**Rare Metal Materials and Engineering**
Volume 49, Issue 5, May 2020
Available online at www.rmme.ac.cn

Science Press

**Cite this article as:** Rare Metal Materials and Engineering, 2020, 49(5): 1512-1520.

ARTICLE

# Leaching Behavior and Kinetics of Ilmenite Ore with NaOH Hydrothermal Method

**Gao Minglei**[1,2], **Xue Xiangxin**[1], **Wang Shaona**[3], **Li Lanjie**[2], **Yang He**[1], **Zhao Beibei**[2], **Chang Fuzeng**[2]

*[1] Northeastern University, Shenyang 110819, China; [2] HBIS Group ChengSteel, Chengde 067102, China; [3] National Engineering Laboratory for Hydrometallurgical Cleaner Production Technology, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China*

**Abstract:** The leaching behavior and kinetics of ilmenite ore in NaOH hydrothermal system were researched, and an innovative metallurgical process of leaching titanium from ilmenite ore by NaOH hydrothermal method was proposed to overcome the severe dilute $H_2SO_4$ waste water pollution of current titanium extraction process in industry. Results that the optimal reaction conditions are as follows: the reaction temperature 240 °C, NaOH concentration 400 $g \cdot L^{-1}$, the mass ratio of alkali to ore 3.5:1, partial oxygen pressure 0.5 MPa, reaction time 2 h, agitation speed 600 r/min, and ore particle size <75μm, and the leaching degree of titanium can reach 95%. Based on XRD analyses and SEM microstructure observation, the decomposition behavior of ilmenite ore was investigated and the generating of sodium titanium particles was observed. The producing phenomenon of the product layer is not found during leaching. The leaching kinetics study shows that the leaching rate of ilmenite ore in NaOH hydrothermal system is controlled by the solid product layer diffusion with the apparent activation energy of 47.39 kJ/mol, and the empirical rate equation is "$1-2X/3-(1-X)^{2/3}=[735.09\exp(-47389.8/RT)]t$".

**Key words:** ilmenite ore; NaOH hydrothermal method; titanium leaching degree; leaching behavior; kinetics

Titanium dioxide is regarded as one of the important raw materials in chemical industry, which is widely used in coatings, plastics, papermaking, etc [1-3]. Production of extracting titanium dioxide from ilmenite ($FeTiO_3$) is predominant. However, there are many problems in the process, such as large discharge of three wastes, toxic gas release, and serious environmental pollution [4, 5]. Traditionally, the main methods for producing titanium dioxide are sulphate process and chloride process [6-9]. Sulphate process is currently the most popular titanium extraction process in China. It is a simple technology and is widely applied, accounting for over 90% of China's titanium production. In the sulphate method, ilmenite $FeTiO_3$ has to be dissolved under the condition of high-acidity (85%~90% $H_2SO_4$) and high temperature (160~200 °C). Therefore the emission of toxic steam of sulfuric acid is unavoidable during the hydrolysis process. It is impossible to recover the waste acid because of the high concentration of the dissolved acid [10-13]. In general, the dilute waste water with the concentration of 20% is treated via lime neutralization method, and as a result, a large amount of red plaster is discharged, which results in serious environmental problems. Due to its limited waste discharging method, the chloride method has great advantages[14-16]. However, in order to increase the content of $TiO_2$ by pyrometallurgical and/or hydrometallurgical processes, careful upgrading of low grade ilmenite deposits is required. The partial reduction from iron to divalent iron at elevated temperatures, which can be easily leached by acid, or the pre-oxidation process followed by high temperature reduction to metallic iron with coal is involved in

---

Received date: May 26, 2019
Foundation item: Natural Science Foundation of Hebei Province (E2017318007); Key Program of National Natural Science Foundation of China (U1502273)

Corresponding author: Xue Xiangxin, Ph. D., Professor, School of Metallurgy, Northeastern University, Shenyang 110819, P. R. China, E-mail: xuexx@mai.neu.edu.cn

these pyrometallurgical and/or hydrometallurgical processes. Alternatively, ilmenite ore can be smelted in an electric furnace in the presence of carbonaceous reducing agents, in which the iron with high quality together with titanium-rich slag can be gained, which is different from ilmenite from chemical and mineralogical sides[17,18].

Digesting ilmenite with dilute acid is beneficial for recycling waste acid as well as reducing the gas emission. In order to solve the mentioned serious environmental problems of the titanium dioxide pigment industry in China, many alternative methods have been proposed, such as the NaOH molten salt system[19], hydrochloric acid leaching process[20, 21], and high leaching speed and acid regeneration technology[22, 23]. Among them, the NaOH molten salt decomposition process is regarded as the most promising process since it takes the advantages of acid digesting. The titanium-bearing materials are decomposed by NaOH molten salt in this process, forming the intermediate product of $Na_2TiO_3$ with NaCl-type crystal structure[24, 25]. The gained intermediate product is washed with water in order to recycle the NaOH reaction medium and to obtain the layered $H_{2-x}Na_xTiO_3$ intermediate. The $H_{2-x}Na_xTiO_3$ intermediate can be easily converted into the $TiOSO_4$ solution under the condition of low-temperature and low-acidity sulphuric acid solutions[26]. The final $TiO_2$ pigment can be obtained afire hydrolysis of the titanylsulfate solution. However, the obtained 20 wt% NaOH solution is still difficult to be recycled into the NaOH molten salt in roasting process because of the high energy consumption of evaporation.

