>28.01~28.95</u>	<u>16.36~19.13</u>	<u>2.25~2.77</u>	<u>90.91~92.33</u>
	28.47	17.38	2.53	91.12

Notes:  $\frac{\text{Min} \sim \text{Max}}{\text{Mean}}$

**Table 3.** Results of the magnetic separation test.

Oxidized ore		Concentrate		Tail	
TiO <sub>2</sub> /%	SiO <sub>2</sub> /%	TiO <sub>2</sub> /%	SiO <sub>2</sub> /%	TiO <sub>2</sub> /%	SiO <sub>2</sub> /%
<u>47.13~48.25</u>	<u>2.05~2.69</u>	<u>47.47~49.36</u>	<u>1.35~1.83</u>	<u>35.20~39.21</u>	<u>14.06~16.52</u>
47.92	2.17	48.71	1.46	37.56	15.65

Notes:  $\frac{\text{Min} \sim \text{Max}}{\text{Mean}}$

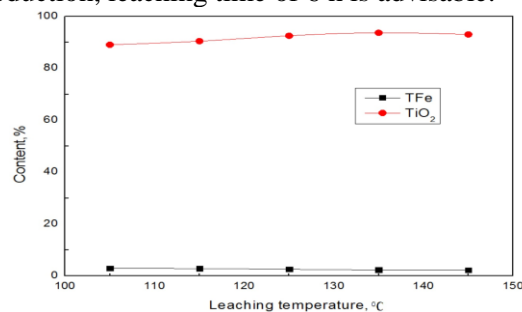
*Effect of leaching temperature and pressure*

Oxidized ore was leached at 105, 115, 125, 135 and 145 °C in a solution consisting of 220 g/l HCl, for 6 h at a S/L ratio of 1:4 and 0.12MPa pressure to determine the effect of temperature on Ti and Fe leaching. The results in Fig.5 reveal that by increasing leaching temperature, Fe and other impurities are dissolved and the TiO<sub>2</sub> content in the residue increases but the recovery decreases due to high titanium losses in the solution. Before the ferrous leaching rate of 90%, the leaching speed is controlled by the chemical reaction, at this stage the pressurized way and higher reaction temperature are favorable, which can significantly improve the response speed. When the temperature is elevated from 110°C to 140°C at 0.15 MPa pressure, the reaction rate increases 3.6 times. Therefore, the higher the temperature and pressure, the better is the leaching efficiency. But the higher temperature and the higher pressure in the ball increase the impact on the equipment. Therefore, leaching temperature and pressure were controlled at 135°C and 0.12MPa pressure in the current study.

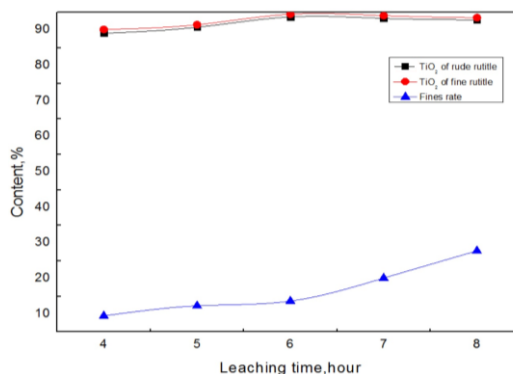
*Effect of leaching time*

The effect of leaching time on the leaching efficiency of oxidized ore was examined between 4 and 8 h using 220 g/l HCl, temperature of 135°C, S/L ratios of 1:4 and 0.12MPa pressure. The results presented in Fig.6 indicate that the residue obtained within 6 h has a maximum TiO<sub>2</sub> content (93.7%). This is due to the higher solubility of iron in hydrochloric acid. At this time about 95% of Fe<sub>2</sub>O<sub>3</sub> is brought into solution. By increasing the iron dissolution efficiency, the recovery of TiO<sub>2</sub> in the

residue as titanium dioxide concentrate decreases from 93.7% to 90.5% by increasing the leaching time from 7 to 8 h and the finesse rate increases. After leaching for more than 6 h, because the soluble impurities content in the titanium concentrate grain is already low, further extending the leaching time, reduces the degree of synthetic rutile. Therefore, considering factors such as product quality and efficiency of industrial production, leaching time of 6 h is advisable.



