

Article

Kinetics of the Carbonate Leaching for Calcium Metavanadate

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Abstract: The sodium salt roasting process was widely used for extracting vanadium due to its high yield rate of vanadium. However, the serious pollution was a problem. The calcium roasting process was environmentally friendly, but the yield rate of vanadium was relatively lower. Focusing on the calcium metavanadate produced in the calcium roasting process of vanadium minerals, the mechanism of the carbonate leaching for calcium metavanadate and its leaching kinetics of calcium metavanadate were studied. With the increase of the leaching agent content, the decrease of the particle size, the increase of the temperature and the increase of the reaction time, the leaching rate of vanadium increased, and the constant of reaction rate increased. In the carbonate leaching process, the calcium carbonate was globular and attached to the surface of calcium metavanadate. In the solution containing bicarbonate radical, lots of cracks formed in the dissolution process. However, the cracks were relatively fewer in the solution containing carbonate. In the present study, the carbonate leaching for calcium metavanadate was controlled by diffusion, the activation energy reached maximum and minimum in the sodium bicarbonate and the sodium carbonate solution, respectively. The activation energy value in the ammonium bicarbonate solution was between those two solutions. The kinetic equations of the carbonate leaching for calcium metavanadate were as follows: $1 - 2/3\eta - (1 - \eta)^{2/3} = 4.39[\text{Na}_2\text{CO}_3]^{0.75}/r_0 \times \exp(-2527.06/T)t$; $1 - 2/3\eta - (1 - \eta)^{2/3} = 7.89[\text{NaHCO}_3]^{0.53}/r_0 \times \exp(-2530.67/T)t$; $1 - 2/3\eta - (1 - \eta)^{2/3} = 6.78[\text{NH}_4\text{HCO}_3]^{0.69}/r_0 \times \exp(-2459.71/T)t$.

Keywords: calcium metavanadate; carbonate leaching; kinetics; microanalysis

1. Introduction

Vanadium, as one of the important industrial raw materials, is widely used in fields such as iron and steelmaking, chemical industry, aerospace and electronics industry [1,2]. The raw materials of vanadium extraction were mainly stone coal and vanadium slag produced from the smelting of vanadium titanomagnetite. The main widely used process for extracting vanadium is sodium or calcium roasting process [3–5]. Although the sodium salt roasting process has a higher yield rate of vanadium than calcium roasting process, it is strict with the quality of the vanadium slag. The CaO in the vanadium should be less than 2%. Moreover, low roasting temperature, long reaction time, and the harmful gases formed in the roasting process such as HCl, Cl₂, SO₂, and SO₃ lead to environmental pollution and equipment erosion, restricting its wide application. The calcium roasting process has potential due to its high roasting temperature, short roasting time, and absence of pollution. However, the leaching rate of calcium vanadates in the carbonate leaching process is relatively low because the calcium vanadates are too stable. To solve this problem, researchers have conducted a variety of investigations. Housheng Chen studied the calcium roasting process of vanadium slag [6], in the conditions of oxidizing roasting, the phase change process related to the interaction between CaO

and the vanadium containing phases was as follows: at 210–600 °C, the spinel (FeV_2O_4) was firstly oxidized, $\text{Ca}(\text{VO}_3)_2$ formed at 600 °C, $\text{Ca}_2\text{V}_2\text{O}_7$ formed at 650 °C, and the $\text{Ca}_3(\text{VO}_4)_2$ formed at 800 °C. With the pH value of 2.5–3.0, the proper value of $\text{CaO}/\text{V}_2\text{O}_5$ was 0.5–0.6. The grade of V_2O_5 was 93%–94%, the leaching rate of vanadium was 90%–92%, and the total yield rate of vanadium could reach 85%–88%. Qirong He [7] has extracted a purity of 99.9% V_2O_5 from stone coal with the yield rate over 80% by calcium roasting method. Xiaoyong Zou et al [8] achieved the best leaching result with the granular V_2O_5 with the sizes ranged from 0.154–0.170 mm and the $\text{V}_2\text{O}_5/\text{Ca}$ mass ratio of 1:1.37. To sum up, three V-containing phases (calcium metavanadate, calcium orthovanadate, and $\text{Ca}_2\text{V}_2\text{O}_7$) are usually formed in the calcium roasting process. There has been uncertainty as to which phase is more beneficial to the formation of vanadates. The effect of carbonating solution on the leaching of V from the vanadates was not well understood. So the leaching behaviors of V from calcium metavanadate in sodium carbonate solution, sodium bicarbonate solution, and ammonium bicarbonate solution were studied by using calcium metavanadate as raw material. The calcium metavanadate was synthesized by pure CaO and V_2O_5 . Aiming at analyzing the kinetic behavior of the migration of V, the restrictive link was discussed by the kinetic model. The results will provide a fundamental basis for the improvement of the calcification V-extraction process.

2. Experimental Methods

2.1. Raw Materials

The pure CaO, V_2O_5 , Na_2CO_3 , NaHCO_3 and NH_4HCO_3 were used in the present study.

2.2. Experimental Equipment

The main experimental equipment is as follows: three-mouth flask, thermometer, stirrer, dryer, and the vacuum filtration system.

2.3. Experimental Procedure

(1) Preparation of calcium metavanadate

The CaO and V_2O_5 were dried at 150 °C for 2 h followed by uniform mixing for 2 h in a planetary ball mill with a mass ratio of 1:1. The mixtures were put into a Al_2O_3 crucible, then the crucible was put into a muffle furnace. After heating for 8 h at 1000 °C, the crucible was cooled in the air. The sample was grinded in the planetary ball mill and screened to the sizes ranging of 120–250 μm , 96–120 μm , and 74–96 μm , respectively. The XRD patterns of the synthetic sample are shown in Figure 1, which is characteristic of calcium metavanadate.