In order to realize the recycle of dilute acid and NaOH solution, and to further optimize the acid solution reaction of titanium dioxide production process, NaOH hydrothermal method was used to realize the leaching of ilmenite in this work. By studying the reaction parameters and the kinetics of ilmenite leaching with NaOH hydrothermal method systematically, the key factors and reaction control step of the process were determined. The obtained intermediate sample was then washed with water for recycling NaOH reaction medium in order to obtain the layered intermediate. Unlike the traditional sulphate process for $TiO_2$ preparation, the intermediate can be easily converted into $TiOSO_4$ solution at low-temperature (50 °C) and low-acidity (20% $H_2SO_4$) in one step, in which the recycling of diluted $H_2SO_4$ solution can be realized. The obtained NaOH solution can also be recycled for ilmenite leaching process after the removal of Al and Si. The leaching process with NaOH can be considered as a mineral activation process, which is beneficial for the suitable and pro-environmental use in the sulphate process for $TiO_2$ preparation. Consequently, the leaching behavior of the ilmenite ores with NaOH hydrothermal method was studied and different influencing factors during leaching were researched in detail. Besides, the leaching kinetics was further investigated to determine the rate controlling steps and corresponding reaction mechanism of ilmenite decomposition and leaching. Furthermore, on the basis of above systematic studies in this work, in order to overcome the severe dilute $H_2SO_4$ waste water pollution of current titanium extraction process in industry, an innovative technology for ilmenite leaching and latter $TiO_2$ preparation was proposed using NaOH hydrothermal method with the process of intermediate product transformation by low concentration acid.

## 1 Materials and Methods

### 1.1 Experimental materials

The ilmenite ore sample was obtained after crushing, grinding and dry sieving, and adopted for latter experiments. The chemical composition of the ilmenite ore is shown in Table 1, and the main phase is shown in Fig.1, from which it is found that the predominant titanium-bearing phase of the ilmenite ore is $FeTiO_3$. The sodium hydroxide and sulphuric acid used in the experiments were of analytical grade and obtained from the Xilong Chemical Group. Deionized water was produced by the water super-purification machine (Millipore-Q, Millipore) and then used throughout the experiments.

### 1.2 Experimental apparatus

The diagrammatic sketch of experimental device is shown in Fig.2. The experiments were performed in a stainless steel autoclave with an effective volume of 1.0 L. The autoclave was equipped with a temperature control unit which was composed of a thermocouple and a regulator of heating furnace, a magnetic driven agitator with the standard turbine propeller, and an internally mounted cooling

**Table 1 Chemical composition of ilmenite ore (wt%)**

| Component | $TiO_2$ | FeO | $Al_2O_3$ | $SiO_2$ | MgO |
|---|---|---|---|---|---|
| Content | 41.02 | 35.48 | 15.42 | 4.85 | 2.89 |

Note: total chemical composition is not 100% because of burning loss

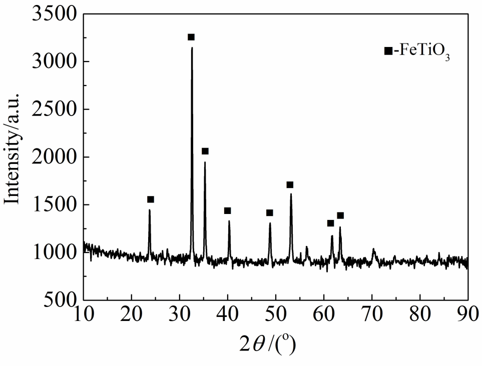
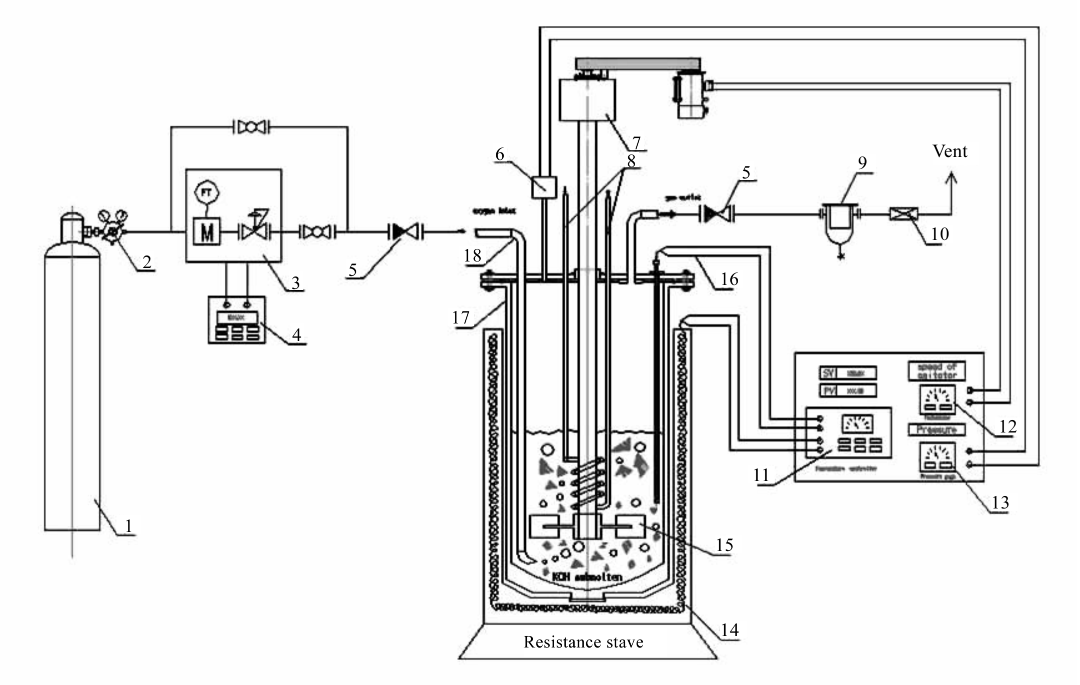


