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A novel method to extract vanadium from vanadium-bearing steel slag using sodium carbonate solution

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Abstract: A new method using sodium carbonate solution to treat a vanadium-bearing steel slag is proposed. The effects of the particle size, solid-to-liquid ratio, initial concentration of sodium carbonate solution, leaching temperature and stirring speed on the leaching rate of vanadium were investigated. The leaching kinetics of vanadium from the vanadium-bearing steel slag was studied, which indicated that the leaching rate was controlled by the step of diffusion through the solid layer around the unreacted core. The apparent activation energy for the process was 13.75 kJ/mol. By using this process, vanadium could be extracted effectively with the leaching rate of more than 80%.

Keywords: vanadium-bearing steel slag, leaching, vanadium, kinetics

1. Introduction

Vanadium, as an important nonferrous metal, is widely used in a metallurgical industry due to its ability to enhance the mechanical properties such as tensile strength, hardness, and fatigue resistance of steels (Liao et al., 1985; Zhao, 2002; Qiu et al., 2011). As a consequence, over 85% of vanadium has been applied in the iron and steel industries worldwide (Hayes, 1961; Moskalyk et al., 2003), which contributed to its versatile application on the preparation of catalysts for the sulfuric acid industry (Liang et al., 2006), aircraft engines, space cabin skeletons, hydrofoils and implants for ships, steam turbine blades and rocket launchers as well (Moskalyk et al., 2003). At present, vanadium-titanium magnetite is the main raw material for vanadium extraction, accounting for about 90% of the vanadium production (Zhao, 2002; Li et al., 2011). During the steelmaking process, the vanadium compounds are oxidized and enriched into the steel slag, constituting the so-called vanadium slag. The content of V₂O₅ in the vanadium slag is above 10%, very valuable source for direct vanadium extraction (Huang, 2000).

The vanadium-bearing steel slag is the major by-product that is generated in the steelmaking process by using vanadium titanium magnetite as the raw material. There are two ways to produce such slag (Yang et al., 2002; Preblinger, 2002): the first way is the oxidation of residual vanadium in semi-steel and enrichment into the steel slag, while the second way is the vanadium-bearing pig iron directly for steelmaking without any chemical conversion of vanadium slag. In this regard, however, it is very difficult to recover vanadium from the vanadium bearing steel slag because of its high content of calcium, iron, and relatively low concentration of vanadium. Further, the element of vanadium has been identified in a variety of mineral phases for vanadium bearing steel slag (Zhao et al., 2014), the complex description of which constitutes another obstacle for effective vanadium extraction. As a result, nearly million tons of the vanadium-bearing steel slag is generated annually in China, which not only pollutes the environment but also causes a significant loss of vanadium resources. According to the literature, there are two major ways to recover vanadium from the vanadium-bearing steel slag. The first one is to return the vanadium-bearing steel slag to the iron-making and steel-making system for producing the high-grade vanadium slag. Thereafter, the concentrated vanadium slag is used for vanadium extraction or smelting ferro vanadium. The pilot-scale and full-scale tests have been conducted in last century in

China (Shi, 1989). Although this process can synergistically recover iron, vanadium and other valuable elements, the element of phosphorus is enriched in the pig iron as well, and consequently increases the difficulty for slag dephosphorization (Gao et al., 2011). Meanwhile, steel slag impurities as well as the less reactive CaO further reduce the grade of sintered ore and increase the overall energy consumption of the iron-making process. Therefore, such method cannot be extensively applied. The other way is roast-leaching or directly leaching vanadium from the vanadium-bearing steel slag, and they include: sodium roasting-leaching, acidic leaching, alkaline leaching and etc. With respect to the method of sodium roasting-leaching, sodium salts (NaCl, Na₂CO₃) are used as an additive to convert vanadium into soluble sodium salts, followed by leaching with water or carbonation leaching (Xiao et al., 2010). However, the sodium roasting technique has some disadvantages. 1) The use of sodium salt leads to the emission of pollutant gases, such as HCl, Cl₂, SO₂, and et al.; 2) The consumption of sodium salts is relative high, because the content of vanadium in the steel slag is very low; 3) Due to the high content of CaO, the conversion rate of vanadium is low. Therefore, the process is not suitable for treating the converting steel slag with high CaO contents. Many researchers proposed the direct acid leaching method (Horlin et al., 1973; Lu et al., 1993; Smith, 1973), which can obtain high conversion rate of vanadium by leaching with either H₂SO₄ or HCl solutions. However, a large amount of acid is consumed in this process due to the high CaO contents in the vanadium-bearing steel slag. Furthermore, impurities, such as Ca, Fe, P, etc., are leached out and need to be separated effectively. Our previous work (Gao et al., 2011; Gao et al., 2013) proposed the direct alkaline leaching method using high concentration NaOH or KOH solutions as leaching agents. The leaching rate was above 80% and there was no waste water and gas produced. However, the concentration of alkali was very high, which led to the high energy consumption of evaporation. Until now, there is no an effective and clean extraction method to be widely applied in the industry.

