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# Vanadium–Titanium Magnetite Concentrate, Calcium–Magnesium Composite Roasting and Sulfuric Acid Leaching for Vanadium Extraction from Pellets

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**Abstract:** This paper investigated a pellet ore production process in which vanadium was extracted from vanadium and titanium magnetite concentrates using sulfuric acid leaching. Calcium and magnesium were added to the iron ore concentrate during pellet production to produce calcium vanadate and magnesium vanadate after roasting. The pellets were leached with sulfuric acid solution to extract $V^{5+}$. The resulting pellets had a compressive strength of 3375 N after primary roasting, a good pellet morphology after acid leaching, and simple liquid–solid separation. Under the optimal experimental conditions, the vanadium leaching rate in the pellets reached 77.86%, while the iron leaching rate was only 1.17%. The pellets did not fragment, which was an improvement upon existing vanadium extraction methods. The strength of the pellets after vanadium extraction decreased to 563 N, but after secondary roasting, the compressive strength of the pellets reached 2578 N, which was suitable for blast furnace ironmaking. The roasting and acid leaching experiments showed that the vanadium extraction process resulted in suitable pellet properties. The use of low compound additives can effectively improve the leaching effect, while avoiding the previous problems of too many additives, pellet iron grade reduction, or the pursuit of high vanadium extraction rate pellet breakage and serious high secondary use process costs.

**Keywords:** vanadium–titanium magnetite concentrate; calcium–magnesium composite roasting; acid leaching vanadium extraction; pellet performance

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## 1. Introduction

Vanadium is widely used in the steel, alloying, pharmaceutical, and aerospace industries because of its excellent physicochemical properties [1–3]. Vanadium and titanium magnetite is the main raw material for vanadium production, and there are currently two main methods of extracting vanadium from it [4]. One method obtains vanadium from vanadium-containing ironmaking slag, and the other obtains it directly from iron ore concentrate.

Vanadium slag extraction is the main method of vanadium extraction [5]. During vanadium extraction from vanadium slag, the slag is typically roasted to convert insoluble vanadium oxide into soluble vanadate [6–8]. Currently, sodium roasting–water leaching [9,10], calcium roasting–acid leaching [11,12], and salt-free roasting–acid leaching processes [13] are mainly used for vanadium extraction. The sodium roasting–water leaching process is more mature, but it generates harmful gases, produces agglomerates, and corrodes equipment during the roasting process [14]. Less vanadium is recovered from the calcium roasting-acid leaching process than from sodium roasting [15]. Salt-free roasting/acid leaching may oxidize and partially volatilize vanadium, making the subsequent acid leaching difficult [16]. The vanadium extraction rate is generally low due to the low vanadium content in the vanadium slag [17].

The direct vanadium extraction method, in which vanadium is extracted from vanadium–titanium magnetite ore before ironmaking, has a high vanadium recovery rate [18,19]. The roasting process has a crucial effect on vanadium recovery [20,21]. When the roasting temperature is lower than 1200 °C, increasing the temperature improves the vanadium leaching efficiency, but temperatures above 1250 °C result in over-burning and the partial encapsulation of vanadium by silicates, which prevents vanadium conversion [22]. To enhance subsequent vanadium extraction, roasting aids are often added during the roasting process, but traditional sodium and potassium salt additives have many problems [23–25]. Zhang et al. [26] used sodium roasting–water leaching to extract vanadium from vanadium–titanium magnetite. This process had a high vanadium leaching rate, but large amounts of iron also entered the solution, and the tailings were difficult to handle. Wen et al. [27] used sodium salt roasting–ammonium sulfate leaching to separate vanadium chromium. Li et al. [28] used $K_2SO_4$/KCl combination roasting to extract vanadium from vanadium–titanium magnetite, and the vanadium leaching rate was substantially increased compared with either individual $K_2SO_4$ or KCl, but harmful gases such as $SO_2$ and $Cl_2$ were produced. Luo et al. [29] used a calcium roasting process for vanadium–titanium magnetite pellets, followed by sulfuric acid leaching, which selectively leached vanadium with a lower iron leaching rate.

The pelletizing of magnetite is a better way to extract vanadium. It can a comprehensive use of vanadium and titanium magnetite resources and improve the vanadium recovery rate. Previous pellet-based vanadium extraction processes have pursued high vanadium extraction rates without investigating the pellet properties, which produced environmental pollution. The use of excessive additives reduced the pellet iron grade, making it difficult to use the pellets after leaching. M. Meraj found that the addition of MgO improved the reduction degree and porosity of the pellets [30]. MgO is a recoverable roasting additive that improves the high-temperature performance of pellets [31,32]. Xiang et al. found that the generation of acid-soluble vanadate was accelerated during CaO/MgO complex roasting, which inhibited the precipitation of calcium sulfate and also accelerated the leaching kinetics [33]. Calcium oxide and magnesium oxide have significant effects on vanadium extraction, and the decomposition of calcium hydroxide during roasting increases the pellet porosity, which promotes vanadium extraction. Many studies have shown that sulfuric acid can separate vanadium and iron [34]. Therefore, this paper used $Ca(OH)_2$/MgO composite roasting to extract vanadium via sulfuric acid leaching. The vanadium and titanium magnetite concentrate pelletizing, roasting, acid leaching, and secondary roasting processes were investigated. Pellets were created to meet the vanadium extraction requirements using fewer additives, and the pellets showed good performance before and after leaching. This process is simple, increases the vanadium leaching rate, is environmentally friendly, and the pellets can be used as iron ore pellets.

## 2. Experimental

### *2.1. Experimental Procedure*

In this study, vanadium and titanium magnetite concentrate provided by a company in Sichuan was used as the raw material. The calcium–magnesium composite roasting–sulfuric acid leaching process was used to extract vanadium, and the process flow chart is shown in Figure 1.