Fig.1 XRD pattern of the raw materials of ilmenite



1-oxygen cylinder; 2-pressure reducing valve; 3-flow controlling valve; 4-flowmeter; 5-check valve; 6-pressure transmitter; 7-magnetic stir; 8-cooling coil; 9-condenser; 10-distribution valve; 11-temperature control system; 12-agitator control system; 13-pressure gauge; 14-heating wire; 15-stirring blade; 16-thermocouple; 17-pressure vessel; 18-oxygen pipe

Fig.2 Diagram of experimental set-up

coil. The temperature of the reactor was controlled by a programmable temperature controller, with a precision of ±1 °C. The oxygen enters the bottom of autoclave through the gas pipe, and the oxygen flow rate was set and controlled by the flow control device in the reaction process.

### 1.3 Experimental procedure

For each experiment, 75 g ilmenite ore particles, 265 g sodium hydroxide (the mass ratio of alkali to ore was 3.5:1) and the ultra-pure water (NaOH concentration was 200~500 $g \cdot L^{-1}$) were used. The sodium hydroxide was put in and dissolved, and then ilmenite ore particles were added. When the autoclave was sealed, the magnetic stir was opened at 200 r/min to mix the slurry completely. Then the reaction was heated at a predetermined temperature and oxygen flow. Subsequently, the reaction was initiated by speeding up the agitation, and about 10 g slurry was withdrawn at each time and then separated to obtain titanium intermediate at selected time intervals. The intermediate was washed with hot ultra-water and then dissolved by acid solution reaction in order to obtain the titanium leaching materials. All experimental data was calculated as the average values collected from three parallel experiments. The titanium leaching degree ($X_{Ti}$) and ferrum leaching degree ($X_{Fe}$) were calculated using the following equations:

$$X_{Ti} = \left(1 - \frac{[Ti]_r \times M_r}{[Ti]_0 \times M_0}\right) \times 100\% \tag{1}$$

$$X_{Fe} = \left(1 - \frac{[Fe]_r \times M_r}{[Fe]_0 \times M_0}\right) \times 100\% \tag{2}$$

where $[Ti]_r$ is Ti concentration of the residues (wt%), $[Ti]_0$ is Ti concentration of the ilmenite ore (wt%); $[Fe]_r$ is Fe concentration of the residues (wt%), $[Fe]_0$ is Fe concentration of the ilmenite ore (wt%); $M_r$ is mass of residues (g), $M_0$ is mass of ilmenite ore (g).

The chemical composition of ilmenite ore and the residues was measured by ICP-OES (PE Optima 5300DV, PerkinElmer), and the mineral phases of ilmenite ore and residues were determined by X-ray diffraction (XRD, Phillips PW223/30). The microstructure and micro area composition of ilmenite ore and residues were observed and analyzed by SEM-EDS (FEI MLA 250, Australia). The water applied for the analysis above was of ultra-purified level produced by the water super-purification machine (Milli-Q, Millipore).

## 2 Results and Discussion

### 2.1 Leaching behavior

#### 2.1.1 Effect of oxygen pressure

Ilmenite ($FeTiO_3$) can be oxidized by the oxygen in NaOH hydrothermal medium based on the following chemical reactions:

$$FeTiO_3+2NaOH+1/2O_2 \rightarrow Na_2TiO_3+1/2Fe_2O_3+H_2O \quad (3)$$

$$2FeTiO_3+2NaOH+1/2O_2 \rightarrow Na_2Ti_2O_5+Fe_2O_3+H_2O \quad (4)$$

$$3FeTiO_3+2NaOH+3/4O_2 \rightarrow Na_2Ti_3O_7+3/2Fe_2O_3+H_2O \quad (5)$$

The standard Gibbs free energies of the reactions at the temperature of 350~600 K were determined based on the standard Gibbs energy data of corresponding reactive species during the oxidation process, as presented in Fig.3. It is shown that the $\triangle_r G^\theta$ values of the chemical oxidation reactions are all negative in the temperature range of 350~600 K, so it can be concluded that the above three reactions are thermodynamically feasible. Furthermore, it is obtained that the generating of $Na_2TiO_3$ is more thermodynamically favorable compared with the generating of $Na_2Ti_3O_7$ and $Na_2Ti_2O_5$.