Aimed at the high Ca-containing feature of the vanadium-bearing steel slag, the leaching of vanadium from the vanadium-bearing steel slag using Na₂CO₃ solutions was presented in this work. The effects of the particle size, solid-to-liquid ratio, the initial concentration of Na₂CO₃ solution, leaching temperature and stirring speed on the leaching behavior of vanadium were investigated. Furthermore, the leaching mechanisms and the leaching kinetics were proposed for developing a new method to extract vanadium from the vanadium-bearing steel slag.

2. Experimental

2.1 Materials

The vanadium-bearing steel slag used in the experiments was supplied by HBIS Group ChengSteel, HeBei, P.R. China. The chemical composition and the mineralogical analysis were performed by inductively coupled plasma optical emission spectrometry, as shown in Table 1, and the X-ray diffraction analysis, as shown in Fig. 1, respectively. The results show that the content of V₂O₅ in the vanadium-bearing steel slag is 2.57% which is similar to the vanadium slags used in other literatures.

2.2 Experimental procedure

Leaching experiments were carried out in a 500 cm³ SUS316 autoclave equipped with a thermometer and a mechanical stirrer. Temperature of the reactor was controlled by a programmable temperature controller, with a precision of ±2 °C, and the experimental device is shown as following. For each experiment, calculated amount of Na₂CO₃ and deionized water were mixed completely to generate the Na₂CO₃ solution. A predetermined amount of Na₂CO₃ solution and vanadium-bearing steel slag were measured and put into the autoclave. Then, the reaction was heated at predetermined temperature and time. After leaching, the slurry was filtered, washed and dried respectively to obtain residue. The contents of V, Cr, Si, Fe, Al, Mn, Ti, Na and other elements in the tailings were analyzed by ICP-OES (PE Optima 5300DV, PerkinElmer). The mineralogical phases of vanadium-bearing steel slag and tailings were determined with X-ray diffraction (XRD, Phillips PW223/30). The SEM-EDS results of vanadium-bearing steel slag and tailings were determined with FEI MLA 250 (Australia).

Because Fe in the original slag cannot be leached out with a high content, this value was calculated on the basis of Fe content. The calculation of formula is:

$$X_n = 1 - \frac{m_{Fe} \cdot m'}{m'_{Fe} \cdot m} \quad (1)$$

where: m_{Fe} is the Fe content of original slag, m' is the V content of tailings, m'_{Fe} is the Fe content of tailing, and m is V content of original slag

Table 1. Composition of HBIS Group ChengSteel's vanadium-bearing steel slag (%)

components	V ₂ O ₅	CaO	TiO ₂	MnO ₂	Cr ₂ O ₃	FeO	Al ₂ O ₃	SiO ₂	MgO	P ₂ O ₅
Wt. %	2.57	41.91	1.90	1.57	0.57	24.28	1.85	7.94	11.90	2.45