The experiments were conducted in three stages. In the first stage, the vanadium titanium magnetite concentrate powder was mixed with $Ca(OH)_2$, MgO, and bentonite in proportion. The balls were made on an 800 mm × 165 mm disc ball-making machine with an inclination angle of 48° and a speed of 23 r/min. The effects of particle size distribution (iron concentrate −0.074 mm, accounting for 50%, 60%, 70%, 80%, 90%, and 100%), bentonite addition (0%, 0.25%, 0.50%, 0.75%, 1.00%, and 1.25%), and pelletizing time (5 min, 10 min, 15 min, 20 min, 25 min, and 30 min) on pellet properties were investigated. We selected balls with a diameter of 8 to 20 mm from the prepared green balls and dried them at 120 °C for 2 h for later use. In the second stage, the raw pellets were roasted to investigate the effects of the additive ratio (0, 0.25:1, 0.5:1, 0.75:1, and 1:1), roasting

temperature (800 °C, 900 °C, 1000 °C, 1100 °C, 1200 °C, and 1300 °C), time (0.5 h, 1.0 h, 1.5 h, 2.0 h, 2.5 h, and 3.0 h), and bentonite addition amount (0.2%, 0.4%, 0.6%, 0.8%, 1.0%, and 1.2%) on the pellet performance and vanadium leaching rate. In the third stage, the roasted pellets were leached in sulfuric acid to investigate the effects of acidity (1.0 moL/L, 1.5 moL/L, 2.0 moL/L, 2.5 moL/L, 3.0 moL/L, and 3.5 moL/L), liquid-to-solid ratio (1:1, 2:1, 3:1, 4:1, 5:1, and 6:1), leaching temperature (40 °C, 50 °C, 60 °C, 70 °C, 80 °C, and 90 °C), time (15 h, 30 h, 45 h, 60 h, 75 h, and 90 h), and pellet size (8–12 mm, 12–16 mm, and 16–20 mm) on the leaching rate of ferrovanadium.

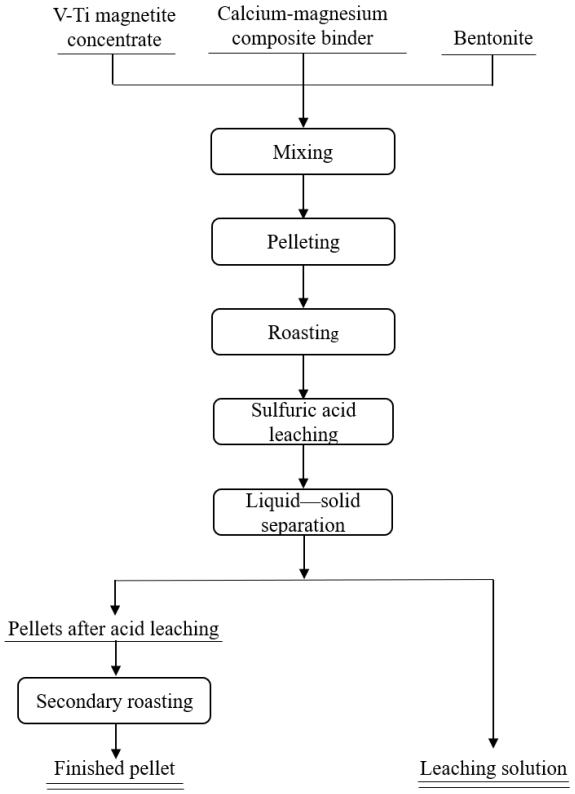



**Figure 1.** Flow chart of calcium magnesium composite roasting acid leaching for vanadium extraction.

### *2.2. Equipment and Analysis Methods*

A Winner 2000 particle size analyzer (QL-1075, Shenzhen Qunlong Instrument & Equipment Co., Shenzhen, China) was used to analyze the particle size of vanadium and titanium iron ore concentrates, and an X-ray diffractometer (XRD, Panalytical Empyrean. Marvin Panaco, The Netherlands) for physical phase characterization, and the XRD patterns were analyzed by MDI JADE software (Stat-Ease, Inc., Minneapolis, MN, USA). An inductively coupled plasma atomic emission spectrometer (ICP-OES, Gangyannake Testing Technology Co., Ltd., Beijing, China) was used to analyze the chemical composition of ferrovanadium in the pellets and leachate before and after leaching. The compressive strength of pellets was tested using a digital display pellet pressure tester (SEM-EDS, Quanta Q 400, FEI Company, Hillsboro, OR, USA). The compressive strength of pellets was tested using a digital display pellet pressure tester (KYS-10, Jinan Testing Instrument Factory, Jinan, China).

## 3. Results and Discussion

### *3.1. Characterization of the Iron Concentrate*

The main components of the iron concentrate are shown in Table 1, in which the Fe content was 52.00% and the V content was 0.31%. The physical phase analysis of the iron ore concentrate is shown in Figure 2; the iron ore concentrate was mainly composed of magnetite and ilmenite phases. Figure 3 shows that the particle size range of the iron ore

concentrate was 0–300 μm, while the percentage of ore fines with particle size less than 74 μm was about 40.15%.

**Table 1.** Chemical composition of vanadium and titanium iron ore concentrate.

| Element | Fe | Ti | Si | Ca | Mg | V | Na | S |
|---|---|---|---|---|---|---|---|---|
| Content (wt.%) | 52.00 | 8.84 | 1.96 | 0.58 | 0.43 | 0.31 | 0.03 | 0.79 |

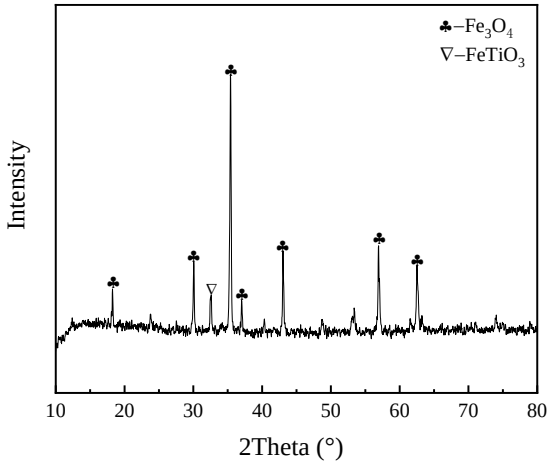



**Figure 2.** XRD patterns of vanadium–titanium magnetite.

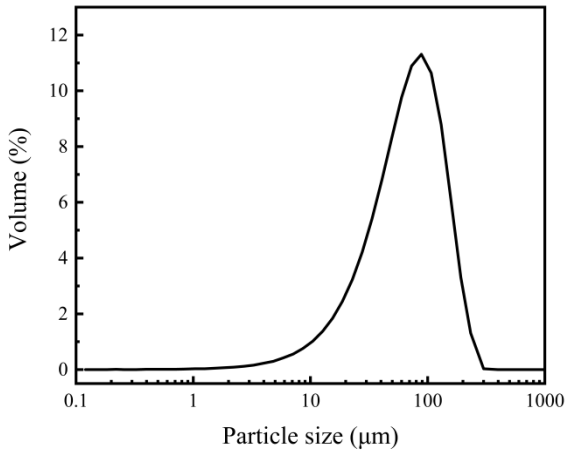



**Figure 3.** Particle size distribution of vanadium–titanium magnetite.

### *3.2. Pelletizing Experiments*

The iron ore concentrate was coarse and unsuitable for pelletizing. First, the effect of grinding time on the particle size percentage of −0.074 mm iron ore concentrate was investigated. Grinding reduced the solid particle size and increased the specific surface area of the particles, which promoted pellet formation. The grinding process also destroyed the structure of the ore powder, making the vanadium within it more susceptible to oxidation. Figure 4 shows that extending the grinding time produced a finer particle size of iron ore concentrate. A total of 90% of the iron ore concentrate powder particle size was less than 0.074 mm after 8 min of grinding. Further increasing the grinding time greatly reduced the grinding effect and also increased the energy consumption. Therefore, the grinding time was set to 8 min.