Fig.4 summarizes the leaching degree under initial oxygen pressure from 0.3 MPa to 1.0 MPa in 400 g·L$^{-1}$ NaOH solution, with alkali-to-ore mass ratio of 3.5:1, reaction temperature of 240 °C, stirring speed of 600 r/min, reaction time of 2 h, and mineral particle size <75 μm. It can be seen from Fig.4 that the leaching degree of titanium can be increased from 0% to 60.25%, and 94.74% when the partial pressure of oxygen is set to 0, 0.3 and 0.5 MPa, respectively. It is suggested that increasing the oxygen pressure can promote the leaching process when the oxygen pressure is lower than 0.5 MPa. However, no obvious change in leaching degree is observed with further increasing the oxygen pressure to 0.5 MPa.

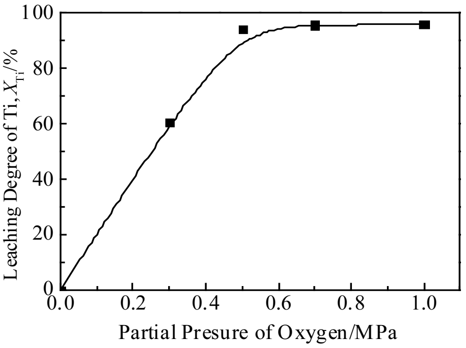


Fig.4 Effect of partial pressure of oxygen on titanium leaching

### 2.1.2 Effect of alkali concentration

In order to gain the optimal conditions of chemical oxidation reaction during leaching, the effect of the concentration of alkali (200, 300, 400, and 500 g·L$^{-1}$) was examined under standard conditions: reaction temperature 513 K, alkali to ore mass ratio 3.5:1, partial oxygen pressure 0.5 MPa, stirring speed 600 r/min, reaction time 2 h, and mineral particle size <75 μm. The results of the experiment are exhibited in Fig.5, from which it is demonstrated that the leaching degree of titanium and iron exhibits a parabolic trend with increasing the concentration of alkali. The reason for this phenomenon is derived from the increased activity of the dissolved oxygen, the decreased oxygen solubility, and the decreased mass transfer efficiency. As the medium becomes more concentrated, the activity coefficient of the component increases evidently, so it is suggested that the high NaOH concentration is more beneficial for the oxidation reactions on the consideration of its thermodynamic properties. In addition, with increasing the NaOH concentration, the viscosity of the medium increases obviously, and the salting-out effect is greatly enhanced, bringing about the vital decrease of the mass transfer efficiency and also the oxygen solubility.

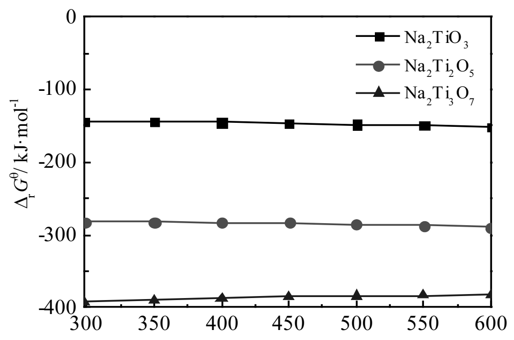


Fig.3 Relationship between $\triangle_r G^\theta$ and temperature under oxidative condition

### 2.1.3 Effect of temperature

The leaching temperature is another significant parameter that has great effects on the leaching of titanium and ferrum from both thermodynamic and kinetic aspects. Fig.6 exhibits the effect of temperature on the leaching degree of titanium and ferrum under the standard conditions: NaOH

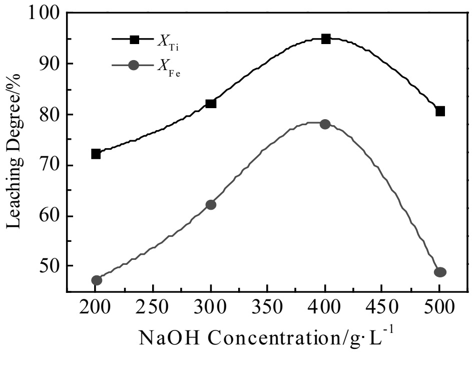


Fig.5 Effect of NaOH concentration on titanium and ferrum leaching

concentration 400 g·L$^{-1}$, alkali to ore mass ratio 3.5:1, partial oxygen pressure 0.5 MPa, stirring speed 600 r/min, reaction time 2 h, and mineral particle size <75 μm. Similar to the effect of the concentration of alkali, the influence of the reaction temperature on the leaching of titanium and ferrum presents a parabolic characteristic, and this is due to the fact that the oxygen dissolution is restricted whereas the mass transfer is beneficial because of the reduction of medium viscosity at high temperature. And the solubility and mass transfer efficiency of oxygen are more significant for controlling the leaching kinetics of titanium and ferrum. The reaction temperature of 240 °C was chosen as the optimal temperature for leaching and thus adopted for the following experiments.

### 2.1.4 Effect of reaction time

The effect of reaction time on leaching of titanium and ferrum from the ilmenite was investigated under the following conceived conditions: reaction temperature 240 °C, NaOH concentration 400 g·L$^{-1}$, alkali to ore mass ratio 3.5:1, partial oxygen pressure 0.5 MPa, stirring speed 600 r/min, reaction time 2 h, and ore particle size <75 μm. The leaching degree of titanium and ferrum at different reaction time is presented in Fig.7, and it is shown that the leaching degree of titanium and ferrum increases with increasing the reaction time, and the leaching degree reaches the maximum and then remains at the reaction time of 2 h.