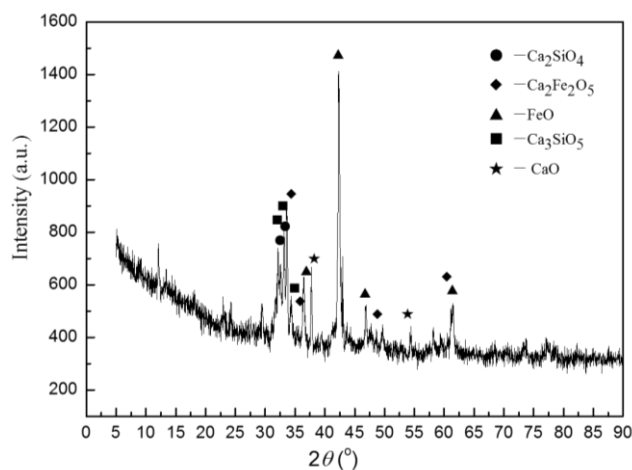


Fig. 1. XRD pattern of the vanadium-bearing steel slag

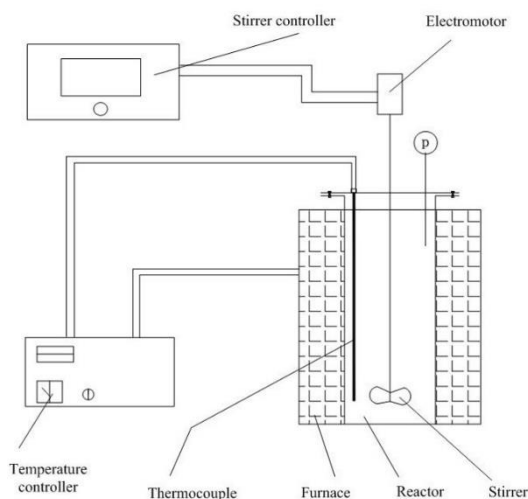


Fig. 2. The diagram of the experiment set-up

3. Results and discussion

3.1 Characteristics

Table 1 shows the chemical composition of the vanadium-bearing steel slag, indicating that calcium, iron, magnesium, silicon are the main elements. Fig. 1 shows that the main mineral composition are dicalcium silicate (C2S), tricalcium silicate (C3S), calcium ferrite, ferrous oxide and free lime. The phases of vanadium are hard to be identified because of its low grade. The backscattered electron image of the vanadium-bearing steel slag in Fig. 3 suggests three obvious phases (the points of A, B, C) within the

slag and the results are illustrated in Fig. 4. It is observed that the phase (A) mainly contains of Fe and Ca, which is mainly the calcium ferrite phase. The phase (B) mainly contains of Si and Ca, which is mainly the calcium silicate (C2S, C3S) phase. The phase (C) mainly contains of Fe and Ca, which is the solid phase of iron oxide and calcium ferrite phase. Vanadium is distributed in these three phases and combined with Ca as a solid solution.

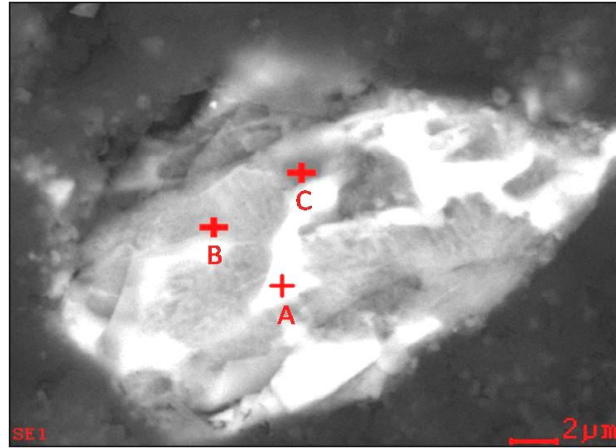


Fig. 3. SEM of vanadium-bearing steel slag

Table 2. Elemental compositions of different phases in vanadium-bearing steel slag

Wt./%	O	Al	Si	P	Ca	Ti	V	Fe
A	26.58	3.01	3.24	2.37	26.91	0.26	1.38	25.19
B	32.95	0.76	6.28	4.39	22.66	0.09	0.46	2.51
C	11.64	0.63	2.41	2.09	20.91	0.25	0.54	11.05