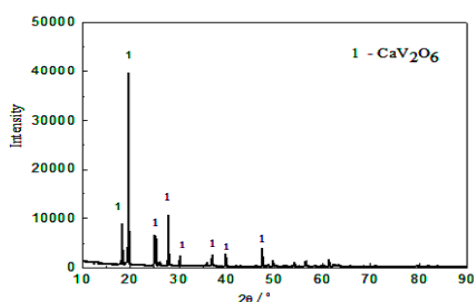


Figure 1. XRD patterns of the synthetic sample.

(2) Leaching kinetics of calcium metavanadate

The calcium metavanadate of different granularity and the carbonation leaching agent (Na_2CO_3 , NaHCO_3 and NH_4HCO_3) were weighted, 400 mL carbonation leaching agent was prepared.

The parameters are listed as follows: the concentration were 0.5, 0.75, 1, and 1.25 mol/L, the liquid-solid ratio was 8:1, the temperature were 20, 40, 60, and 80 °C, the revolution of the stirrer was 90 r/min, and the leaching time was 5, 10, 20, 40, and 60 min. When the predetermined time reached, the stirring of leaching solution stopped and settled for 30 s. 2 mL of the leaching solution were used for the content detection of vanadium which is only 0.5% of the leaching solution. The effect of the sampling can be neglected. After the leaching experiment, the leaching solution was subjected to filtration and separation. The leaching residues were dried in the oven at 120 °C for 2 h for the subsequent X-ray diffraction analysis. The schematic diagram of the experimental apparatus is shown in Figure 2.

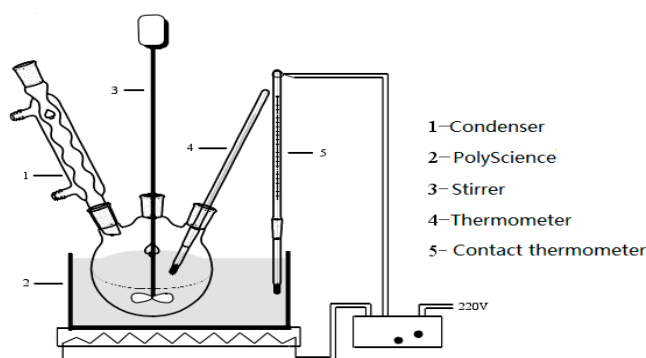


Figure 2. Schematic diagram of experimental apparatus.

(3) Microcosmic leaching of calcium metavanadate

The synthetic calcium metavanadate samples were cut into a cube with a size of 20 mm × 20 mm × 10 mm, then one side of the cube with a size of 20 mm × 20 mm was polished by sand paper of. The sample was then further polished in a polishing machine. 300 mL carbonation leaching agents (Na_2CO_3 , NaHCO_3 , and NH_4HCO_3) were prepared in a beaker, then the beaker was put into the thermostat water bath and the temperature was controlled at 20 and 60 °C. When the solution reached the set temperature, the cubic sample was put into the solution, the polished side was upward. Then the sample was taken out after 5, 10, 20 and 30 min. It was washed three times with deionized water and then washed with absolute ethyl alcohol three times. After dried, the sample was treated by metal spraying, the corrosion morphology was observed by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) analysis. The schematic diagram of experimental apparatus for the leaching process is shown in Figure 3.

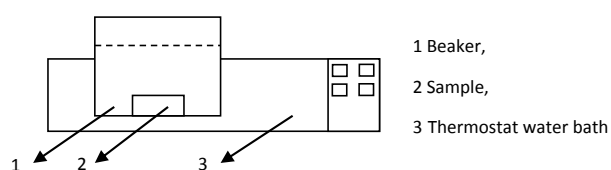


Figure 3. Schematic diagram of the leaching apparatus.

2.4. Analytical Method

- (1) Analyzing by X-ray diffraction (XRD). X-ray diffractometer of the D/Max-2500 PC (Rigaku, Tokyo, Japan,) type was used, which determines on the conditions of $K\alpha$ radiation excited by Cu target with a wavelength of 1.544426 Å, working voltage of 40 KV, scanning range of 2θ , diffraction angle from 10° to 80°, and a scanning speed of 2°/min. Synthetic samples and leaching lags were measured by XRD in order to determine their phases.
- (2) Analyzing by SEM. The SSX-550 scanning electron microscopy (Shimadzu, Kyoto, Japan) was used to observe micro structures and to identify elements on the surface of the samples.

- (3) Analyzing by chemical testing. According to the standard of GB/T 8639.1-1988, the chemical analyzing method of potassium permanganate—ferrous ammonium sulfate measured the element of vanadium in the solution. A formula to calculate the leaching rate of vanadium element is as follows:

$$\eta = (A \times C/M) \times 100\% \quad (1)$$

In the formula: η is the leaching rate of vanadium element for partial vanadate calcium, %. A is the volume of the leaching solution, L. C is the content of vanadium element in the leaching liquid, kg/L. M is the total mass of vanadium element for the sample, kg.