### 2.1.5 Effect of agitation speed

The effect of the agitation intensity was researched under the following conditions: reaction temperature 240 °C, NaOH concentration 400 g·L$^{-1}$, alkali to ore mass ratio 3.5:1, partial oxygen pressure 0.5 MPa, reaction time 2 h, and ore particle size <75 μm. The stirring speed in the range of 200~1000 r/min was studied, and results are shown in Fig.8. The leaching of ilmenite ore is independent of the agitation when the stirring speed is higher than 600 r/min, from which it is suggested that the distribution of oxygen and particle suspension are appropriate. Consequently, the agitation speed was kept at 600 r/min in the subsequent experiments in order to exclude agitation intensity as a variable in the kinetics study.

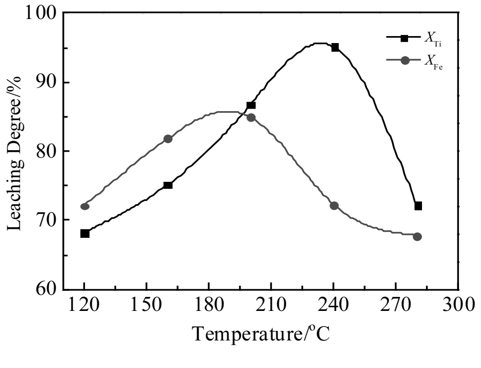


Fig.6 Effect of temperature on titanium and ferrum leaching

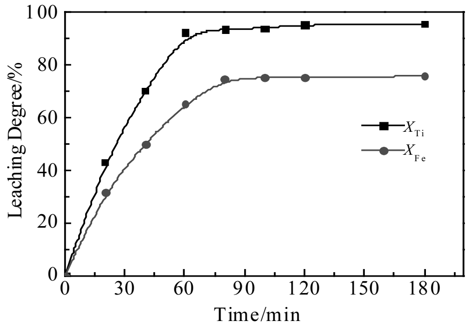


Fig.7 Effect of reaction time on titanium and ferrum leaching

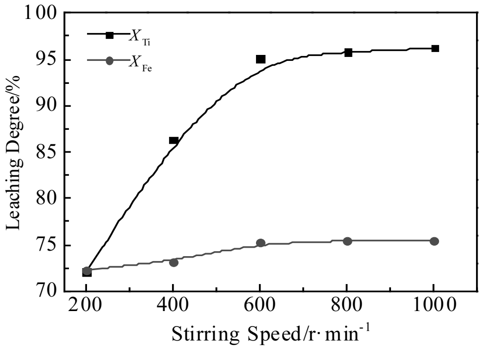


Fig.8 Effect of stirring speed on titanium and ferrum leaching

## 2.2 Leaching kinetics

To investigate the mechanism of the leaching process of ilmenite ore, the mineral phase analysis and microstructure characterization of the ilmenite ore and tailing particles were performed by XRD and SEM, respectively, and corresponding patterns and images are shown in Fig.9 and Fig.10, respectively. The results show that the unreacted ilmenite particles have smooth compact surfaces, and with the proceeding of the reactions, the surfaces gradually become loose and porous because of the decomposition of ilmenite. The diffraction peaks of the ilmenite ore almost disappear after 2 h reactions, so it is suggested that $FeTiO_3$ in the ilmenite ore is completely decomposed, and the diffraction peaks of $Fe_2O_3$ and sodium titanate appear and the corresponding peak intensity is strengthened as the reaction proceeds.

According to Ref.[27, 28], it is suggested that the reaction rate can be generally controlled by one of the following steps: the diffusion of reactants through the liquid boundary layer, the solid product layer, or the chemical reaction at the surface of the unreacted core from the shrinking core model. Accordingly, there are three possible rate-controlling steps: liquid boundary layer diffusion, solid product layer diffusion

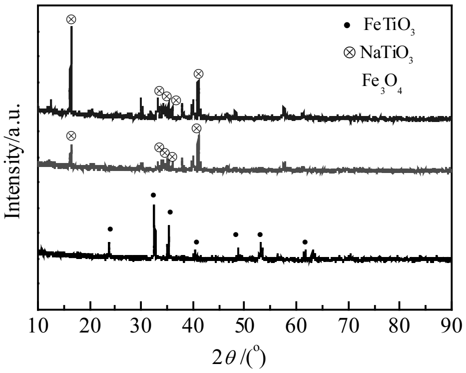


Fig.9 XRD patterns of reaction products

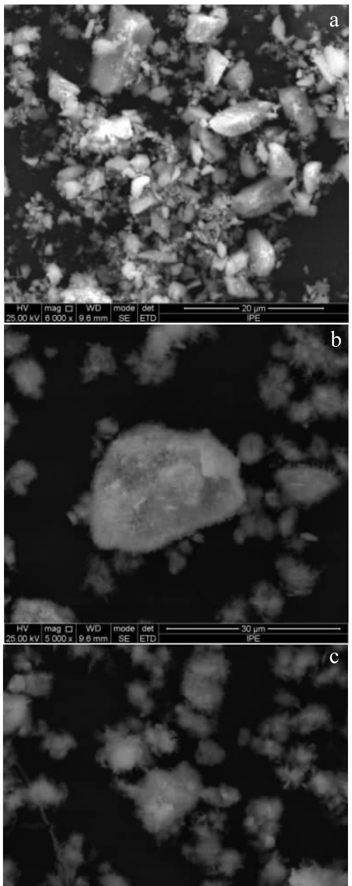


Fig.10 SEM images of reaction products: (a) 0 min, (b) 60 min, and (c) 120 min

and surface chemical reaction. If the leaching process of ilmenite ore is controlled by liquid boundary layer diffusion, Eq.(6) can be adopted for small particles:

