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Calcium recovery from waste carbide slag via ammonium sulfate leaching system

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ABSTRACT

Waste carbide slag (WCS) is a typical industrial solid waste with high calcium content, which shows highly potential in preparation of CaCO₃ by CO₂ mineralization technology. This study demonstrated the feasibility of efficient calcium leaching from WCS using ammonium sulfate ((NH₄)₂SO₄) under mild conditions (\leq 40 °C , 0.1 MPa). Nearly 90% calcium was converted into calcium sulfate dihydrate (CaSO₄·2H₂O) in about 15 min, and after impurity separation the CaSO₄·2H₂O with about 90% whiteness and 94% purity was effectively collected. In addition, a surface coverage kinetics model suitable for this leaching system was proposed. It was found that, kinetics behavior followed the chemical reaction control mechanism within the first minutes and then switched to the product islands diffusion-control along with CaSO₄·2H₂O crystallization. Accordingly, calcium leaching in (NH₄)₂SO₄ system could be reinforced by readjusting S/L after reaching equilibrium. This process provides a potential path for the resource treatment of industrial solid wastes such as calcium carbide slag and desulfurization gypsum.

1. Introduction

The reduction of anthropogenic carbon emissions is critical for mitigating global warming. Carbon capture and utilization (CCU) is a promising technique for CO_2 mitigation. Mineral carbonation has the potential to permanently sequester CO_2 by combining alkaline earth metals (primarily Ca and Mg) with CO_2 to form carbonates.

Waste carbide slag (WCS), containing nearly 85 wt% CaO is a solid waste in the production of polyvinyl chloride (PVC), with an annual yield of ~ 5.6×10^7 t/y in the world (Zhang et al., 2016). Besides the occupation of a large amount of land, long-term open storage of WCS also causes serious environmental concerns ranging from groundwater pollution to soil alkalization (Jimoh et al., 2016; Zhang et al., 2016). The single of mineral compositions in WCS such as calcium hydroxide (Ca (OH)₂) and calcium oxide (CaO) have a high potential for CO₂ fixation. Nowadays, WCS is primarily used as a raw material in cement manufacture in China. It is also feasible for WCS to replace the hydrated lime in the desulfurization process (Li et al., 2015). Furthermore, previous research (Li et al., 2022; Y. Wang et al., 2020) demonstrated that WCS could be employed as a calcium source to prepare ultrafine calcium carbonate (CaCO₃) via CO₂ mineralization. The ultrafine CaCO₃ could

be utilized as a filler material in paper, plastics and adhesives owing to its unique particle size and morphology (Chen and van de Ven, 2016; Thenepalli et al., 2015). However, it is relatively easy for the pure calcium-based materials such as CaO and Ca(OH)₂ to prepare CaCO₃ by CO₂ mineralization. And considering the separation of calcium components and impurities in WCS, it is an essential step to leaching process in the entire CaCO₃ preparation process.

The effective leaching of calcium components is a critical issue in preparing ultrafine CaCO₃ particles from WCS. Various types of strong acids such as HCl, HNO₃, and H₂SO₄ showed a relatively high leaching efficiency (Maroto-Valer et al., 2005; Teir et al., 2007). Moreover, the weak acid like acetic acid combined with organic solvent tributyl phosphate (TBP) was used as a calcium leaching medium to effectively extract the calcium ions from steelmaking slag (Maroto-Valer et al., 2005). Nowadays, considering the leaching efficiency and capital cost, the recycled ammonium salts (He et al., 2016), including NH₄NO₃, CH₃COONH₄ or NH₄Cl were employed to extract calcium from waste slag. It was found that approximately 70% calcium was selectively extracted within 1M CH₃COONH₄, NH₄Cl and NH₄NO₃ solutions at a solid to liquid ratio of 5–50 g/L under ambient conditions (Jo et al., 2014; Said et al., 2013). Furthermore, pH swing technology extracted

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nearly 100% reactive components (Ca²⁺, Mg²⁺) from feedstocks with 1.4 M NH₄HSO₄ in 3 h at 100 °C (Wang and Maroto-Valer, 2011). Multiple crystal phase transformations of calcium contribute to controlling the particle size of CaCO₃. Research (Y. Wang et al., 2020) had shown that calcium leaching efficiency could be significantly increased with the help of the coordination effect of citrate anions, which also displayed a strong surface effect during the nano-sized CaCO₃ crystallization. Recently, the thermal reduction technology of multi stage precipitation was proposed, in which the blast furnace slag was firstly roasted with (NH₄)₂SO₄ at 300–450 °C to convert the calcium component into sulfates, and then carbonated with NH₄HCO₃/(NH₄)₂CO₃ solution at relatively mild conditions (Hu et al., 2017; Wang et al., 2018).