3. Mechanism Analysis of the Carbonate Leaching of Calcium Metavanadate

Figure 4 shows the micro erosion morphology and the EDS results of calcium metavanadate. With increasing the reaction time, the corrosion of the surface of calcium metavanadate aggravated gradually, amounts of spherical calcium carbonate attached to the surface of calcium metavanadate. Moreover, the particle size of calcium carbonate increased with the increasing reaction time.

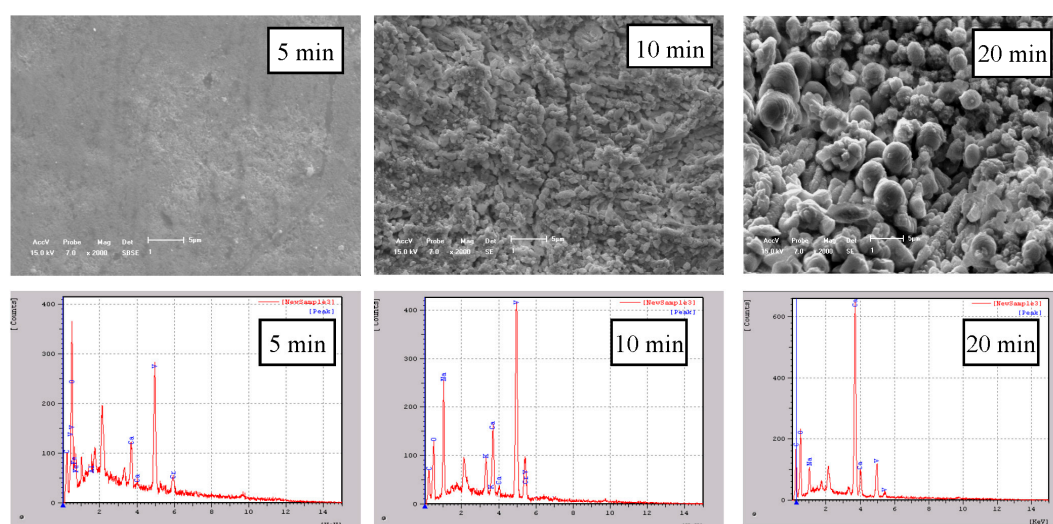


Figure 4. SEM images and EDS analysis of the surface of calcium metavanadate at different leaching time (20 °C, sodium carbonate).

Figure 5 shows the micrographs of the surface of calcium metavanadate in different carbonate solutions. After leaching at 60 °C for 30 min, calcium carbonate particles formed on the surface of calcium metavanadate in all three solution systems. The particle size of calcium carbonate in sodium carbonate solution was bigger, and the particle size was smallest in the ammonium bicarbonate solution. Judging from the corrosion morphology, there were obvious changes, the surface was relatively bright and clean after leaching in sodium carbonate solution. However, cracks appeared on the surface of calcium metavanadate leached in sodium bicarbonate solution. There were more cracks present for the sample leached in ammonium bicarbonate solution.

To sum up, the corrosion mechanisms of the three carbonate solution are different. In sodium carbonate solution, it is a dissolution process of the surface of calcium metavanadate, the product on the surface is relatively little. In sodium bicarbonate solution, it is a dissolution process of the surface of calcium metavanadate, but the dissolution accompanies the formation of cracks on the surface. In ammonium bicarbonate solution, there are lots of cracks on the surface of calcium metavanadate, and the cracks develop in depth and breadth. It indicates that the leaching mechanisms in carbonate solution are quite different from that in bicarbonate radical solution. The difference of the leaching behavior in the different leaching agents is explained the next section.

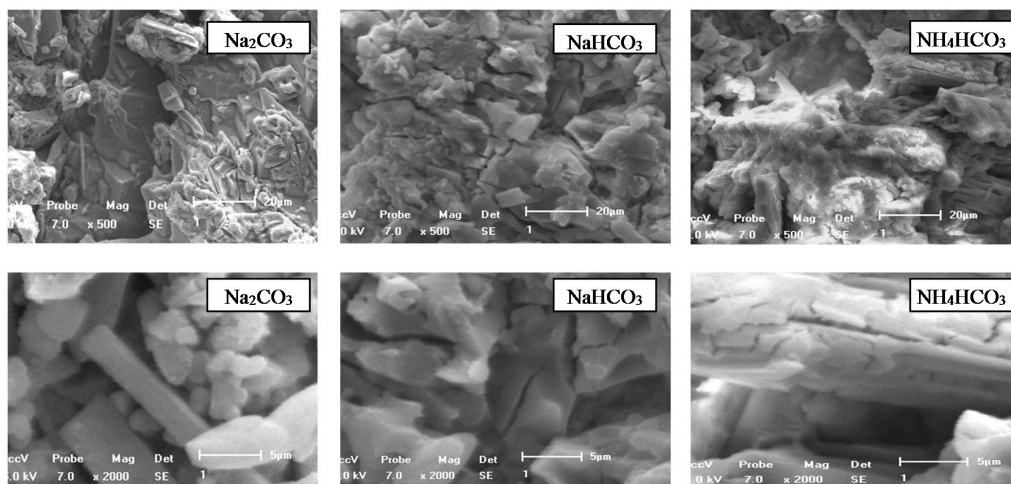
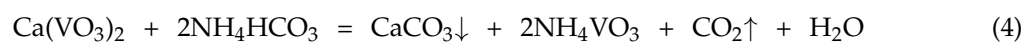
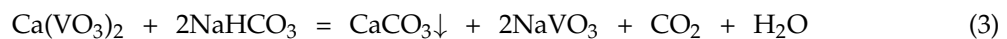
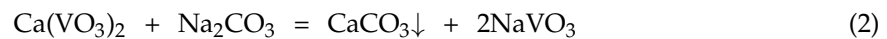


Figure 5. SEM images of the surface of calcium metavanadate under different leaching conditions (60 °C, 30 min).