$$X = \frac{3k_{\mathrm{M}}MC_0}{\sigma\rho_{\mathrm{S}}R_0}t \tag{6}$$

Similarly, if the process is controlled by the surface chemical reaction, the integral rate Eq.(7) is used, and if the process is controlled by the step of diffusion through solid layer around the unreacted core, the integral rate Eq.(8) is used:

$$1-(1-X)^{1/3} = \frac{k_{\mathrm{rea}}MC_0}{\sigma\rho_{\mathrm{S}}R_0}t \tag{7}$$

$$1+2(1-X)-3(1-X)^{2/3} = \frac{6D_{\mathrm{e}}MC_0}{\sigma\rho_{\mathrm{S}}R_0^2}t \tag{8}$$

where $X$ is titanium leaching degree (%), $k_{\mathrm{M}}$ is mass-transfer coefficient of the medium in liquid boundary layer, $k_{\mathrm{rea}}$ is reaction rate constant, $D_{\mathrm{e}}$ is mass transfer coefficient of the cluster in the product layer, $M$ is molar weight of ilmenite ore (g), $C_0$ is initial concentration of the cluster at $t$=0 min (mol/L), $R_0$ is average radius of ilmenite particles investigated (cm), $\sigma$ is stoichiometric coefficient, $\rho_{\mathrm{s}}$ is density of ilmenite ore (g/cm$^3$), $t$ is reaction time (min). The kinetic data can be fitted by Eq.(6~8) to study the kinetics of the leaching reaction.

To understand the rate controlling steps of the titanium leaching process, the data of leaching degree of titanium at 180 °C was used to fit the kinetic Eq.(6~8) above, with the results shown in Fig.11. It can be concluded that the experimental data is perfectly fitted with Eq.(8), with Pearson $R$ correlation of 0.9954, and the kinetics of the leaching rate is controlled by the solid product layer diffusion.

The titanium leaching degree over time at different temperatures was also investigated, and the results are exhibited in Fig.12, Fig.13 and Table 2. It is found from Table 2 that the reaction rate constant $k$ presents an increased feature with the increase of temperature in range of 140~200 ºC. Furthermore, the leaching process is controlled by the solid product layer diffusion under the optimal reaction conditions. In view of above discussions, it is appropriate to conclude that the titanium leaching process can be further promoted with enhancing the mass transfer efficiency.

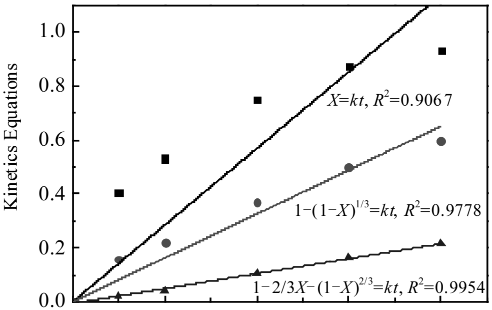


Fig.11 Titanium leaching degree versus time at 180 °C fitted by three kinds of kinetic equations

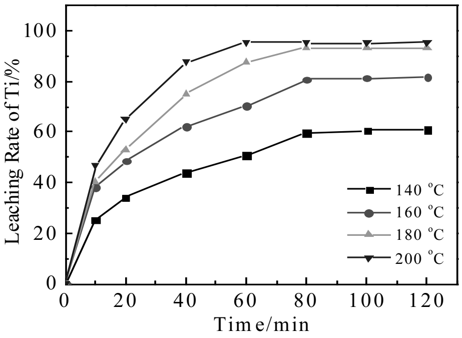


Fig.12 Effect of temperature on titanium fractional conversion

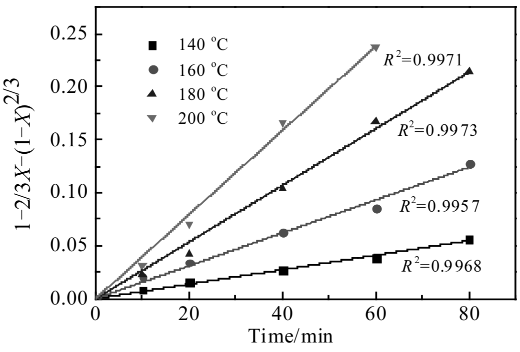


Fig.13 Plot of leaching kinetics under various reaction temperatures

**Table 2 Rate constants of the reaction at different temperatures**

| $T$/K | $k$/min$^{-1}$ | ln$k$ | $T^{-1}$/×10$^{-3}$ K$^{-1}$ |
|---|---|---|---|
| 413.15 | 0.00068 | −7.13 | 2.42 |
| 433.15 | 0.00155 | −6.49 | 2.31 |
| 453.15 | 0.00267 | −5.89 | 2.21 |
| 473.15 | 0.00397 | −5.50 | 2.11 |

