CrossMark

Pressure leaching of converter vanadium slag with waste titanium dioxide

Guo-Quan Zhang, Ting-An Zhang*,
Ying Zhang, Guo-Zhi Lv, Yan Liu,
Zhuo-Lin Liu

Abstract The process of pressure leaching the converter vanadium slag with waste titanium dioxide without roasting was studied. Mineralogy analysis indicates that the converter vanadium slag contains mainly three mineral phases: magnetite, titanium magnetite, and silicate phase. Vanadium is in combination with iron, titanium, manganese, aluminum, and silicon. The impacts of leaching temperature, leaching time, stirring speed, liquid-to-solid ratio, and initial leaching agent concentration were investigated on the waste titanium dioxide leaching process. The results indicate that under the optimal conditions, the vanadium and the iron leaching rates are 96.85 % and 93.50 %, respectively, and the content of titanium is 12.6 % in the residue. The main mineral phases for the residues under the optimal operation conditions are quartz, ilmenite, anatase, and silicate phase, and the residues can be reused as the extraction of titanium raw materials for titanium dioxide production technology by the sulfate method.

Keywords Vanadium; Waste titanium dioxide; Pressure leaching; Resource utilization

1 Introduction

Vanadium is widely distributed in the nature, accounting for about 0.02 wt% of the crust, and there is a symbiotic

G.-Q. Zhang, T.-A. Zhang*, Y. Zhang, G.-Z. Lv, Y. Liu,
Z.-L. Liu
Key Laboratory of Ecological Utilization of Multi-Metal
Intergrown Ores of Ministry of Education, School of Materials
and Metallurgy, Northeastern University, Shenyang 110819,
China
e-mail: zta2000@163.net

relationship among vanadium, iron, titanium, and uranium in the mineral [1]. China is rich in the resources of titano-magnetite, mostly deposited around the Panzhihua, Sichuan, Chengde, and Hebei areas [2, 3]. As the titanomagnetite smelting process produces the converter slag containing about 3 %–15 % vanadium, it is usually used as the main raw material for vanadium extraction [4, 5]. The traditional technique of vanadium recovery from vanadium-containing minerals consists in chloridizing roasting, water leaching, deposition, alkali melting, and thermal decomposition. During the roasting process, the vanadium minerals were converted to a solubility phase. Then, the leaching process was conducted with the roasted materials for the vanadium separation. However, the main disadvantage of the process is the release of HCl and Cl_2, which pollute the environment severely. However, low-vanadium recovery (<60 %) and high-energy consumption make the traditional process uneconomical to be used in practice [6–8].

Titanium dioxide production technology by the sulfate method is based on ilmenite ($FeTiO_3$) decomposition by means of concentrated sulfuric acid. The decomposition product dissolves in water, and insoluble particles are removed by means of clarifying. This waste material, such as ferrous sulfate containing marked quantities of sulfuric acid, represents a specific waste, with large concentrations of heavy metals that could potentially damage health and the environment if not adequately managed. Though the TiO_2 waste is usually neutralized with calcium carbonate to produce the waste product gypsum, the red gypsum disposed of in landfills is close to the titanium dioxide plant, representing a high cost to the company for managing the same [9–11].

In recent years, researchers have been focusing on the study of transformation of the roasting process and the leaching procedure during the vanadium extraction process, for avoiding the environmental pollution and increasing the

Table 1 Chemical composition of converter vanadium slag (wt%)

Fe$_2$O$_3$	SiO$_2$	V$_2$O$_5$	MnO	TiO$_2$	Cr$_2$O$_3$	CaO	Al$_2$O$_3$	MgO	P$_2$O$_5$	SO$_3$	K$_2$O	Nb$_2$O$_5$
41.79	14.76	13.22	11.70	9.03	3.43	3.16	1.79	0.67	0.25	0.09	0.06	0.05

vanadium recoveries [12–15]. Vanadium, titanium, and iron commonly occur in the converter vanadium slag. As the E–pH diagrams of V–Ti–H$_2$O system and V–Fe–H$_2$O system as well as thermodynamic calculations show, stable regions of the soluble ions V^{3+}, VO^{2+}, and VO^{2+} are contained in the stable regions of ions Fe^{3+}, Fe^{2+}, and TiO$_2$, which reveal that vanadium and iron are dissolved in the leachate, as well as that titanium oxides are enriched in the residue by means of the pressure acid leaching of the converter slag [4, 5, 16]. The process of pressure leaching involves the chemical dissolution of minerals within a solid ore or concentrate, carried out in closed autoclaves, thus permitting higher temperatures and pressure than those in the open tanks [17]. The process of pressure leaching of the converter vanadium slag by waste titanium dioxide without roasting was investigated in this work, and the optimal leaching condition for effectively separating vanadium, iron, and titanium was obtained based on the test result. The process may practically reduce the discharge of waste titanium dioxide and avoid the emission of toxic gases from the roasting process.