4. Kinetic Analysis of the Carbonation Leaching Behavior of Calcium Metavanadate

The main reactions in the carbonation solution for calcium metavanadate are as follows:



4.1. The Choice of Reaction Model for Carbonate Leaching Calcium Metavanadate

The carbonate leaching reaction of calcium metavanadate mainly belongs to liquid-solid heterogeneous reaction. There are commonly two models used in the process of the liquid-solid heterogeneous reaction, namely the overall reaction model and the contracting and nonreactive nuclear model [9]. The chemical reaction of leaching agent and calcium metavanadate was conducted on the surface of solid particle, but with the whole reaction carried through, vanadium existing in calcium metavanadate came into the solution and formed VO_3^- , subsequently, solid (non-dissolved) calcium carbonate was formed from Ca^{2+} combined with CO_3^{2-} deposited on the surface of nonreactive particles of calcium vanadate. The layer of sediment seen from the Figure 4 was relatively loose, having no impact on the leaching solution permeating inside. As a result, it is more suitable that the leaching adopted the contracting and nonreactive nuclear model. The mechanism of the carbonate leaching of calcium metavanadate is shown in Figure 6.

In the present study, the carbonate leaching reaction of calcium metavanadate can be described as follows:

- (1) Firstly, CO_3^{2-} or HCO_3^- diffuses to the surface of the particle through the liquid film of the blast furnace containing Ti.
- (2) CO_3^{2-} or HCO_3^- diffuses to the surface of the unreacted particles through the product film on the surface of calcium metavanadate.
- (3) CO_3^{2-} or HCO_3^- reacts with calcium metavanadate, which can be considered as the reaction between Ca^{2+} and CO_3^{2-} or the reaction between Ca^{2+} and HCO_3^- .
- (4) The reaction product, calcium carbonate, forms on the surface of the particle, which shows a loose deposition condition.
- (5) The other reaction product, VO_3^- , diffuses to the solution from the surface of the particle through the liquid film.

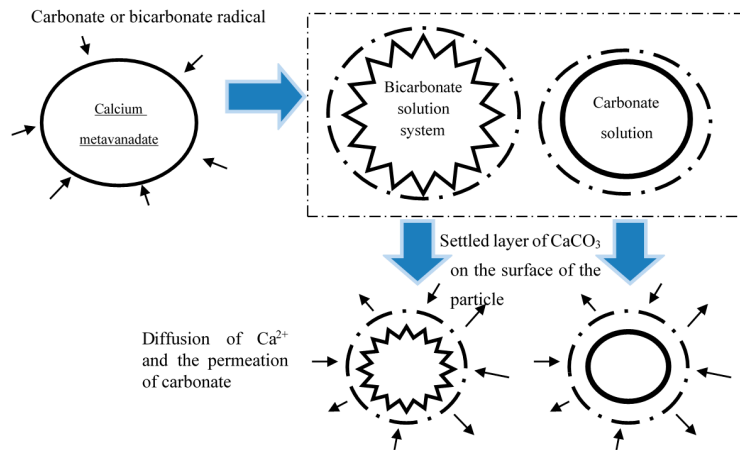


Figure 6. Reaction mechanism of the carbonate leaching reaction of calcium metavanadate.

4.2. Restricted Links of the Carbonate Leaching of Calcium Metavanadate

In order to confirm the restricted links of the carbonate leaching of calcium metavanadate, the following three equations were used to fit the experimental data [10]. The results are shown in Figure 7.

- (1) The leaching rate is controlled by the diffusion in the liquid boundary layer: $\eta = Kt$;
- (2) The leaching process is controlled by the diffusion in the solid product layer: $1 - 2/3\eta - (1 - \eta)^{2/3} = Kt$;
- (3) The leaching process is controlled by the chemical reactions: $1 - (1 - \eta)^{1/3} = Kt$.

From Figure 7, the correlation coefficient R^2 is 0.992 when $1 - 2/3\eta - (1 - \eta)^{2/3} = Kt$ is used to fit the experimental data. The results indicate that the carbonate leaching of calcium metavanadate is controlled by the diffusion in the solid product layer.

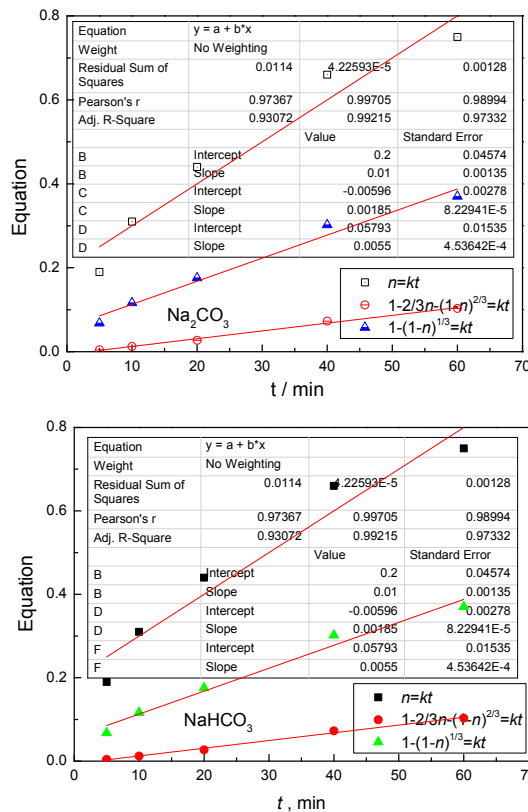


Figure 7. Cont.