According to above analyses, from the Arrhenius equation, the apparent activation energy can be calculated by Eq.(9), with the result shown in Fig.14.

$$\ln k = \ln A - E_a / RT \tag{9}$$

where $k$, $A$, $E_a$, $R$, and $T$ are kinetics constant, pre-exponential factor, apparent activation energy (J/mol), molar gas constant (J/(mol·K) ), and the Kelvin temperature (K), respectively. From the kinetic data, following kinetic Eq.(10) is gained, which can be applied to describe the present leaching process of ilmenite ore under certain partial oxygen pressure conditions in the 400 g·L$^{-1}$ solution.

$$1-2X/3-(1-X)^{2/3} = \left[735.09\exp(-47389.8/RT)\right]t \tag{10}$$

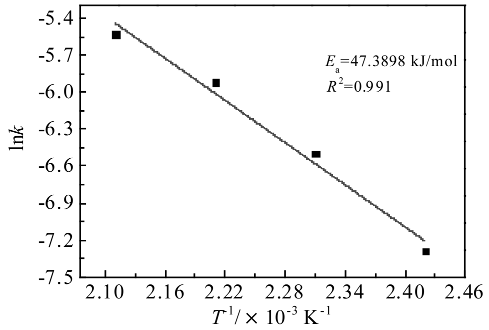


Fig.14 Relationship between ln$k$ and $T^{-1}$

## 2.3 Development of a new method for ilmenite ore treatment

On the basis of aforementioned theoretical and experimental results, an innovative process for leaching $TiO_2$ from ilmenite ore was proposed and the flow sheet of this process is shown in Fig.15. Ilmenite ore is thermally decomposed by sodium hydroxide. The liquid alkali solution can be directly recycled. After washing, the formed sodium

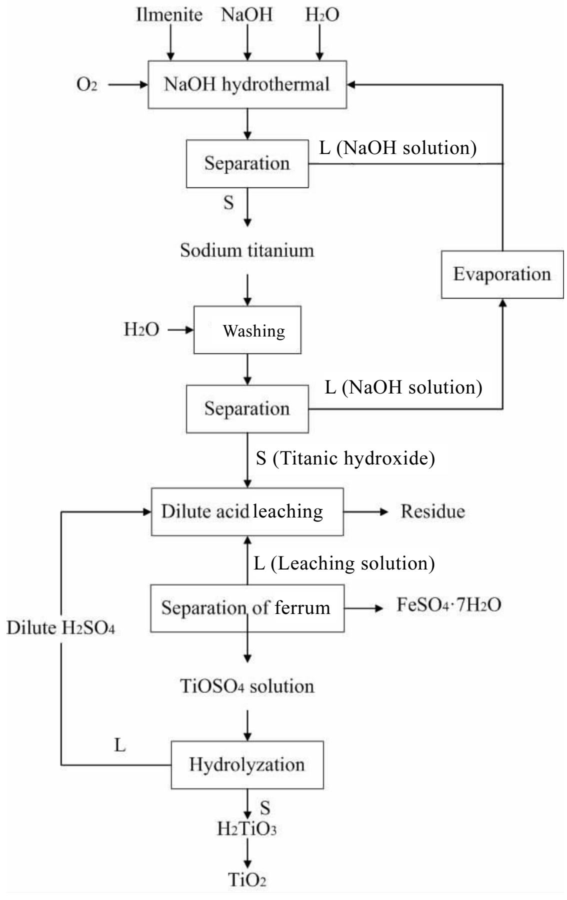


Fig.15 Principal flow chart of ilmenite ore treated by hydrothermal method

titanate can be transformed to titanate intermediately and the washing solution can be evaporated to return to the decomposition step to realize the circulation of alkali medium. Titanate intermediate is then dissolved by dilute acid to prepare $TiO_2$, and dilute acid is returned to the leaching step after treatment to realize the circulation of acid medium. The new clean production technique for titanium extraction has the advantages of high conversion degree of titanium from less than 90% by traditional sulfuric acid process to more than 95%. Moreover, the consumption of acid and alkali is greatly reduced and there is no waste water produced throughout the whole flow sheet. It is considered a green preparation process of titanium oxide.

## 3 Conclusions

1) An improved innovative metallurgical process for the leaching of ilmenite ore using NaOH hydrothermal medium is proposed, which is proven to be effective and feasible, and is greatly beneficial for overcoming the severe dilute $H_2SO_4$ waste water pollution of current titanium extraction process in industry. Under optimal reaction conditions (reaction temperature 240 °C, NaOH concentration 400 $g\cdot L^{-1}$, alkali-to-ore mass ratio 3.5:1, partial oxygen pressure 0.5 MPa, reaction time 2 h, agitation speed 600 r/min, and ore particle size <75 μm), the leaching degree of titanium can reach 95%.

2) The leaching process of ilmenite ore and the generating of sodium titanium particles are investigated, observed and confirmed through XRD and SEM analysis. It is concluded that no product layer is produced during leaching. The activation energy of the ilmenite ore leaching process is 47.39 kJ/mol, and a valid rate equation is obtained to describe the NaOH hydrothermal leaching process. It is indicated that the leaching process of ilmenite ore is controlled by the solid product layer diffusion according to the kinetics investigation.