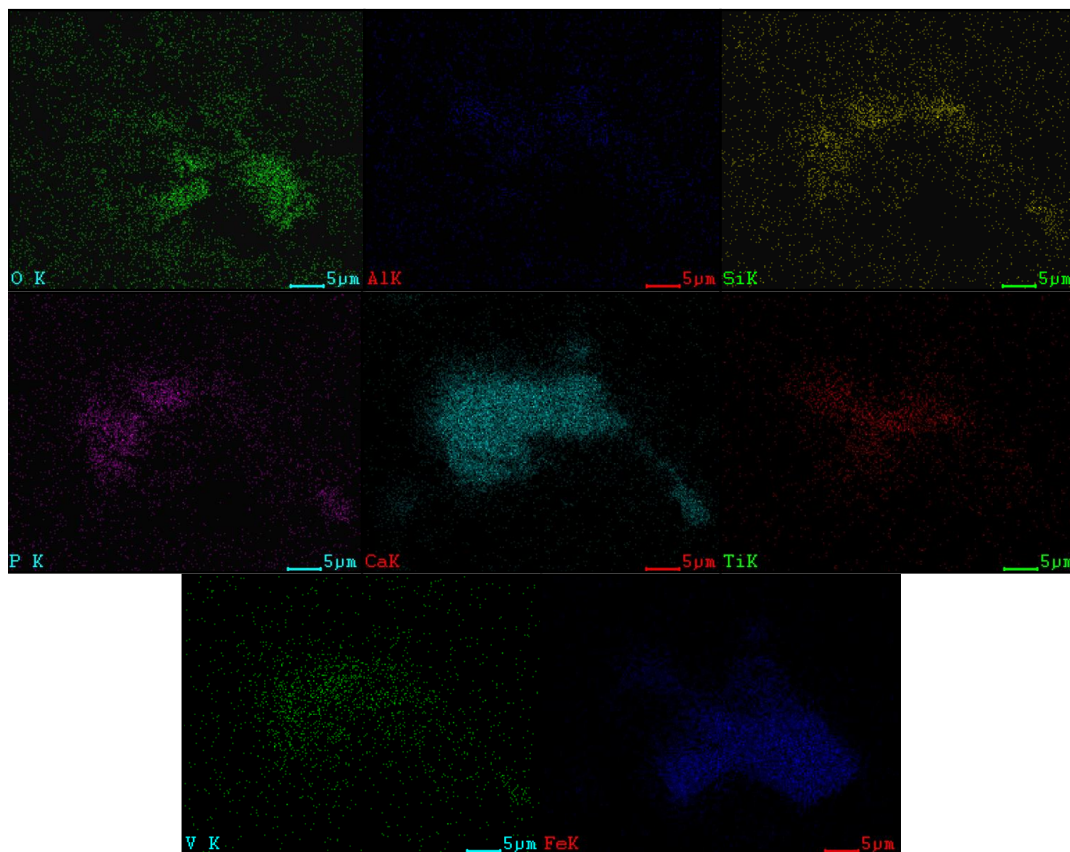


Fig. 4. The elements distribution of the vanadium-bearing steel slag

3.2 Effect of particle size

The effect of the particle size on the leaching rate was investigated under the conditions of the fixed leaching temperature of 180 °C, initial Na_2CO_3 concentration of 20 wt.%, solid-to-liquid ratio of 1:4 (by weight), and stirring speed of 600 rpm. The results are shown in Fig. 5. By increasing the particle size, the leaching rate of V_2O_5 decreased as expected. The leaching rate at the particle size smaller than 38 μm presented the optimized leaching rate while it decreased a little when the particle size increased to 74 μm . Further increasing the particle size to larger than 124 μm , the leaching rate dropped obviously. A small particle size obviously benefits the leaching process. However, milling is a high energy-consumption operation. Too small particle size will increase the milling energy consumption and decrease the filtration property. So, the narrow particle size of 38-74 μm was used in this work.

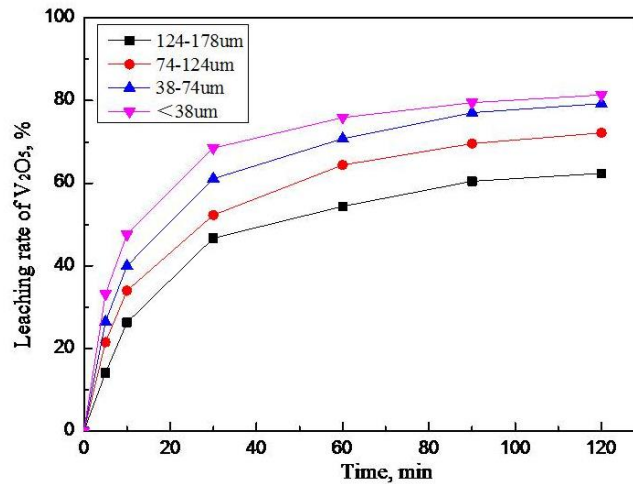


Fig. 5. Effect of the particle size on the leaching rate of vanadium

3.3 Effect of leaching temperature

The effect of the leaching temperature on the leaching rate was investigated at 130, 160, 180, 200, and 220 °C with the particle size of 38-74 μm , solid-to-liquid ratio of 1:4 (by weight), initial Na_2CO_3 concentration of 20 wt.%, and the stirring speed of 600 rpm. Typical leaching rate curves are shown in Fig. 6. It is observed that the leaching rate is highly sensitive to the leaching temperature and increasing with the leaching temperature. Leaching temperature was optimized in the range of 180–220 °C. The leaching rate of V_2O_5 at 120 min increased about 20% when the leaching temperature increased from 130 to 180 °C. However, only 1% was increased when the temperature increased from 180 to 220 °C. At 180–220 °C, the leaching rate can attain 80% at 120 min. In the consideration of the energy consumption, 180 °C was chosen as the optimal temperature for leaching.