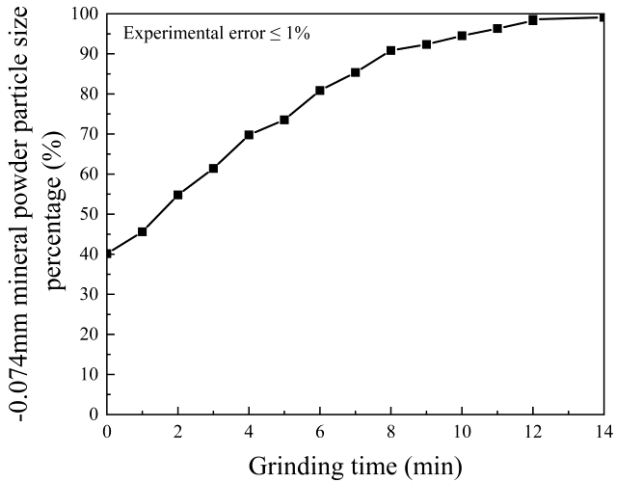



**Figure 4.** The effect of grinding time on the particle size of iron concentrate.

The effects of mineral powder −0.074 mm particle size ratio, bentonite addition, and pelletizing time on pellet performance were investigated, and the results are shown in Figure 5. We adjusted the addition amount of bentonite to 1% and the pelletizing time to 15 min.

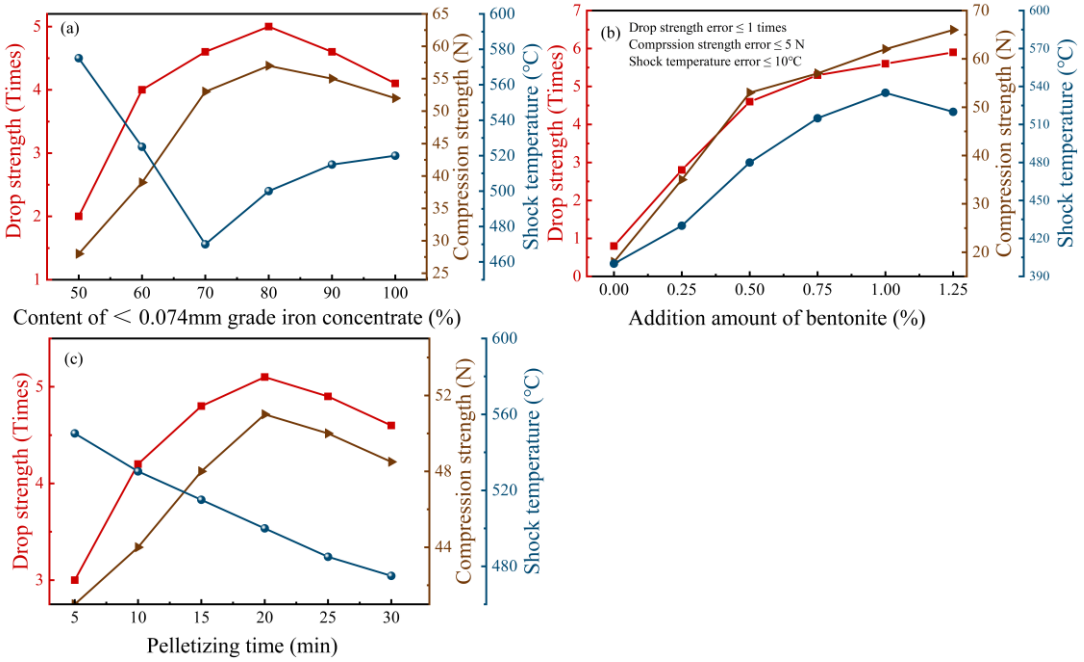



**Figure 5.** Influence of pelletizing factors on falling strength, compressive strength, and bursting temperature of raw balls: (**a**) the effect of iron concentrate −0.074mm particle size ratio, (**b**) the effect of addition amount of bentonite, (**c**) the effect of pelletizing time.

Figure 5a shows that the falling strength and compressive strength of raw pellets increased with the percentage of −0.074 mm iron ore concentrate particles. The best strengths were obtained at 80%. Continuing to increase the percentage of −0.074 mm particles decreased the falling strength and compressive strength of pellets. When the iron ore concentrate was too fine, irregular needle particles were destroyed, and the particle size distribution did not promote pellet formation. The bursting temperature of raw pellets decreased as the percentage of −0.074 mm particles increased. The finer the particle size, the denser the pellet, and the lower the pellet porosity, which made water migration difficult during roasting, resulting in uneven pellet shrinkage and cracking. When −0.074 mm particles accounted for more than 70%, the pellet bursting temperature increased. The

production of finer pellets required less moisture, which decreased the bursting tendency. Therefore, 80% was the optimal portion of −0.074 mm particles during pelletizing.

Figure 5b shows that increasing the bentonite addition amount increased the falling strength, compressive strength, and bursting temperature of raw pellets. However, excess bentonite introduced impurities that decreased the pellet iron grade. A more compact pellet structure produced many cracks or directly burst the pellet during roasting, which also decreased the porosity of the pellets, prolonged the acid leaching time, and made the acid leaching effect worse. Therefore, a bentonite addition amount of ≥0.7% was used during pelletizing.

Figure 5c shows that the falling strength and compressive strength of raw pellets continually increased with the pelletizing time, showing the best results at 20 min. Upon continuing to increase the pelletizing time, the pellet moisture evaporated, and the strengths of raw pellets decreased due to collisions between them. Bursting temperature will continue to decline with the extension of the ball-making time; the longer the ball-making time, the more closely bound the particles in the pellets are, and the roasting process moisture escapes difficulties caused by pellet cracking, so the extension of ball-making time will play a negative role in the bursting temperature. An excessively long pelleting time decreased the pellet yield and increased the energy consumption. Therefore, the pelleting was set to 20 min.