2 Experimental

2.1 Materials

The raw converter vanadium slag was taken from the Panzhihua District in Sichuan Province, China. The chemical composition of converter vanadium slag is shown in Table 1. The major minerals identified by X-ray diffraction (XRD) analysis are shown in Fig. 1, and the scanning electron microscope (SEM) images of the raw converter vanadium slag are shown in Fig. 2. It can be seen
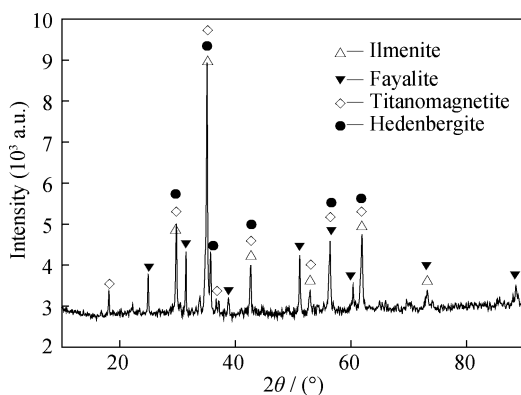
Fig. 1 XRD pattern of raw converter vanadium slag
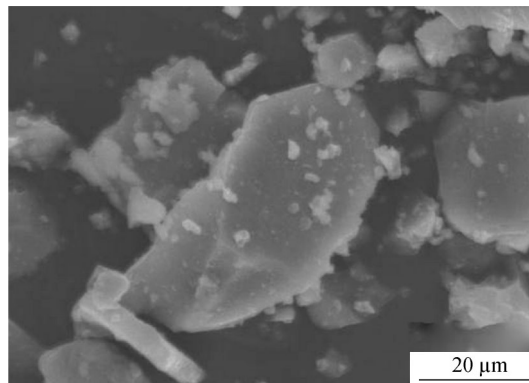
Fig. 2 SEM image of raw converter vanadium slag

Table 2 Chemical composition of waste titanium dioxide (g·L^{-1})

H$_2$SO$_4$	Fe^{2+}	Mg^{2+}	Al^{3+}	Mn^{2+}
200.00	30.50	2.50	1.57	2.70

clearly that there are three mineral phases: magnetite, titanium magnetite, and silicate phase. Vanadium is found to co-occur with iron, titanium, manganese, aluminum, and silicon. The waste titanium dioxide used in this study was synthesized according to the composition of the industrial waste TiO$_2$. The main components of the waste acid include ferrous sulfate, magnesium sulfate, manganese sulfate, and aluminum sulfate, as shown in Table 2.

2.2 Methods

The converter vanadium slag and the waste titanium dioxide solution were added to a KCFD2-10 autoclave. The effects of leaching temperature, leaching time, stirring speed, liquid-to-solid ratio, and initial leaching agent concentration were investigated. After leaching, the autoclave was rapidly water cooled, and the solution was filtered for collecting the solid residues. The solid residue and the solution were chemically analyzed, and extractions of vanadium, iron, and titanium were calculated from the solid chemical analysis.

3 Results and discussion

3.1 Effect of temperature on leaching process

The effect of temperature on the leaching process with the liquid–solid ratio of 10:1 (ml:g), the concentration of waste
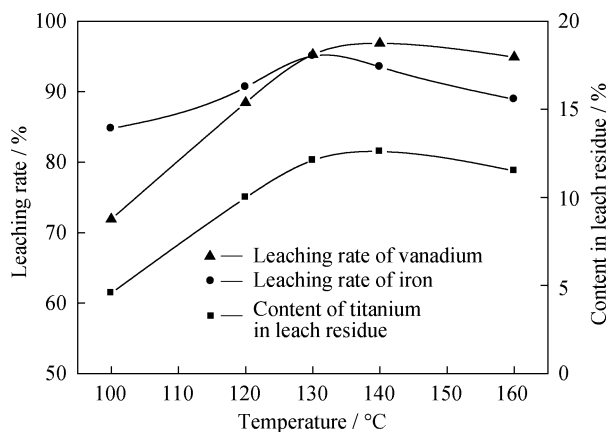
Fig. 3 Effect of reaction temperature on leaching process

Fig. 4 Effect of time on leaching process

acid at 200 g·L^{-1}, the stirring speed of 500 rpm, and a reaction time of 90 min is shown in Fig. 3.