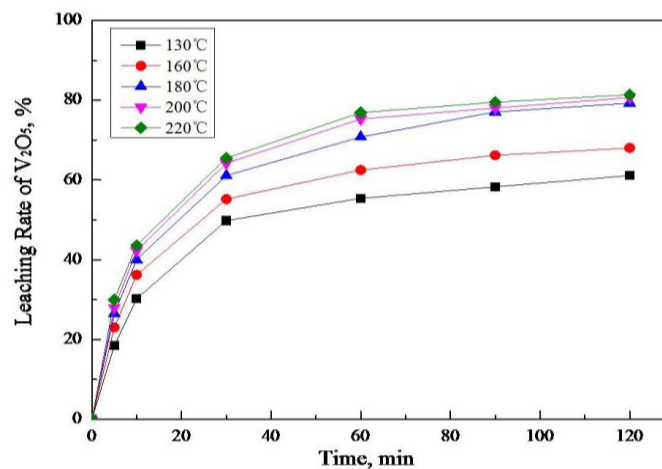


Fig. 6. Effect of the leaching temperature on the leaching rate of vanadium

3.4 Effect of the initial concentration of Na₂CO₃ solution

The effect of the initial concentration of the sodium carbonate solution (C) on the leaching rate was studied with the initial Na₂CO₃ concentrations of 15, 18, 20, 25, and 30 wt.% at the fixed leaching temperature of 180 °C. In the experiments, the particle size of 38-74 μm was used with the solid-to-liquid ratio of 1:4 and the stirring speed of 600 rpm. According to the results shown in Fig. 7, the leaching rate of vanadium increased with the increase in the initial concentration of Na₂CO₃ solutions, which can be explained by the increasing amount of Na₂CO₃. The final leaching rate was as low as about 60% with the initial Na₂CO₃ concentrations of 15%. Further, when the initial Na₂CO₃ concentrations increased to 20 wt.% the leaching rate of vanadium was about 80%. However, when Na₂CO₃ concentration increased to 30% the leaching rate only slightly increased. In the process of Na₂CO₃ leaching, the CaO and calcium vanadates in the vanadium-bearing steel slag react with Na₂CO₃ to form calcium carbonate and sodium vanadate. So, the amount of Na₂CO₃ gradually decreased when the reaction proceeded. It can provide enough amount of Na₂CO₃ when the initial concentrations increased to 20 wt.%. In consideration of the cost, the initial Na₂CO₃ concentration was optimized to be 20 wt.%.

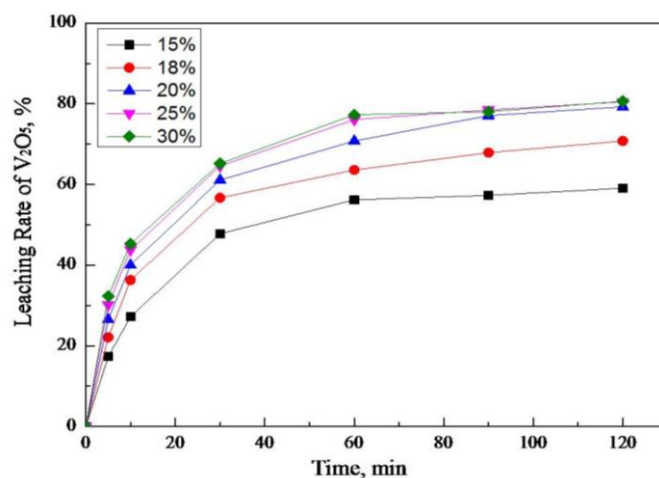


Fig. 7. Effect of the initial concentration of Na₂CO₃ on the leaching rate of vanadium

3.5 Effect of solid-to-liquid ratio

The effect of the solid-to-liquid ratio (S/L) on the dissolution rate was studied with the ratios varied from 1:3, 1:4, 1:5, to 1:6 at the fixed leaching temperature of 180 °C. In the experiments, the particle size was 38-74 μm, initial Na₂CO₃ concentration was 20% wt.%, and the stirring speed was 600 rpm. As seen in Fig. 8, decreasing the solid-to-liquid ratios facilitates the leaching rate, which can be explained by the increased amount of free Na₂CO₃ and diffusibility of reaction medium during the reaction. The leaching rate increased slightly when the solid-to-liquid ratio increased from 1:4 to 1:6 and reached the maximum at 1:6. To decrease the amount of leaching agent, the solid-to-liquid ratio of 1:4 was utilized.

3.6 Effect of stirring speed

The effect of the stirring speed on the leaching rate was studied for the stirring speeds of 200, 400, 600, and 800 rpm at the fixed leaching temperature of 180 °C. In the experiments, the particle size was 38-74 μm, and the initial Na₂CO₃ concentration was 20 wt.%, and the solid-to-liquid ratio (S/L) was 1:4 (by weight). The experimental results presented in Fig. 9 clearly show that with the increasing of stirring speed, the leaching rate of vanadium gradually increased, and increased rapidly when the stirring speed reached 600 rpm. It was due to the fact that increasing the stirring speed facilitated diffusion and the mass transfer at the leaching progress. The final leaching rate was only 50% with the stirring speed of 200 rpm, while the leaching rate of about 67 and 80% was obtained at the stirring speed of 400 and 600 rpm, respectively. When the stirring speed increased to 800 rpm, leaching rate slightly increased by only 2%. Based on this analysis, the stirring speed of 600 rpm was chosen as the optimal stirring speed.