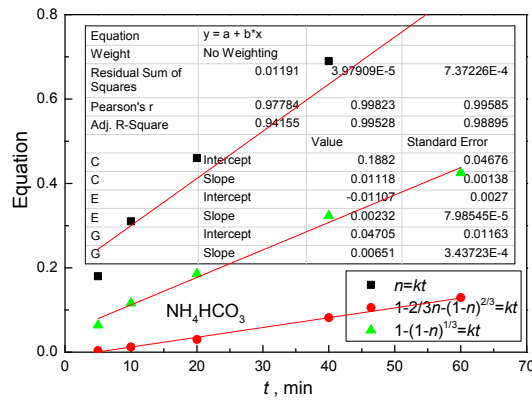


Figure 7. Linear fitting correlations of different rate equations (concentration of sodium carbonate: 1 mol/L, temperature: 60 °C, particle size: 96–120 μm, stirring rate: 90 rpm).

4.3. Kinetic Behavior Analysis of the Carbonate Leaching of Calcium Metavanadate

Figure 8 shows the relationship between t and $1 - 2/3\eta - (1 - \eta)^{2/3}$ with different concentrations of leaching agent. The slope of the fitted line is the synthesis reaction rate constant K . All the correlation coefficients are more than 0.99, the carbonate leaching of calcium metavanadate in three different solutions is controlled by the diffusion process. With the increase of the concentration of the three leaching agents, the slopes of the fitted lines increase, the synthesis reaction rate constant K increases gradually. The results indicate that a higher concentration of leaching agent can lead to a quicker leaching rate of vanadium, which is beneficial to the reactions.

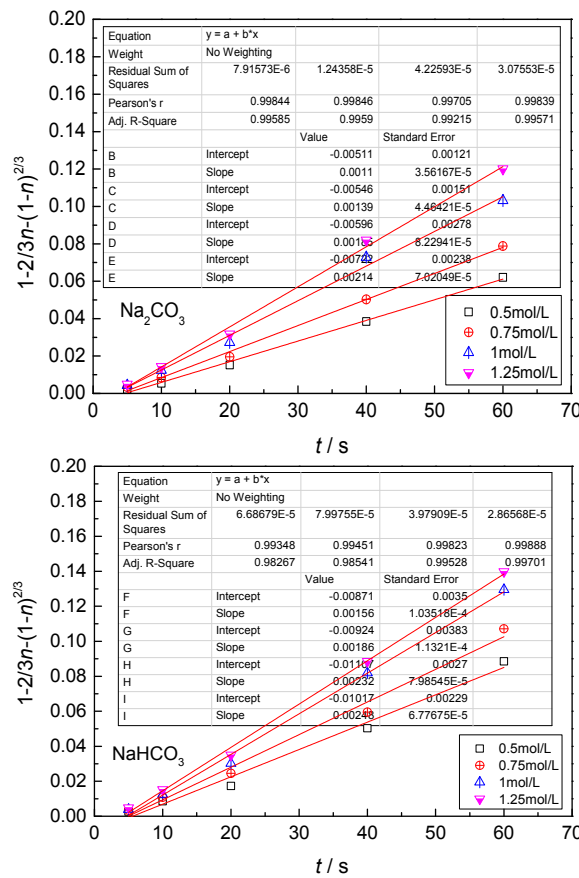


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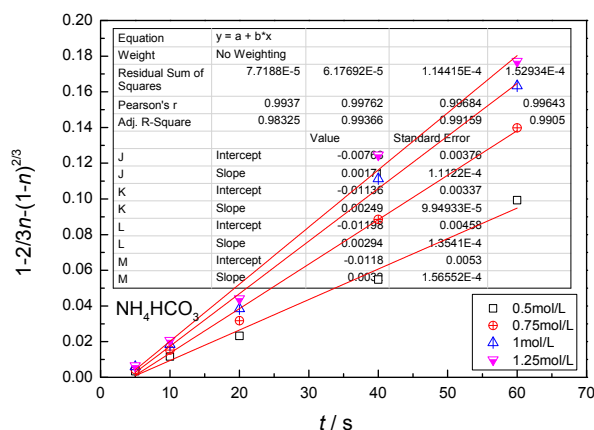


Figure 8. Linear relation between the leaching time and $[1 - 2/3\eta - (1 - \eta)^{2/3}]$ (60 °C, particle size: 96–120 μm, stirring rate: 90 rpm).

Figure 9 shows the relation between the concentration of the leaching agent and the logarithm of the synthesis reaction rate constant. As shown in Figure 10, the slope of the fitted line is the reaction order. The maximum reaction order is 0.746 in the sodium carbonate solution system, and the minimum reaction order is 0.531 in the sodium bicarbonate solution system. The reaction order can reflect the influence of leaching agent on the reaction rate. With a larger reaction order, the leaching agents show more remarkable influence on the reaction rate. In the present study, sodium carbonate shows the most remarkable influence on the leaching reaction of vanadium, and the least remarkable one is ammonium bicarbonate.