It is obvious that the temperature has an important impact on the selected leaching process. With the temperature increasing from 100 to 160 °C, both the leaching rates of vanadium and iron and the content of titanium in the leached residue show an upward trend, but after the leaching temperature reaches 140 °C, the vanadium leaching rate tends to decrease. The result in Fig. 3 shows that the extraction of vanadium reaches peak values 96.85 % at 140 °C, and the content of titanium in the leached residue is 12.6 % at the same time. Therefore, the optimal leaching temperature of vanadium is selected to be 140 °C.

3.2 Effect of time on leaching process

The effect of time on the leaching process was investigated with the liquid–solid ratio of 10:1, the concentrations of waste acid at 200 g·L^{-1}, the stirring speed of 500 rpm at 140 °C. The results are shown in Fig. 4.

As shown in Fig. 4, the leaching rates of vanadium and iron increase with the prolonging time, but after the leaching time reaches about 90 min, the vanadium leaching rate rises slowly, and the content of titanium in the leached residue changes little. The reason might be that the relatively longer reaction time makes a unit time processing amount decrease and the production capacity decline. It is necessary to consider a higher leaching rate with the shorter reaction time in industrial production. Therefore, 90 min is selected as the optimal reaction time.

3.3 Effect of stirring speed on leaching process

Figure 5 shows the effect of stirring speed on the leaching process with the liquid–solid ratio of 10:1, the concentration of waste acid at 200 g·L^{-1}, and the reaction time of 90 min at 140 °C.
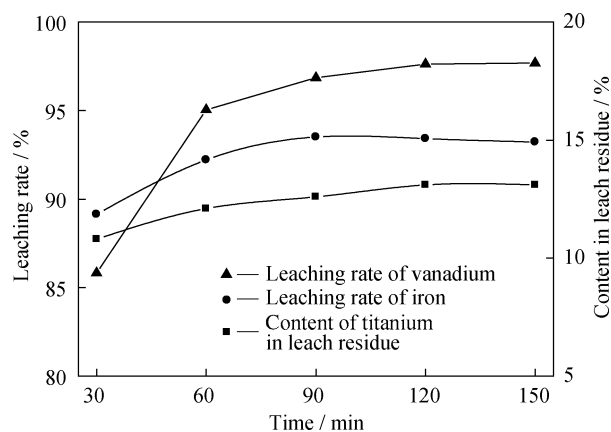
As shown in Fig. 5, a relatively higher speed increases the vanadium leaching rate. This phenomenon is attributed to the fact that the faster stir facilitates the flow of the leaching agent and promotes the reaction process. However, it is not appropriate to select a much faster stir, which results in the reduction of the mixing pulp's service life. A stirring speed of 500 rpm is considered as the best.

3.4 Effect of liquid-to-solid ratio on leaching process

The effect of liquid-to-solid ratio on the leaching process with the 500 rpm stirring speed, the concentration of waste acid at 200 g·L^{-1}, and the reaction time of 90 min at 140 °C is shown in Fig. 6.

It can be seen from Fig. 6 that the vanadium leaching rate does not increase significantly with the increasing liquid-to-solid ratio within the scope of the study. Leaching reaction is a typical solid–liquid reaction model. Both the diffusion speeds of leaching agent into the surface of the solid particles and that of the reaction product from the interior of the particle to the outside have an impact on the leaching rate. A relatively low liquid-to-solid ratio increases the slurry viscosity and affects the reaction speed. On the other hand, a high liquid-to-solid ratio decreases the vanadium concentration in the leaching liquid, which is not conducive to the subsequent extraction process. Therefore, a liquid-to-solid ratio of 10:1 is appropriate.

3.5 Effect of initial acid concentration on leaching process

Figure 7 shows the effect of initial acid concentration on the leaching process with the stirring speed of 500 rpm, the liquid–solid ratio of 10:1, and the reaction time of 90 min at 140 °C.