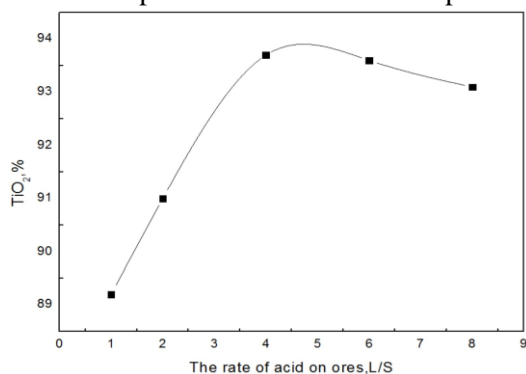
**Fig. 5.** Effect of HCl concentration on TiO<sub>2</sub> content in the rutile product.



**Fig. 6.** Effect of leaching time on TiO<sub>2</sub> content in the rutile product.

*Effect of solid/liquid (S/L) ratio*

Several leaching experiments were performed using hydrochloric acid of concentration 220 g/l HCl with S/L ratios of 1:1, 1:2, 1:4, 1:6 and 1:8. In these experiments, leaching was performed at 135°C for 6 h, with S/L ratio of 1:4 and 0.12MPa pressure. From the results plotted in Fig. 7 it is evident that with increasing S/L ratio, the total iron leaching efficiency increases, but after S/L=1:4 it decelerates. By decreasing the S/L ratio or increasing acid consumption the titanium dissolution also increases. Therefore for decreasing acid consumption and titanium dissolution S/L=1:4 is selected as optimum amount for the experiments.



**Fig. 7.** Effect of acid/ore (L/S) on TiO<sub>2</sub> content in the rutile product.

*Characterization of titanium dioxide concentrate*

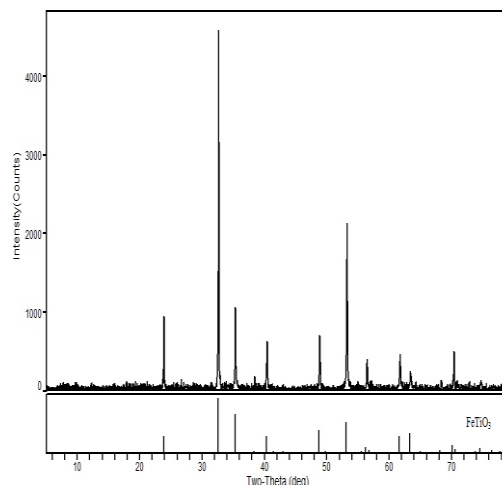
The produced titanium dioxide concentrate at the optimum conditions was washed and calcined at 900°C. Comparing with the raw materials shown in Fig. 8, rutile in this concentrate (Fig. 9) is the dominant phase but Ti<sub>2</sub>O<sub>3</sub>, anatase and iron oxide phases are also found. The chemical analysis of the calcined product obtained under optimum conditions is presented in Table 4.

**Table 4.** Chemical composition of the rutile product

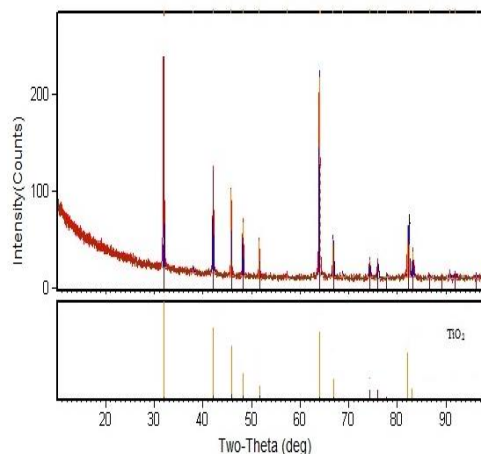
Constituent	TiO <sub>2</sub>	TFe	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	SiO <sub>2</sub>
Content (wt.%)	93.70	2.31	1.27	0.10	0.6	1.35

The product of HCl leaching contains about 93.7% TiO<sub>2</sub> and only 2.31% Fe. The SEM images of the raw materials and rutile products by hydrochloric acid leaching are compared in Figs.10 and 11. These images indicate that the texture and morphology of the product obtained by HCl leaching and raw materials are very different. The morphology of titanium dioxide produced by HCl leaching is more granular than that of the raw materials. In the product of HCl leaching, the grains are mostly circular with a clear and sharp boundary while the product of the raw materials is more