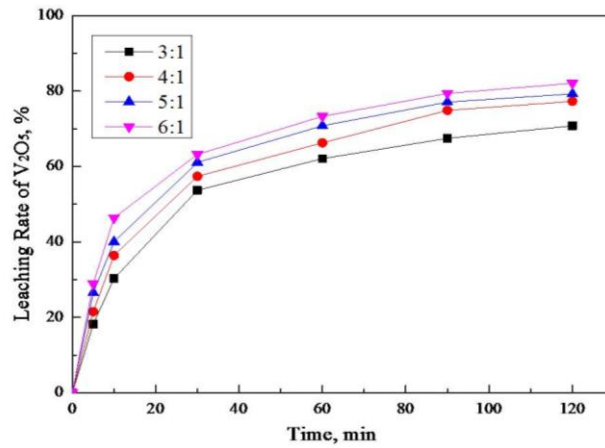


Fig. 8. Effect of the solid-to-liquid ratio on the leaching rate of vanadium

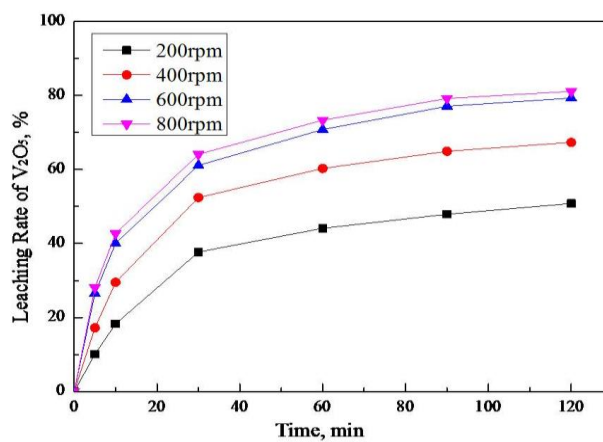


Fig. 9. Effect of the stirring speed on the leaching rate of vanadium

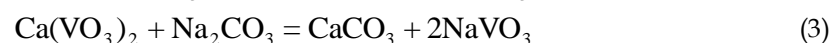
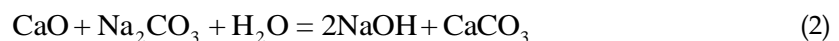
3.7 The characteristics of the leaching residue

The tailing was obtained under the optimal conditions of particle size of 38-74 μm, leaching temperature of 180 °C, initial Na₂CO₃ concentration of 20 wt.%, solid-to-liquid ratio (S/L) of 1:4, and stirring speed of 600 rpm. The typical composition of tailing is listed in Table 3. In comparison with Table 1, the content of vanadium obviously decreased to 0.51% and the leaching rate of vanadium reached up to 80%. In addition, the other element contents decreased slightly because the product of calcium carbonate had the diluted content of other elements within tailings.

Table 3. Typical composition of the leaching residue

component	TiO ₂	MnO ₂	V ₂ O ₅	Cr ₂ O ₃	FeO	Al ₂ O ₃	SiO ₂	CaO	MgO	P ₂ O ₅
Wt. %	1.54	1.26	0.51	0.47	20.21	1.68	5.58	34.44	9.69	1.54

The change of phases of vanadium-bearing steel slag is shown in Fig. 10. The diffraction patterns of dicalcium silicate (C2S), tricalcium silicate (C3S), calcium ferrite disappeared, and the diffraction patterns of calcium carbonate are found in tailings. In the process of Na₂CO₃ leaching, the CaO and all calcium vanadates in the vanadium-bearing steel slag react with Na₂CO₃ solution according to the following reactions:



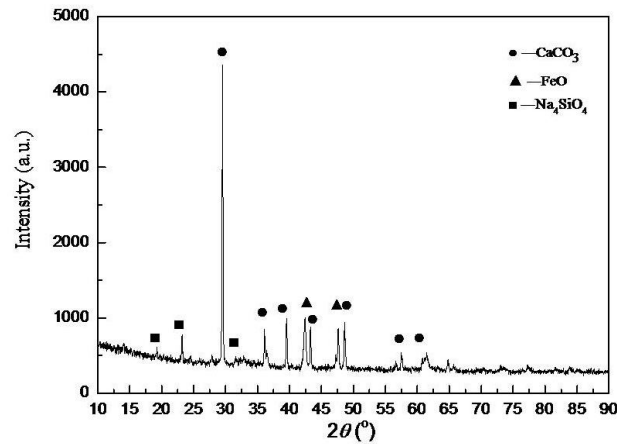
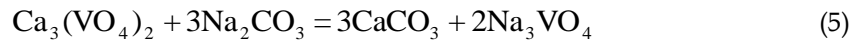
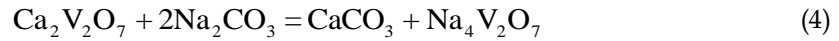