### *3.3. Roasting Experiments*

According to previous experiments, the highest vanadium leaching rate was achieved when 2% $Ca(OH)_2$ was added. Therefore, the total addition of ($Ca(OH)_2$+MgO) was fixed at 2%. The pelletizing conditions were iron concentrate with a particle size of −0.074 mm, accounting for 80%, and the pelletizing time was 20 min. The roasting conditions were roasting temperature of 1100 °C, roasting time of 1 h, and addition of 0.8% bentonite. The leaching conditions were a sulfuric acid concentration of 2 mol/L, liquid–solid ratio of 2:1, leaching temperature of 90 °C, and leaching time of 90 h. The effect of the mass ratio of MgO/($Ca(OH)_2$+MgO) on the compressive strength of the pellets and vanadium leaching rate was studied, and the results are shown in Figure 6.

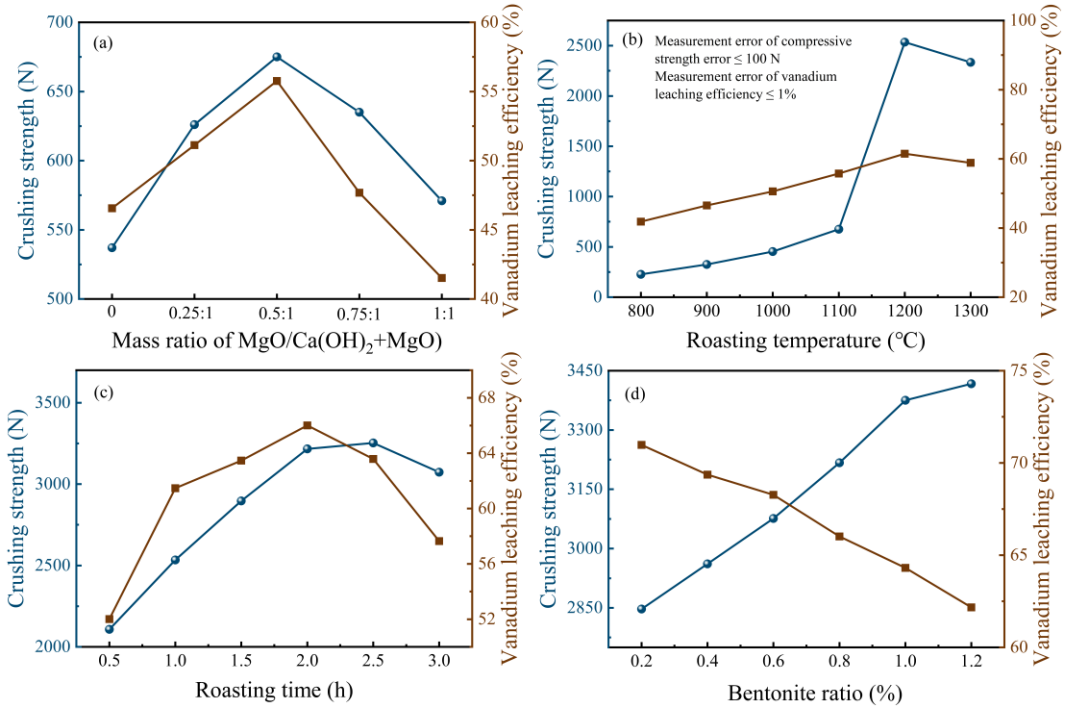



**Figure 6.** Influence of roasting conditions on compressive strength and vanadium leaching rate of pellets: (**a**) the effect of roasting, (**b**) the effect of roasting temperature, (**c**) the effect of roasting time, (**d**) the effect of bentonite ratio.

Figure 6a shows that the compressive strength and vanadium leaching rate of pellets increased and then decreased as the mass ratio of MgO/($Ca(OH)_2$+MgO) increased. When the mass ratio of MgO/($Ca(OH)_2$+MgO) was 0%, the only additive was $Ca(OH)_2$, and the calcium vanadate generated after roasting entered the acid solution after acid leaching. The generated calcium sulfate precipitated from the solution, but the calcium sulfate generated inside the pellet had difficulty entering the solution, which hindered vanadium leaching. Upon increasing the MgO content, the leaching kinetics were accelerated, which inhibited the calcium sulfate precipitation. The highest vanadium leaching rate was achieved when the mass ratio of MgO/($Ca(OH)_2$+MgO) was 50%. Continuing to increase the mass percentage of MgO/($Ca(OH)_2$+MgO) to 100% decreased the vanadium leaching rate to 58.86%. When only MgO was added, roasting generated less soluble vanadate, which was not conducive to vanadium leaching. When calcium and magnesium were both added, they promoted each other and improved the leaching kinetics. When the MgO content was low, CaO reacted with $Fe_2O_3$ to form CaO-$Fe_2O_3$, which enhanced the solidification of molten pellets and increased the pellet strength. When the MgO mass fraction continued to increase, $Mg^{2+}$ reacted with magnetite to form a high-melting MgO-$Fe_2O_3$ solid, resulting in a lower calcium ferrate content, which was unfavorable to pellet solidification. Therefore, the optimal MgO/($Ca(OH)_2$+MgO) mass ratio was determined to be 50%.

Figure 6b shows that increasing the roasting temperature from 700 to 1200 °C continuously increased the compressive strength of the pellets. At 1100 °C, the pellet strength was only 675 N. When the temperature was increased to 1200 °C, the pellet compressive strength increased sharply to 2534 N. Continuing to increase the roasting temperature decreased the compressive strength of pellets. When the roasting temperature was low, the pellet consolidation reaction was incomplete, and when the temperature was too high, the pellet was overmelted and sintering occurred. At 1200 °C, the optimal vanadium leaching rate of 61.47% was obtained. The vanadium leaching rate decreased when the temperature increased to 1300 °C. At higher temperatures, calcium, magnesium, and silicon in the pellets reacted and formed new inclusions that prevented vanadium from being leached from the pellets. Therefore, 1200 °C was the optimal roasting temperature.

Figure 6c shows that when the roasting time was less than 2 h, the leaching effect of vanadium was affected by time because the solid-phase reaction of pellets occurred from the outside to the inside. When the roasting time was too short, the oxidation reaction of $V^{3+}$ into $V^{5+}$ was incomplete, making it difficult for low-valent vanadium to react with the sulfuric acid solution that remained in the pellets. This lead to a poor acid leaching effect. As the roasting time increased from 0.5 h to 2 h, the vanadium leaching rate increased rapidly to 66.01%. However, as the roasting time increased to 3 h, the leaching effect of vanadium decreased slightly. The oxidation of vanadium in the pellets was more complete at this point, but the low melting point of the calcium silica–magnesium salts produced hindered the leaching of vanadium. As the roasting time increased, the compressive strength of the pellets continued to rise and reached a maximum at 2 h. The solidification of pellets required a certain reaction time, and when the roasting time was too long, the pellets underwent over-melting and were bonded to each other, which reduced their compressive strength. Therefore, the optimal roasting time was 2 h.