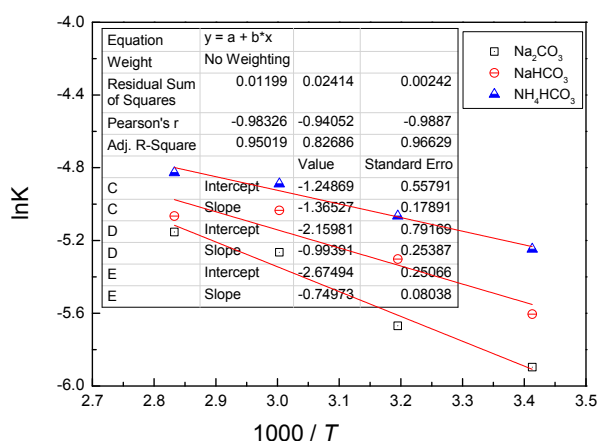


Figure 9. Relation between the concentration of leaching agent and the synthesis reaction rate.

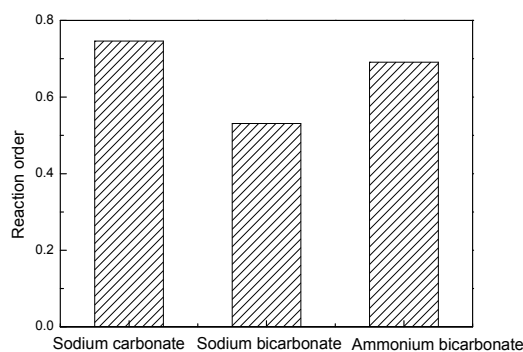


Figure 10. Relation between the leaching agent and the reaction order.

Figure 11 shows the relation between the reaction time and $1 - 2/3\eta - (1 - \eta)^{2/3}$ at different leaching temperatures. With increasing the temperature, the slope of the curve increases, the synthesis reaction rate constant of the leaching reaction of vanadium increases gradually.

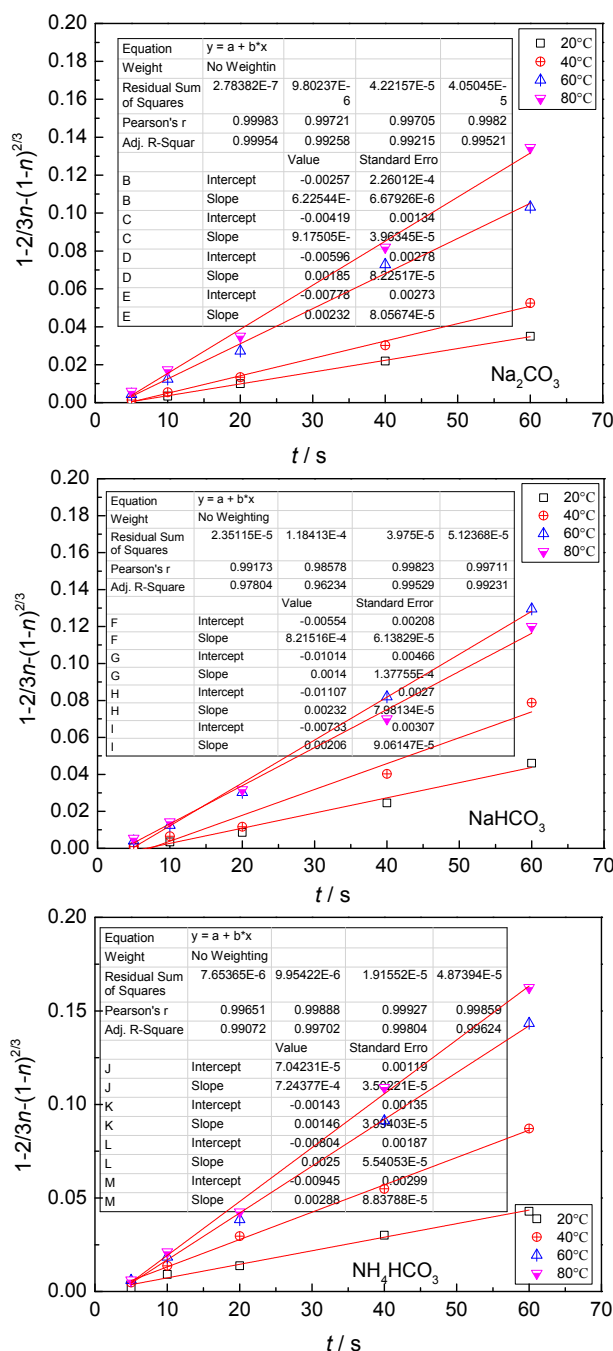


Figure 11. Linear relation between the leaching time and $[1 - 2/3\eta - (1 - \eta)^{2/3}]$ (concentration of leaching agent: 1 mol/L, particle size: 96–120 μm , the stirring rate: 90 rpm).

The relation between the reaction rate constant and the temperature can be obtained by the Arrhenius equation.

$$K = A \times \exp(-E/RT) \tag{5}$$

K is the reaction rate constant; A is the frequency factor, s^{-1} ; E is the apparent activation energy, mol/L; R is the gas constant, 8.314 J/mol·K; T is the reaction temperature, K.