Fig. 10. XRD patterns of leaching residue

3.8 Kinetics analysis

Fluid–solid heterogeneous reaction systems have many applications in chemical and hydrometallurgical processes. In such systems, the reaction rate can be generally controlled by one of the following steps: diffusion through the fluid film, diffusion through the ash, or chemical reaction at the surface of the core of un-reacted materials. To determine the kinetic parameters and rate-controlling step in the dissolution of vanadium from vanadium-bearing steel slag in Na_2CO_3 solutions, the experimental data were used to study kinetics on the basis of the shrinking-core model. The basic equation, as shown in Eq. 6, is used to describe the extraction kinetics of vanadium (Sun et al., 2009; Zhang et al., 2010; Liu et al., 2012):

$$\frac{1}{3K_M}x + \frac{R_0}{6D_e}[1 - 3(1-x)^{\frac{2}{3}} + 2(1-x)] + \frac{1}{K_r} \times [1 - (1-x)^{\frac{1}{3}}] = \frac{MC_0}{\sigma\rho R_0} \quad (6)$$

where x is the extraction rate of vanadium, K_M is the mass-transfer coefficient of the reactant from reagents in the liquid boundary layer, R_0 is the radius of the vanadium bearing steel slag particle, D_e is the mass-transfer coefficient of the reactant in the product layer, K_r is the reaction rate constant, t is the reaction time, M is the molar weight of vanadium bearing steel slag, C_0 is the concentration of the reactant at $t=0$, ρ is the density of vanadium bearing steel slag, and σ is the coefficient of Na_2CO_3 .

Under different rate-controlling steps, the kinetics equations can be simplified as:

1) if the process is controlled by liquid boundary layer diffusion, the integral rate Eq. 7 is used

$$x = \frac{3K_M MC_0}{\sigma\rho R_0} t \quad (7)$$

2) if the process is controlled by the step of diffusion through solid layer around the unreacted core, the integral rate Eq. 8 is used

$$1 + 2(1-x) - 3(1-3x)^{\frac{2}{3}} = \frac{6D_e MC_0}{\sigma\rho R_0^2} t \quad (8)$$

3) if the process is controlled by the surface chemical reaction, the integral rate Eq. 9 is used

$$1 - (1-x)^{\frac{1}{3}} = \frac{K_r MC_0}{\sigma\rho R_0} t \quad (9)$$

Fig. 6 shows the relationship between leaching rate of vanadium from the vanadium-bearing steel slag in Na_2CO_3 solutions and time at different temperatures for the particle size of 38-74 μm , solid-to-liquid ratio of 1:4 and initial Na_2CO_3 concentration 20 wt.% with the stirring speed of 600 rpm. The

leaching kinetics equation of vanadium can be determined. It is observed that the leaching rate is highly sensitive to leaching temperature. It increased rapidly in the first 30 minutes and slowed down after 30 minutes, that is, the leaching efficiency of vanadium was high in the initial 30 minutes of the reaction. The reason was that Na₂CO₃ medium had higher concentration which was benefits diffusibility at the initial reaction. As the reaction time extended, the concentration of Na₂CO₃ gradually decreased, and the formation of calcium carbonate hindered the progress of the reaction. In order to study the kinetics of the leaching reaction, the leaching rate of vanadium in the initial 30 minutes was used to fit the kinetic equation. The trend of changes of vanadium leaching rate at different temperatures was similar, and the data collected at 180 °C were taken as the object study. The conversion data in Fig. 6 were fitted into Eqs. 3, 4, and 5, as shown in Fig. 11. It can be concluded that the equation of $1+2(1-x)-3(1-x)^{2/3}=kt$ fits the experimental data well for vanadium, and the coefficient value is 0.9957. It is indicated that the reaction is rather sensitive to both the particle size and stirring speed. As Figs. 5 and 9 suggest, the conversion rate remarkably increased with the decrease of particle size and the increase of stirring speed as it could destroy the solid product and reduce the diffusion distance in the solid product layer. To confirm the result of these statistical analyses, the leaching rates of vanadium with different temperatures are fitted as well (Fig. 12). From the result of the statistical analyses, it was determined that the integral rate expression obeyed equation:

$$1 + 2(1 - x) - 3(1 - x)^{2/3} = kt . \tag{10}$$

From the Arrhenius equation, the *k* term is:

$$k = Ae^{-\frac{E}{RT}} . \tag{11}$$

The plot of $1-2/3X-(1-X)^{2/3}$ for the reaction temperature is shown in Fig. 13. From the slopes of the straight line in Fig. 13, ln*k* versus ln(1/*T*) is plotted for each value of the temperature, and the following values were obtained: *E_a*=13.75 kJ/mol, *A*=0.074.