Figure 6d shows that upon increasing the bentonite addition amount, the compressive strength of the pellet continually rose, and the vanadium leaching rate decreased. At 0.2% bentonite, the pellet strength was 2847 N, and the vanadium leaching rate was 70.98%. At 1% bentonite, the pellet strength increased to 3417 N, and the vanadium leaching rate decreased to 64.31%. Upon further increasing the bentonite content, the combination between the particles in the pellet was denser, the strength of the pellet compressive strength continually rose, and the leaching effect was worse. Because of this, the optimal bentonite addition amount was 1%.

The reactions occurring in the pellets during roasting are shown in Equations (1)–(14). Figure 7 shows the Gibbs free energy of reactions (1)–(14) in the range of 100–1300 °C. The relevant data were calculated using HSC 6.0 software (Ottokump Research Center, Uusimaa,

Finland). Reaction (9) shows the reaction equation for the thermal decomposition of calcium hydroxide, which displayed a negative Gibbs free energy at 500 °C, indicating that calcium hydroxide began to decompose and form calcium oxide. The other reactions showed negative Gibbs free energies in this temperature range, indicating that these reactions were thermodynamically feasible. Reactions (4), (6), and (11) show the conversion of $V^{3+}$ to $V^{5+}$, and reactions (3), (7), (8), and (12)–(14) show the reaction of vanadium pentoxide with calcium oxide and magnesium oxide to form calcium vanadate and magnesium vanadate. Reaction (5) shows the reaction of silicon dioxide with calcium oxide and magnesium oxide to form silicate, which is detrimental to the leaching of vanadium and should be avoided in the roasting process.

$$4FeTiO_3 + O_2 = 2Fe_2O_3 + 4TiO_2 \quad (1)$$

$$Fe_2O_3 + TiO_2 = FeTiO_5 \quad (2)$$

$$V_2O_5 + 2CaO = Ca_2V_2O_7 \quad (3)$$

$$2V_2O_3 + O_2 = 2V_2O_4 \quad (4)$$

$$CaO + MgO + 2SiO_2 = CaMgSi_2O_6 \quad (5)$$

$$Al(s) \rightarrow Al^{3+} + 3e^- \quad (6)$$

$$V_2O_5 + 2MgO = Mg_2V_2O_7 \quad (7)$$

$$V_2O_5 + CaO = Ca(VO_3)_2 \quad (8)$$

$$Ca(OH)_2 = CaO + H_2O \quad (9)$$

$$4Fe_3O_4 + O_2 = 6Fe_2O_3 \quad (10)$$

$$2V_2O_4 + O_2 = 2V_2O_5 \quad (11)$$

$$V_2O_5 + MgO = Mg(VO_3)_2 \quad (12)$$

$$V_2O_5 + 3MgO = Mg_3(VO_4)_2 \quad (13)$$

$$V_2O_5 + 3CaO = Ca_3(VO_4)_2 \quad (14)$$

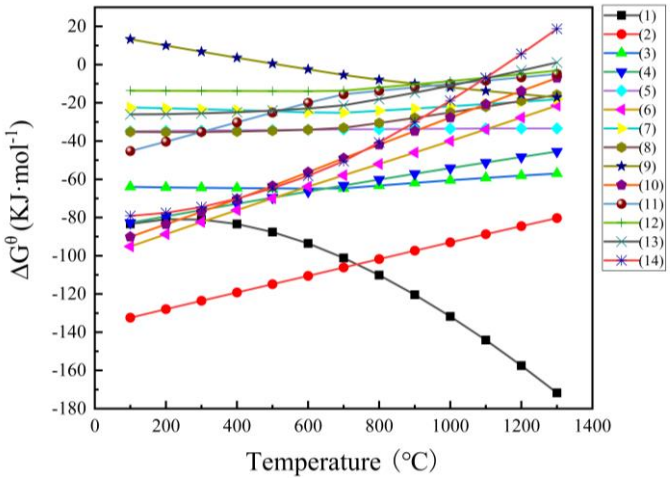



**Figure 7.** ΔG$^{θ}$-T diagram of possible chemical reactions.

Figure 8 shows the XRD patterns of iron ore concentrate pellets after roasting at different temperatures, in which iron mainly existed as $Fe_3O_4$. After roasting, iron was oxidized, and divalent iron was transformed into trivalent iron. The diffraction peaks of $Fe_2TiO_5$ appeared, which is the product of the reaction between $Fe_2O_3$ and $TiO_2$. When the roasting temperature reached 1300 °C, a diffraction peak of silicate appeared. This compound inhibited the consolidation of pellets and vanadium leaching.

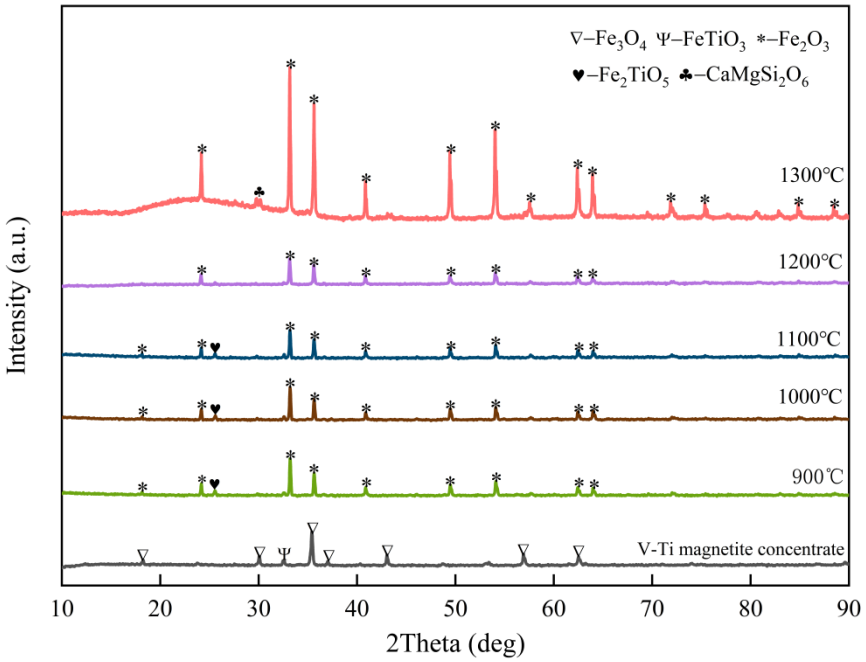



**Figure 8.** Pellet samples under different conditions.

### *3.4. Acid Leaching Experiments*

The effect of acid leaching process parameters on the pellet ferrovanadium leaching rate was investigated under the optimal pelletizing and roasting conditions, and the results are shown in Figure 9. We adjusted the MgO/(Ca(OH)$_2$+MgO) mass ratio to 50%, roasting temperature to 1200 °C, roasting time to 2 h, and added 1% bentonite. The leaching temperature was 60 °C, the leaching time was 60 h, and the liquid–solid ratio was 2:1.