## References

1 Zhang Wensheng, Zhu Zhaowu, Cheng Chuyong. *Hydrometallurgy*[J], 2011, 108(3-4): 177

2 Grätzel M. *Journal of Photochemistry and Photobiology C: Photochemistry Review*[J], 2003, 4(2): 145

3 Firas N, Marc A, Xuao L. *Applied Energy*[J], 2016, 163: 323

4 Taysser A, Lasheen, Ebtsam A *et al. Egyptian Journal of Pure and Applied Science*[J], 2017, 8(3): 17

5 Ramadan A M, Farghaly M, Fathy W M *et al. International Research Journal of Engineering and Technology*[J], 2016, 3(10): 46

6 Alapi T, Sipos P, Ilisz I *et al. Applied Catalysis A: General*[J], 2006, 303(1): 1

7 Anpo M, Thomas J M. *Chemical Communication*[J], 2006, 31: 3273

8 El-Hazek N, Lasheen T A, El-Sheikh R *et al. Hydrometallurgy*[J], 2007, 87: 45

9 Sasikumar C, Rao D S, Srikanth S. *Hydrometallurgy*[J], 2004, 75: 189

10 Li Chun, Liang Bin, Guo Linghong. *Hydrometallurgy*[J], 2007, 89(1-2): 1

11 Li Chun, Liang Bin, Wang Haiyu. *Hydrometallurgy*[J], 2008, 91(1-4): 121

12 Renmin L, Tao L, Yimin Z *et al. Minerals*[J], 2018, 8(1): 1

13 Victor I S, Roman A N, Vladislav V O *et al. Minerals*[J], 2018, 8(1): 15

14 Suchun Z K, Michael J N. *Hydrometallurgy*[J], 2010, 103: 196

15 Abd El-Rahman M K, Youssef M A, Abdel-Khalek N A. *The Journal of Ore Dressing*[J], 2006, 8(16): 19

16 Zhang Yongjie, Qi Tao, Zhang Yi. *Hydrometallurgy*[J], 2009, 96(1-2): 52

17 Gireesh V S, Vinod V P, Nair S K *et al. International Journal of Mineral Processing*[J], 2015, 134: 36

18 Xiong Li, Hua Yixin, Xu Cunying *et al. Journal of Alloys and Compounds*[J], 2016, 676: 383

19 Liu Yumin, Qi Tao, Chu Jinglong *et al. International Journal of Mineral Processing*[J], 2006, 2(81): 79

20 Xue Tianyan, Wang Lina, Qi Tao *et al. Hydrometallurgy*[J], 2009, 95: 22

21 Richard G H, Desiderius K, Ranjeeth R. *Hydrometallurgy*[J], 2016, 163: 198

22 Janssen A, Putnis A. *Hydrometallurgy*[J], 2011, 109 (3-4): 194

23 Mahmoud M H H, Afifi A A I, Ibrahim I. *Hydrometallurgy*[J], 2004, 73(1-2): 99

24 Samal S. *Chemical Engineering Research and Design*[J], 2011, 89(10): 2190

25 Liu Yahui, Zhao Wei, Wang Weijing *et al. Journal of Physics and Chemistry of Solids*[J], 2012, 73: 40

26 Zeng Jianmin, Li Jiahao, Zhu Hongxi. *Advanced Materials Research*[J], 2014, 88: 11 545

27 Chen Gang, Wang Xiaohui, Wang Jiajun *et al. International Journal of Mineral Processing*[J], 2014, 10(131): 58

28 Wang Zhonghang, Du Hao, Wang Shaona *et al. Minerals Engineering*[J], 2014, 57: 16

# 钛铁矿 NaOH 水热体系中浸出行为及动力学研究

高明磊 [1,2]，薛向欣 [1]，王少娜 [3]，李兰杰 [2]，杨　合 [1]，赵备备 [2]，常福增 [2]
(1. 东北大学，辽宁 沈阳 110819)
(2. 河钢集团承钢公司，河北 承德 067102)
(3. 中国科学院过程工程研究所 湿法冶金清洁生产技术国家重点实验室，北京 100190)

**摘　要**：为了解决硫酸法生产钛白存在严重的大量硫酸废水污染问题，提出了 NaOH 水热法分解钛铁矿以浸出钛的全新工艺，研究了钛铁矿在 NaOH 水热体系中的分解行为及动力学。确定最佳的反应条件为：反应温度 240 ℃，NaOH 浓度 400 $g\cdot L^{-1}$，液固比 3.5:1，氧分压 0.5 MPa，反应时间 2 h，搅拌速度 600 r/min，粒度 <75 μm，钛的浸出率可达到 95%以上。通过 XRD 和 SEM 表征，确定了钛铁矿的分解行为及钛酸钠的物相组成。宏观动力学研究表明，钛铁矿中的钛在 NaOH 水热体系中的氧化分解过程符合未反应收缩核模型，过程速度受产物层扩散控制，计算得到浸出过程的表观活化能为 47.39 kJ/mol；钛铁矿在 NaOH 水热体系中浸出动力学方程为：$1-2X/3-(1-X)^{2/3}=[735.09\exp(-47389.8/RT)]t$。

**关键词**：钛铁矿；NaOH水热法；钛浸出率；浸出行为；动力学

---

作者简介：高明磊，男，1984 年生，博士，高级工程师，东北大学冶金学院，辽宁 沈阳 110819，E-mail: gaominglei.nsd@163.com