As shown in Fig. 7, the leaching rate increases with the initial acid concentration increasing from 100 to 250 g·L^{-1},
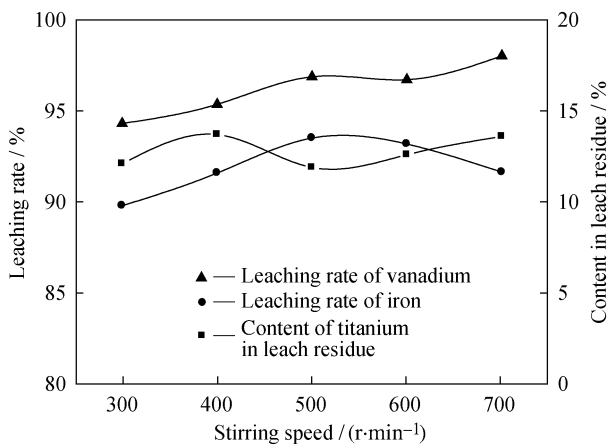
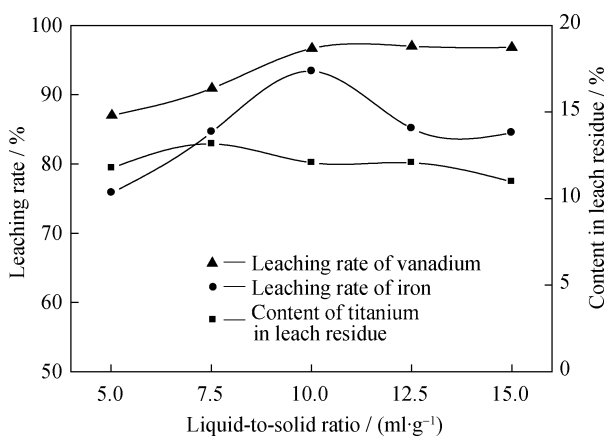Fig. 5 Effect of stirring speed on leaching process

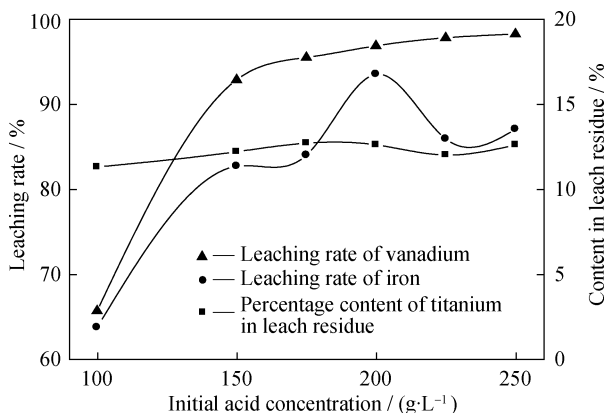Fig. 6 Effect of liquid-to-solid ratio on leaching process

Fig. 7 Effect of initial acid concentration on leaching process

and the leaching rate reaches the peak value of 98.24 % with the initial acid concentration of 250 g·L^{-1}. A larger initial acid concentration will improve the concentration of H^{+}, which plays an important role in accelerating the
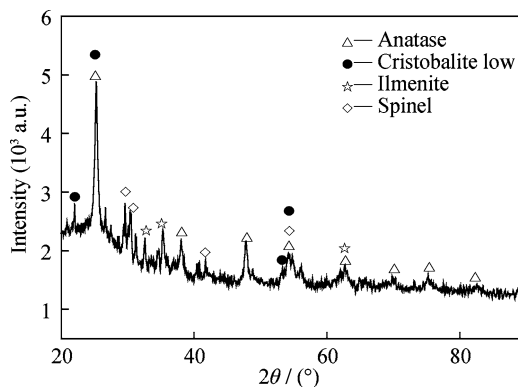

Fig. 8 XRD pattern of optimal operation conditions leaching residue

leaching process. However, the concentration of the industrial waste titanium dioxide is in the range of 200–250 g·L^{-1}. It is inevitable that a variety of losses will occur in industrial production, decreasing the acid concentration. An optimal initial acid concentration is 200 g·L^{-1} for a stable leaching process.

3.6 Characterization of leached residues

XRD was conducted to measure the chemical compositions of the residues under the optimal operation conditions. As the XRD pattern in Fig. 8 shows, constituent phases of the residue change greatly compared with the nonleached converter vanadium slag concentrate. The main composition of the residue is quartz, ilmenite, anatase, and silicate phase. In this work, vanadium exists in converter vanadium slag in the form of magnetite; as shown in Fig. 8, magnetite phase disappears, and the anatase and the ilmenite phases are enriched. The residues as the extraction source of titanium raw materials can be reused for titanium dioxide production technology by the sulfate method.