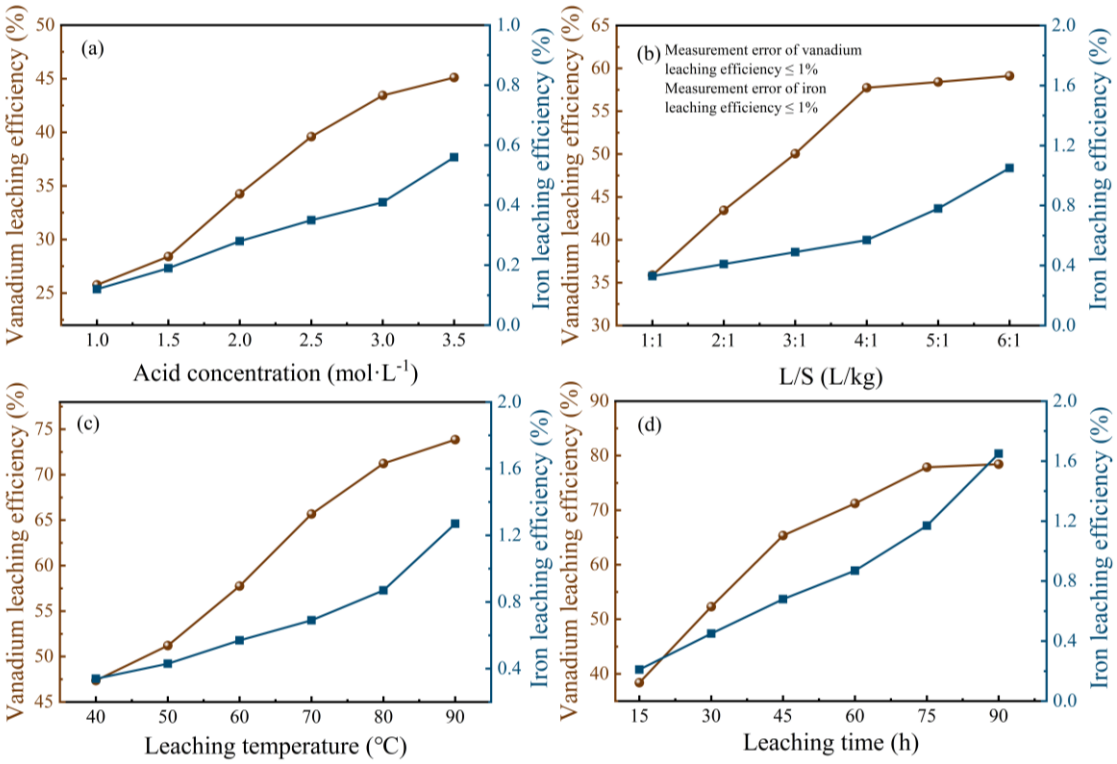



**Figure 9.** Influence of leaching conditions on leaching rate of iron vanadium: (**a**) the effect of acid concentration, (**b**) the effect of L/S, (**c**) the effect of leaching temperature, (**d**) the effect of leaching time.

Figure 9a shows that upon increasing the acid concentration, the vanadium and iron leaching rates all rose and slowed down above 3 mol/L. Upon increasing the sulfuric acid concentration, the concentration of $SO_4^{2-}$ in the solution was too high, and the calcium sulfate generated by the rapid calcification reaction on the surface of the pellet wrapped the pellet. This hindered further reaction between calcium vanadate and sulfuric acid inside the pellet and decreased the leaching rate of vanadium. The pellets were also cracked and broken, making it easier for unoxidized $Fe^{2+}$ to react in the acid solution, increasing the iron leaching rate and decreasing the iron grade of the pellets after leaching. Therefore, to reduce the acid consumption while also reducing the iron leaching, the optimal sulfuric acid concentration was 3 mol/L.

Figure 9b shows that the vanadium leaching rate increased with the liquid-to-solid ratio, reaching a maximum of 57.75% when the liquid-to-solid ratio was 4:1. The vanadium leaching rate did not greatly increase when the liquid-to-solid ratio continued to increase due to the consumption of more sulfuric acid. The vanadium concentration in the solution decreased further, which increased the difficulty of subsequent purification and enrichment. The iron leaching rate was only 0.57% at a liquid-to-solid ratio of 4:1, indicating that vanadium could be selectively separated from iron sulfuric acid leaching. Therefore, to reduce acid consumption while also reducing the leaching of iron, the optimal liquid–solid ratio was 4:1.

Figure 9c shows that the leaching rate of vanadium increased sharply from 47.36% to 73.86% with the temperature, while the leaching rate of iron increased slightly from 0.34% to 1.27%. If the temperature continued to rise, the sulfuric acid solution reacted violently with the surface of the pellet to form an inner and outer layer that made reactions inside the pellet difficult to proceed. The acid concentration dropped sharply due to the evaporation of a large amount of solution, which led to excessive acid loss and higher energy consumption. The breakage of the pellets dislodged and accumulated particles at the bottom of the solution, which hindered the subsequent process. Finally, 80 °C was determined to be the optimal leaching temperature.

Figure 9d shows that the leaching rate of ferrovanadium continuously increased with time. The acid solution first reacted with the surface of the pellet, and as the leaching process proceeded, a reaction also occurred inside the pellet due to osmosis. The optimal rate was reached at 75 h, at which time the reactions of $V^{5+}$ and $SO_4^{2-}$ in the pellet were more complete. The vanadium leaching rate was 77.86%. Continuing to increase the acid leaching time did not greatly increase the vanadium leaching rate, but the iron leaching rate increased. Therefore, the optimal leaching time was determined to be 75 h. Compared with the calcium roasting process for vanadium extraction, the addition of $Ca(OH)_2$ was reduced, the vanadium leaching efficiency was improved by 3.35%, and the generation of calcium sulfate during the acid leaching process was reduced [35].