Consequently, Eq. 5 can be rewritten as

$$1 - \frac{2}{3}x - (1 - x)^{2/3} = 0.074e^{(-13.75/RT)} . \tag{12}$$

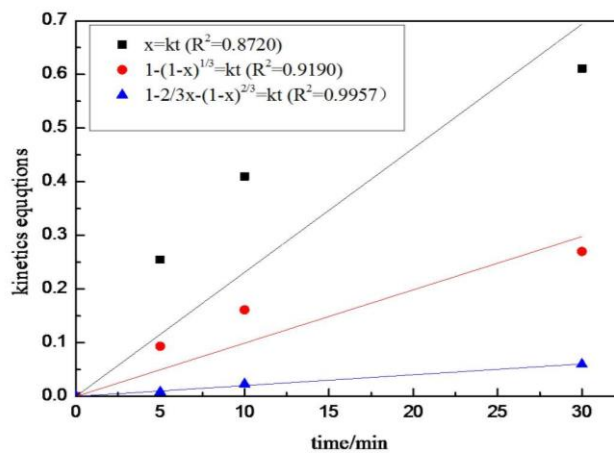


Fig. 11. Vanadium extraction rate vs. time at 180 °C fitted by three kinetics equations

4. Development of a new method of extraction of V₂O₅ from vanadium-bearing steel slag

Based on the previous theoretical and experimental results, a new process for extracting vanadium from the vanadium-bearing steel slag by Na₂CO₃ solutions has been proposed and the process flow sheet was plotted in Fig. 14. This leaching system exhibited intense decomposition effect for vanadium-bearing steel slag, and vanadium can be leached out as sodium vanadate in a short reaction time. The main content in vanadium-bearing steel slag, CaO, converted to CaCO₃ and NaOH was produced simultaneously as shown by Eq. 2. Therefore, the alkalinity increased during the leaching process. To realize the recycle of leaching medium, the leaching solutions need to be carbonated to form new

carbonate. The sodium vanadate products were obtained by crystallization when the V_2O_5 concentration of filter liquor accumulated to 20 g/dm^3 . It can be used to produce high purity vanadium pentoxide (Wang et al., 2017). After crystallization, the Na_2CO_3 solution was returned to the leaching. Therefore, this is an effective and clean extraction vanadium process and there is no waste water produced within the whole flow sheet.

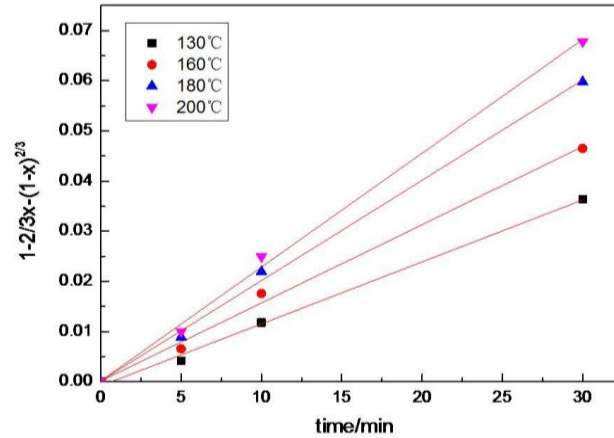


Fig. 12. Plots of extraction kinetics under various reaction temperatures

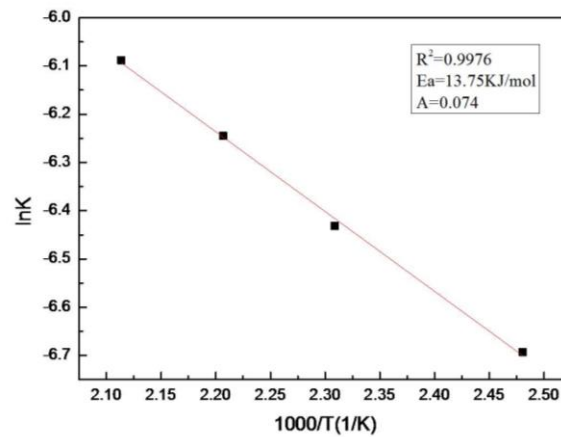


Fig. 13. Nature logarithm of reaction rate constant vs. reciprocal temperature

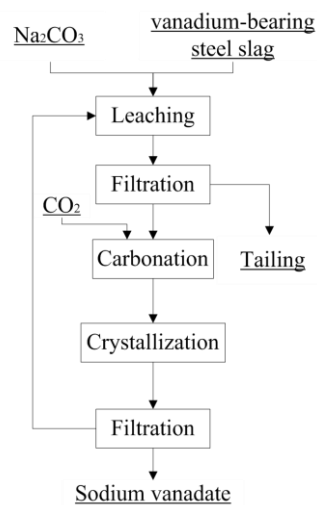


Fig. 14. Flow sheet of the leaching vanadium from vanadium-bearing steel slag

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