4 Conclusion

The mineralogical analysis shows magnetite, titanium magnetite, and silicate phases as the main phases existing in the converter vanadium slag. Vanadium is found to co-occur with iron, titanium, manganese, aluminum, and silicon. The results indicate that under the optimum leaching parameters with the leaching time of 90 min, stirring speed of 500 rpm, the temperature of 140 °C, the waste acid concentration of 200 g·L^{-1}, the vanadium slag particle size of less than 0.0038 mm, and the liquid-to-solid ratio of 10:1 employed, the vanadium and iron leaching rates are 96.85 % and 93.50 %, respectively, while the content of titanium is 12.6 % in the residue. The main mineral phases for the residues under the optimal operating conditions are

quartz, ilmenite, anatase, and silicate phases. The pressure leaching of the converter vanadium slag using waste titanium dioxide is an environmental-friendly process for extracting vanadium, treating, and comprehensively making use of the waste titanium dioxide.

References

[1] Huang DX. Vanadium Steel. Beijing: Metallurgical Industry Press; 2000. 1.

[2] Du XH, Xie B, Lou TP. Research on solid reduction of vanadium-titanium magnetite. J Northeastern Univ Natural Science. 2012;5(33):685.

[3] Yao PH. Records of China's Iron Ore Deposits. Beijing: Metallurgical Industry Press; 1993. 12.

[4] Zhang TA, Mu WZ, Dou ZH, Lv GZ, Liu Y. Potential—pH diagrams for V–Fe–H_2O system during oxygen pressure acid leaching of vanadium-bearing converter slags. Chin J Nonferr Met. 2011;11(21):2936.

[5] Mu WZ, Zhang TA, Dou ZH, Lv GZ, Liu Y. φ-pH diagram of V–Ti–H_2O system during pressure acid leaching of converter slag containing vanadium and titanium. Trans Nonferr Met Soc China. 2011;9(21):2078.

[6] Jena BC, Dresler W, Reilly IG. Extraction of titanium, vanadium and iron from titanomagnetite deposits at pipestone lake, Manitoba, Canada. Miner Eng. 1995;8(1–2):159.

[7] Zhu XB, Zhang YM, Liu T. Experiment and mechanism of vanadium extraction from stone coal by roasting with activators. Chin J Rare Met. 2013;37(2):283.

[8] Aarabi-Karasgani M, Rashchi F, Mostoufi N, Vahidi E. Leaching of vanadium from LD converter slag using sulfuric acid. Hydrometallurgy. 2010;102(1–4):14.

[9] Fauziah I, Zauyah S, Jamal T. Characterization and land application of red gypsum: a waste product from the titanium dioxide industry. Sci Total Environ. 1996;188(2–3):243.

[10] Pérez-Moreno SM, Gázquez MJ, Barneto AG, Bolívar JP. Thermal characterization of new fire-insulating materials from industrial inorganic TiO_2 wastes. Thermochim Acta. 2013;552: 114.

[11] Vondruska M, Bednarik V, Sild M. Stabilization/solidification of waste ferrous sulphate from titanium dioxide production by fluidized bed combustion product. Waste Manag. 2001;21(1):11.

[12] Zou XY, Peng QJ, Ouyang YZ, Tian RG. Research on the roasting process with calcium compounds for silica based vanadium ore. Chin J Process Eng. 2001;1(2):189.

[13] Zhou XJ, Wei C, Xia WT, Li MT, Li CX, Deng ZG, Xu HS. Dissolution kinetics and thermodynamic analysis of vanadium trioxide during pressure oxidation. Rare Met. 2012;31(3):296.

[14] He DS, Feng QM, Zhang GF, Ou LM, Lu YP. An environmentally-friendly technology of vanadium extraction from stone coal. Miner Eng. 2007;20(12):1184.

[15] Chen XY, Lan XZ, Zhang QL, Ma HZ, Zhou J. Leaching vanadium by high concentration sulfuric acid from stone coal. Trans Nonferr Met Soc China. 2012;20(S1):123.

[16] Zhang TA, Mu WZ, Dou ZH, Lv GZ, Liu Y, Zhao QY, He JC, A Hydrometallurgy method for extraction the vanadium from the converter slag containing vanadium and titanium, Chinese Patent, 10514573.8, 2010.

[17] Wang F, Zhang YM, Huang J, Liu T, Wang Y, Yang X, Zhao J. Mechanisms of aid-leaching reagent calcium fluoride in the extracting vanadium processes from stone coal. Rare Met. 2013;32(1):57.