Roasting formed pellets with different sizes. Table 2 shows the percentage of roasted pellets of different sizes from 8 to 20 mm.

**Table 2.** Percentage of pellets of different size specifications.

| Pellet Diameter (mm) | 8~12 | 12~16 | 16~20 |
|---|---|---|---|
| Percentage (%) | 33 | 58 | 9 |

The conditions for pelletizing were 80% iron concentrate with a particle size of −0.074 mm, and the pelletizing time was 20 min. The roasting conditions were MgO/(Ca $(OH)_2$+MgO) mass ratio of 50%, roasting temperature of 1200 °C, roasting time of 2 h, and addition of 1% bentonite. The leaching conditions were sulfuric acid concentration of 3 mol/L, liquid–solid ratio of 4:1, leaching temperature of 80 °C, and leaching time of 75 h. The relationship between pellet diameter, vanadium leaching rate, and compressive strength was studied. The experiments were carried out by heating and stirring pellets of different sizes in three groups in a beaker at a constant temperature according to their specifications. The results in Figure 10 show that the highest vanadium leaching rate of 8–12 mm diameter pellets reached 79.29%, and the highest compressive strength of 12–16 mm diameter pellets was 596 N. When the total mass of pellets was constant, the surface area of small pellets was larger than that of large pellets. This provided smaller pellets with a greater contact area with sulfuric acid, allowing for a more complete and rapid reaction rapid during acid leaching. The interior of the larger pellets was more difficult to oxidize during roasting, which resulted in the incomplete oxidation of some vanadium. This made it more difficult for sulfuric acid to react with the pellets during acid leaching. Therefore, during the pelletizing stage, the optimal pellet diameter range was 12–16 mm.

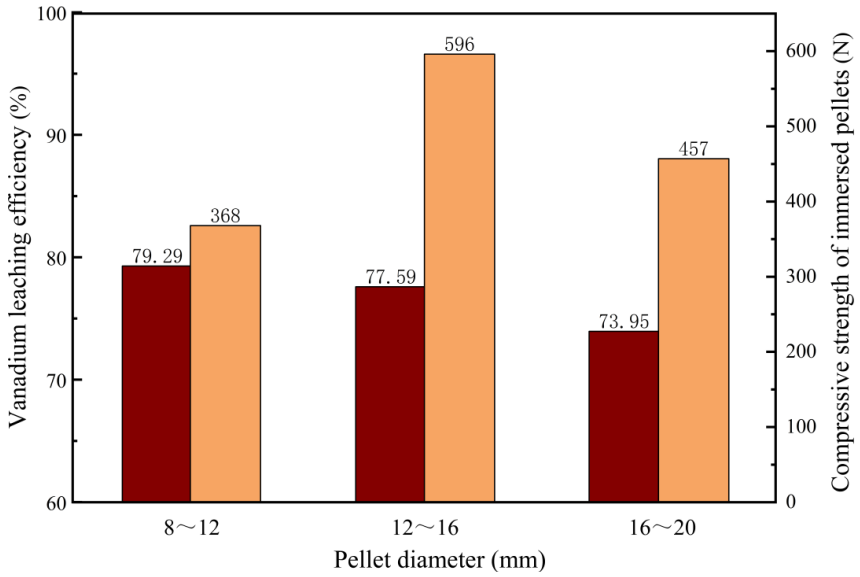



**Figure 10.** Effect of calcined pellet size on vanadium leaching rate and compressive strength of pellets after leaching.

### 3.5. Characterization of the Pellets

The pellets were acid-dipped and washed to remove sulfuric acid and other substances from their surface and then placed on the ground to dry naturally before being loaded into a crucible and roasted in a muffle furnace at 1200 °C for 20 min to obtain the final pellets. Figure 11 reflects the compressive strength of the pellets obtained at different stages. Under the optimal conditions (the conditions for pelletizing were 80% iron concentrate with a particle size of −0.074 mm, and the pelletizing time was 20 min; the roasting conditions were MgO/($Ca(OH)_2$+MgO) mass ratio of 50%, roasting temperature of 1200 °C, roasting time of 2 h, and addition of 1% bentonite), the pellet strength was 3375 N after one roasting. After acid leaching (the sulfuric acid concentration was 3 mol/L, the liquid–solid ratio was 4:1, the leaching temperature was 80 °C, and the leaching time was 75 h), the pellet strength decreased to 563 N. After secondary roasting (roasting temperature of 1200, roasting time of 20 min), the pellet strength was 2578 N, which satisfied the strength requirement of iron making.

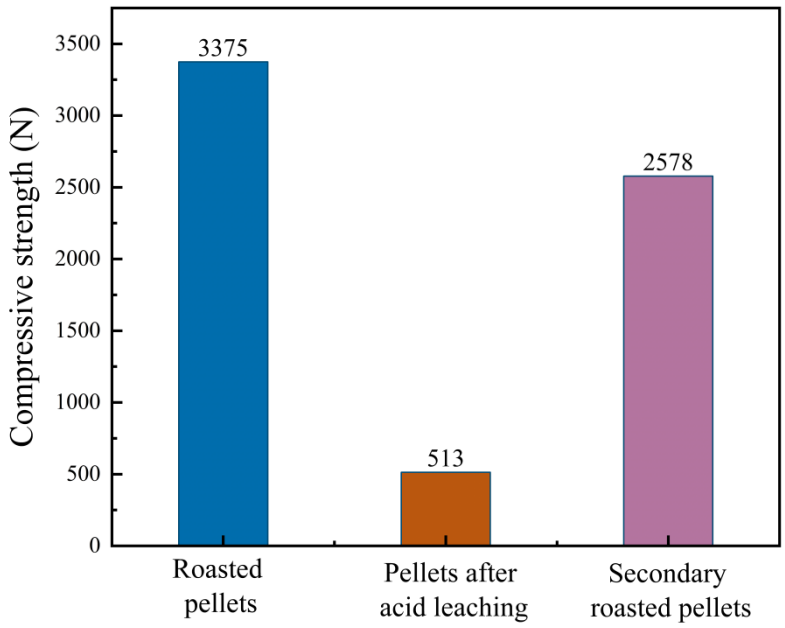



**Figure 11.** Roasted pellets, immersed pellets, and compressive strength of secondary pellets.

SEM-EDS analysis of the raw ore, roasted pellets, pellets after acid leaching, and secondary roasted pellets was carried out. Figure 12a shows that the distributions of vanadium and iron were highly correlated, indicating that vanadium and iron existed as a compound, while the raw ore contained less magnesium and calcium and was more dispersed. In Figure 12b, the distributions of vanadium and iron were different and overlapped with areas containing calcium and magnesium, indicating that after roasting, vanadium formed magnesium vanadate and calcium vanadate. Figure 12c shows that the pellets after acid leaching contained an uneven distribution of small amounts of vanadium, calcium, and magnesium. The distribution of sulfur overlapped with that of calcium. Figure 12d shows that vanadium was sparsely distributed, indicating that most vanadium entered the acid solution after acid leaching, while the distribution of sulfur was reduced. This indicates that most sulfur was removed after secondary roasting.