Figure 12 shows the relation between $\ln K$ and $1/T$. The slope of the fitted line is $-E/R$, and the apparent activation energy can be calculated by this parameter. The apparent activation energies of the carbonation leaching reaction of calcium metavanadate in different solutions are as follows: 20.01 KJ/mol in sodium carbonate, 21.04 KJ/mol in sodium bicarbonate, and 20.45 KJ/mol in ammonium bicarbonate. The frequency factors are as follows: 2.24 min^{-1} in sodium carbonate, 4.6 min^{-1} in sodium bicarbonate, and 3.39 min^{-1} in ammonium bicarbonate. In present study, the reaction in sodium carbonate solution has the minimum apparent activation energy, the reaction in sodium bicarbonate solution has the maximum activation energy, but the frequency factor is the minimum one. The apparent activation energy is less, the reactivity is higher, the carbonation reaction capacity is stronger, and the reaction rate is faster. The frequency factor can express the total effective collision of the activated molecule, if the frequency factor is bigger, there will be more effective collisions of the activated molecule, the reactions will occur more easily, and the reaction will be more complete. The above phenomenon may be related to the ionization of bicarbonate radical.

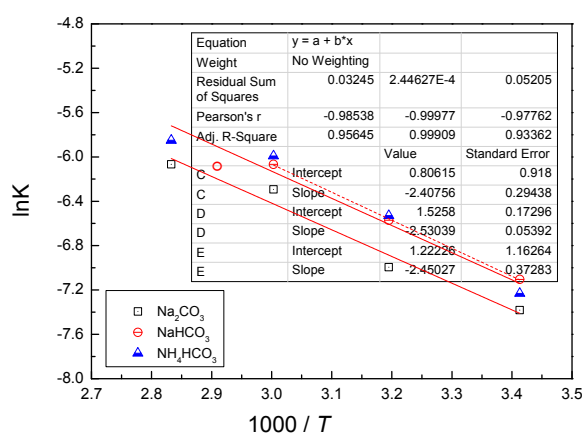


Figure 12. The relation between $\ln K$ and $1/T$ in different solutions.

Figure 13 shows the relation between the reaction time and $1 - 2/3\eta - (1 - \eta)^{2/3}$ under the condition of different particle size. With the decrease of the particle size, the slope of the line increases, and the synthesis reaction rate constant increases gradually.

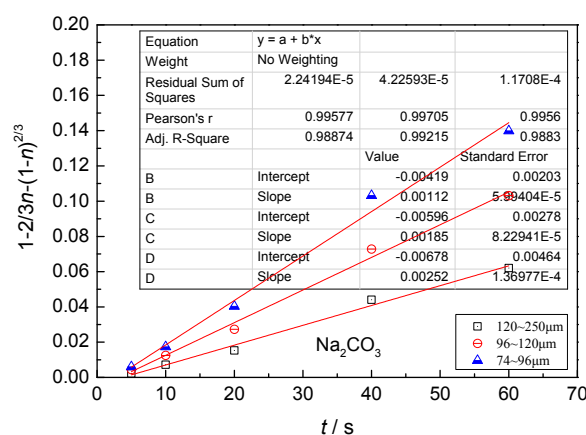


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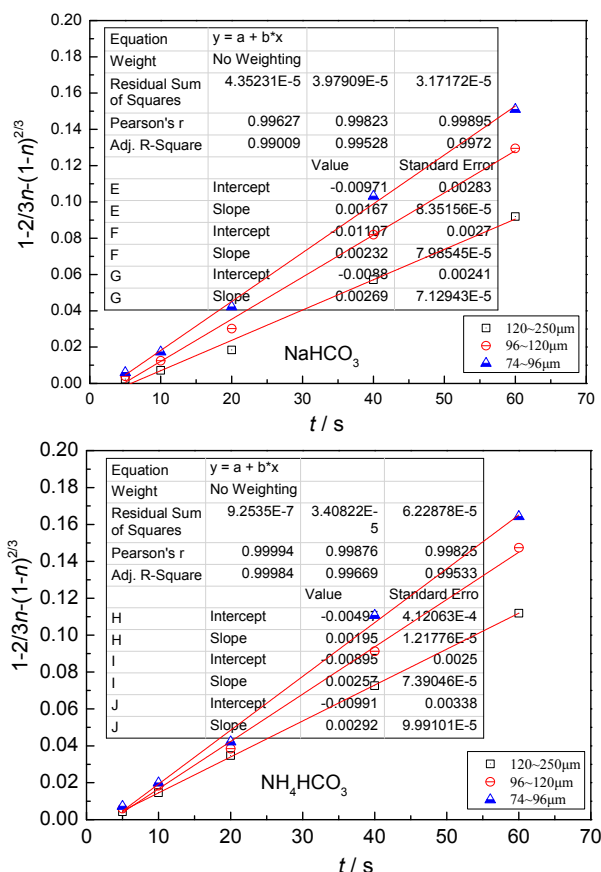


Figure 13. The linear relation between the reaction time and $1 - 2/3\eta - (1 - \eta)^{2/3}$ (1 mol/L, 60 °C, 90 rpm).

According to the kinetic equation, the reciprocal of the average particle size $1/r$ is proportional to the synthesis reaction rate constant K_1 , which is shown in Equation (6).

$$K = K_1/r \tag{6}$$

$$K_1 = A_0C^n/\rho \times \exp(-E/RT) \tag{7}$$

4.4. Kinetic Equations of the Carbonate Leaching of Calcium Metavanadate

The following equation can be derived according to the Arrhenius equation.

$$1 - 2/3\eta - (1 - \eta)^{2/3} = Kt = A_0C^n/\rho r_0 \times \exp(-E/RT)t \tag{8}$$

C is the concentration of the leaching agent, mol/L; n is the reaction order; ρ is the proportion of the reactants, g/cm³; r_0 is the radius of the reactant particle, μm.