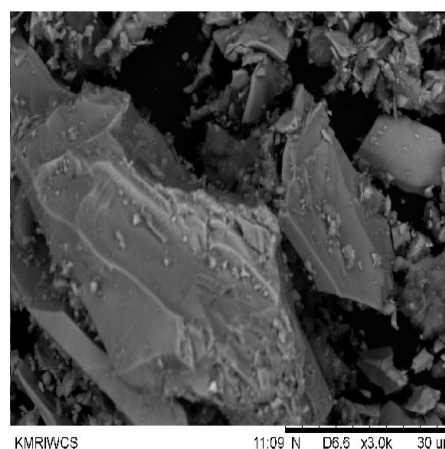
elongated. Size distribution of titanium dioxide particles produced by HCl leaching was also determined by the cumulative percentage of particles analysis method shown in Fig.12. The results indicate that the particles obtained from HCl leaching are mostly sized above 105 μm which can meet the particle size requirements of the raw materials for chlorination processes.



**Fig. 8.** XRD of the raw materials.



**Fig. 9.** XRD of the rutile product.



**Fig. 10.** SEM of the raw materials.

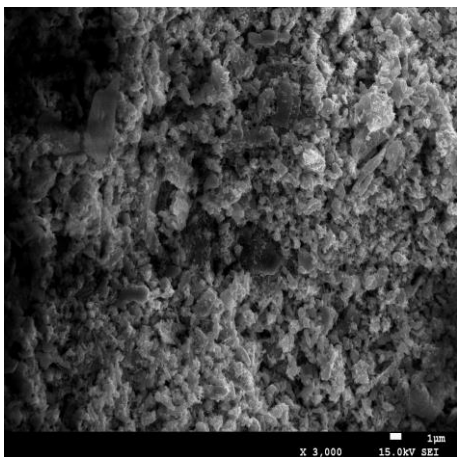


Fig. 11. SEM of the rutile product.

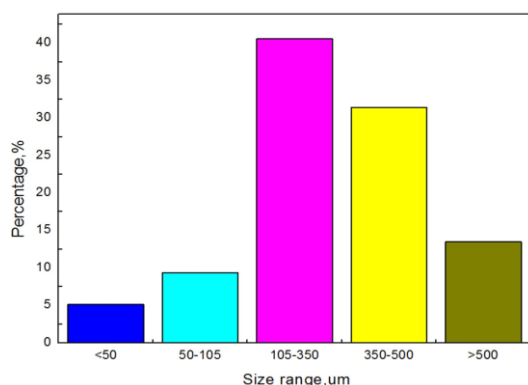


Fig. 12. Size distribution of the rutile product.

### CONCLUSIONS

The pressure leaching of Yunnan ilmenite ores with HCl was found to be much more effective in the presence of oxidation-magnetic separation. Oxidation temperature and time were 900°C, and 30 min, respectively. Magnetic separation conditions were: excitation intensity 5.0A, charging current 1.1A and feeding speed 100 g/min. The optimum leaching conditions used in this study were 220 g/l

HCl at 135°C for 6 h, at S/L ratio of 1:4 and 0.12MPa pressure. Under these conditions, the rutile products were obtained with 93.7% TiO<sub>2</sub> and 2.31% Fe and most particles were sized above 105  $\mu\text{m}$  which can meet the particle size and quality requirements for chlorination processes.

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### ОБОГАТЯВАНЕ НА ИЛМЕНИТ ЧРЕЗ ОКИСЛЯВАНЕ И МАГНИТНА СЕПАРАЦИЯ ПОД НАЛЯГАНЕ

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(Резюме)

Установено е, че процесът на излугване на илменитова руда от Юнан с помощта на окисление, съчетано с магнитна сепарация под налягане е много ефективен. Получава се синтетичен рутил. Изследвани са ефектите на тези три операции за оптимизирането на опитните условия. Оптималните условия за магнитна сепарация са следните: температура 900°C; 30 минути за окисление; интензитет на възбуждане 5.0A; токна зареждане 1.1A; скорост на подаване 100g/min. Концентрацията на солна киселина е 220 g/l при 135°C и налягане 0.12MPa в продължение на 6 часа за излугване, отношението твърда/течна фаза е 1:4. При тези условия синтетичните рутили съдържат 93.7% TiO<sub>2</sub>, 2.31% TiFe, а размерът на частиците е над 105  $\mu\text{m}$ .