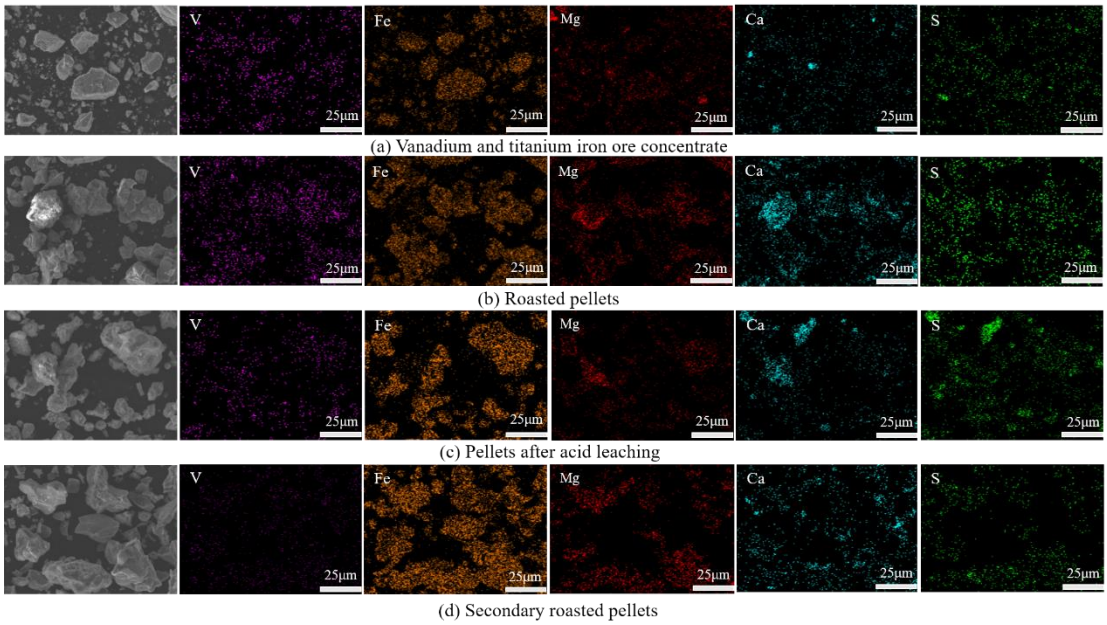



**Figure 12.** Electron microscopic images of raw ore, roasted pellets, leached pellets, and second roasted pellets.

Table 3 shows the ICP analysis of the secondary roasted pellets containing 58.10% Fe, 0.06% V, and 0.02% S. After vanadium extraction, some material in the pellet was leached due to a reaction with the sulfuric acid solution. Therefore, the pellet iron grade rose after vanadium extraction, which promoted subsequent iron smelting. A small amount of vanadium remained in the pellet because it was incompletely oxidized during roasting, and the resulting calcium vanadate remained encapsulated in the pellet. The sulfur content of the pellets was low, indicating that roasting removed sulfur from the pellets.

**Table 3.** Chemical composition of vanadium titanium magnetite concentrate, pellets after acid leaching, and pellets after secondary roasting.

| Element | Fe | Ti | Si | Ca | Mg | V | Na | S |
|---|---|---|---|---|---|---|---|---|
| Content (wt.%) | 58.10 | 8.80 | 2.28 | 0.95 | 0.61 | 0.06 | 0.04 | 0.02 |

### *3.6. Economic Analysis*

At present, the price of $V_2O_5$ is about 100,000 CNY/ton, and the leaching rate of vanadium and vanadium by wet extraction from vanadium titanium iron concentrate is >70%. Treating 1 ton of vanadium titanium iron concentrate can produce approximately 4.0 kg of $V_2O_5$, bringing about economic benefits of about CNY 400. The amount of drugs required to process 1 ton of vanadium titanium iron concentrate: (1) The amount of sulfuric acid used: 50 L/ton; (2) Dosage of flocculant: 3.33~4.44 g/ton; (3) Dosage of gelatin: 25 g~33.33 g/ton; (4) Dosage of $Ca(OH)_2$: 10 kg/ton; (5) MgO dosage: 10 kg/ton; (6) The dosage of bentonite is 10 kg/ton. A total of 49.1 CNY/ton. In addition, in terms of labor costs, repair costs, depreciation costs, water and electricity costs, and other expenses (including the cost of vanadium precipitation), the cost of processing 1 ton of pellets is approximately CNY 240. Therefore, the gross profit brought to the enterprise by processing 1 ton of vanadium titanium iron concentrate is about CNY 110.9.

## 4. Conclusions

For a vanadium–titanium magnetite concentrate, a pellet calcium–magnesium complex roasting method for leaching vanadium was proposed. The pelletizing, roasting, and acid leaching processes were investigated. While improving the vanadium leaching effect,

the pellet performance was further investigated to reduce the influence of the vanadium extraction process on the pellet performance, and the following conclusions were obtained.

The optimal pelletizing conditions were an 8 min grinding time, 80% iron ore concentrate −0.074 mm particle size, bentonite addition ≥0.7%, and 20 min pelletizing time. Under these conditions, the raw pellet drop strength, compressive strength, and bursting temperature were 5.1 times/each, 50.7 N, and 505 °C, respectively, which met roasting requirements.

The optimal roasting conditions for the pellets were a $MgO/(Ca(OH)_2+MgO)$ mass ratio of 50%, temperature of 1200 °C, time of 2 h, and bentonite addition amount of 1%. The compressive strength of pellets produced under these conditions reached 3375 N, and the vanadium leaching rate was 64.31%. The pellet calcium and magnesium complex roasting leaching kinetics were improved, and the subsequent vanadium leaching effect was enhanced.

The optimal conditions for acid leaching were a sulfuric acid concentration of 3.0 mol/L, a liquid-to-solid ratio of 4:1, a leaching temperature of 80 °C, and a time of 75 h. Under these conditions, the leaching rate of vanadium reached 77.86%, while the leaching rate of iron was only 1.17%. The pellet iron grade increased by 6.1% after leaching. After secondary roasting, the pellet strength reached 2578 N, which met the strength requirements for iron making.

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