Based on the experimental data and Equation (8), the relation between $1 - 2/3\eta - (1 - \eta)^{2/3}$ and $C^n/r_0 \times \exp(-E/RT)t$ can be obtained, which is shown in Figure 14. The correlation coefficients in three different solutions are more than 0.96, and the fitting results show good correlation. The value of A_0/ρ in different solutions can be obtained according to the slope of the fitted line and the results are as follows: 4.39 in sodium carbonate solution, 7.89 in sodium bicarbonate solution, and 6.78 in ammonium bicarbonate solution.

According to the reaction order, the value of A_0/ρ , and the activation energy, the kinetic equations of the carbonate leaching for calcium metavanadate in three solutions were as follows:

$$1 - 2/3\eta - (1 - \eta)^{2/3} = 4.39[Na_2CO_3]^{0.75}/r_0 \times \exp(-2527.06/T)t \tag{9}$$

$$1 - 2/3\eta - (1 - \eta)^{2/3} = 7.89[\text{NaHCO}_3]^{0.53}/r_0 \times \exp(-2530.67/T)t \quad (10)$$

$$1 - 2/3\eta - (1 - \eta)^{2/3} = 6.78[\text{NH}_4\text{HCO}_3]^{0.69}/r_0 \times \exp(-2459.71/T)t \quad (11)$$

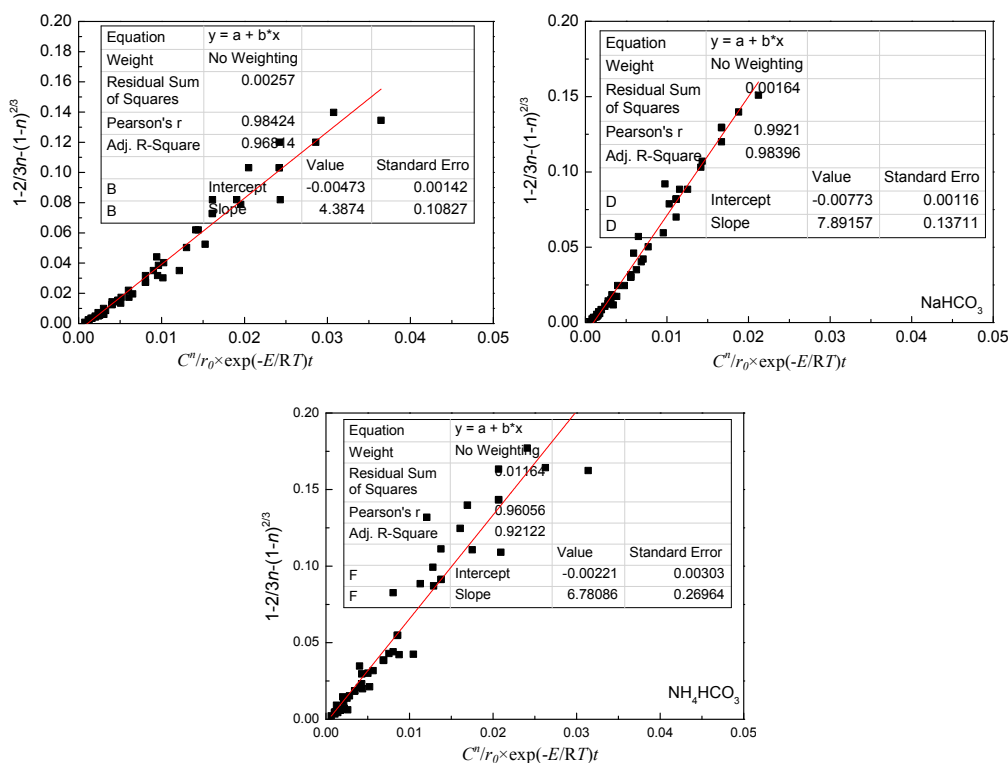


Figure 14. The relation between $1 - 2/3\eta - (1 - \eta)^{2/3}$ and $C^t/r_0 \times \exp(-E/RT)t$ in the solutions for the carbonation of calcium metavanadate.

5. Conclusions

- (1) With increasing the reaction time, calcium carbonate particles formed on the surface of calcium metavanadate, and the particle size increased. The leaching product on the surface of calcium metavanadate was relatively little in sodium carbonate solution. In sodium bicarbonate solution, the dissolution process of the surface of calcium metavanadate accompanied the formation of cracks on the surface. In ammonium bicarbonate solution, more obvious cracks formed on the surface of calcium metavanadate, and the cracks developed in depth and breadth.
- (2) With the increase of the leaching agent content, the particle size decreased, temperature and reaction time increased, the leaching rate of vanadium increased, and the constant of reaction rate increased.
- (3) In the present study, the carbonate leaching for calcium metavanadate was controlled by diffusion, the activation energy was maximum in the sodium bicarbonate solution, and was minimum in the sodium carbonate solution. The activation energy value was median in the ammonium bicarbonate solution. The kinetic equation of the carbonate leaching for calcium metavanadate was as follows:

$$1 - 2/3\eta - (1 - \eta)^{2/3} = 4.39[\text{Na}_2\text{CO}_3]^{0.75}/r_0 \times \exp(-2527.06/T)t;$$

$$1 - 2/3\eta - (1 - \eta)^{2/3} = 7.89[\text{NaHCO}_3]^{0.53}/r_0 \times \exp(-2530.67/T)t;$$

$$1 - 2/3\eta - (1 - \eta)^{2/3} = 6.78[\text{NH}_4\text{HCO}_3]^{0.69}/r_0 \times \exp(-2459.71/T)t.$$

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Conflicts of Interest: The authors declare no conflict of interest.

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