The product of insoluble calcium sulfate dihydrate (CaSO₄·2H₂O) was the important raw material for the preparation of ultrafine calcium carbonate had attracted much attraction (B. B. Wang et al., 2021). Considering the low energy consumption and recycling economy, a previous study proposed and verified the feasibility of employing $(NH_4)_2SO_4$ as a recycling leaching medium to finally prepare CaCO₃ by CO₂ mineralization (Liu et al., 2021). Furthermore, to improve the calcium conversion ratio of the entire process, the kinetics behavior of calcium leaching with $(NH_4)_2SO_4$ solution is an urgent to figure out. The metal leaching was either controlled by product layer diffusion or through a chemical reaction or a combination of these two models (Bao et al., 2017; T. J. Wang et al., 2017). It was revealed that the feedstock with smaller grain size showed a higher mass transfer rate, resulting in higher leaching efficiency (Said et al., 2013). Additionally, the calcium leaching behavior from waste slag was also evaluated by shrinking core model. In the liquid-solid-liquid leaching system, the typical shrinking core model could well describe the influence of the product layer in a solid-liquid multi-phase reaction (Liu et al., 2014; Rao et al., 2015; J. T. Wang et al., 2017; Zhong et al., 2020). Simultaneously with the calcium ions leaching, uniform "product layer" was formed to wrap around the reactant particles, preventing the further reaction and achieving a maximum conversion. However, in solid-liquid-solid leaching system, the calcium leaching from WCS with (NH₄)₂SO₄ solution involved calcium ions leaching and the formation of insoluble gypsum. Thus, the conventional shrinking core model is no longer applicable and research on reaction kinetics under relatively milder conditions in this leaching system is also significant.

In this study, we employed $(NH_4)_2SO_4$ solution to extract calcium from WCS and the effects of key parameters on calcium leaching kinetics were investigated systematically. The results will make a lot of sense for calcium recovery from industrial solid waste.

2. Experimental

2.1. Materials

WCS was obtained from Beiyuan Chemical Group Co., Ltd, Shanxi, China. All WCS samples were pretreated in an oven at a temperature of 80 °C until the weight remained unchanged. Subsequently, the slag sample was crushed and sieved through 150 μ m. The pretreated WCS should be stored in a vacuum dryer to prevent the reaction with CO₂ in the air. The chemical composition was determined by X-ray fluorescence (XRF, Panalytical PW2400), the results were listed in Table 1. In addition, an alkyl complex salt (OBS) as collector for impurity separation was synthesized through oleate and alkylbenzene sulfonate under mild system. All the raw materials (oleate, alkylbenzene sulfonate, sodium silicate (SS), (NH₄)₂SO₄) were analytical grade, purchased from Sigma-Aldrich. The crystalline phase analysis results in Fig. S1 showed that the major mineral phases in WCS were calcium hydroxide (Ca(OH)₂) and calcite (CaCO₃). Notably, the CaCO₃ was probably formatted by the naturally carbonized in open stacking. In addition, the contents of calcium components in WCS were determined using a thermogravimetric method. As we all known that the thermal decomposition temperature of CaCO₃ and Ca(OH)₂ was occurred at the range of 600–850 °C and 350–550 °C, respectively. It could be seen in Fig. S2 that 76.38 wt% Ca (OH)₂, 9.23 wt% CaCO₃ and 20.03 wt% of free CaO was calculated basing on the weight loss of H₂O and CO₂.

2.2. WCS leaching

The leaching process was carried out in a 250 mL three-necked glass flask reactor immersed in a water bath, and the temperature was constantly controlled within the range of 25-80 °C. In addition, it was also equipped with a digital controlled mechanical stirrer, a thermometer and a water-cooled condenser to minimize solution loss due to evaporation (Fig. 1). In each experiment, 10 g of WCS was added to a definite concentration of agitated (NH₄)₂SO₄ solution, which was used as a leaching agent at a certain temperature. The solutions were stirred vigorously at 800 r·min⁻¹ throughout the experiment. The calcium conversion ratio was determined by taking a 1.0 mL slurry sample using a pipette, filtered through a membrane of 0.22 µm pore size at selected time intervals. After a period of time, 100 ml of the suspension was transferred to a 250 mL micro-column cell for flotation. OBS was used as the collector of CaSO₄·2H₂O and SS was added as the inhibitor to prevent the entrainment. Finally, the float product was filtered, washed with pure water, and dried at 65 °C for 24 h.

2.3. Measurement of calcium conversion ratio

Since the CaSO₄·2H₂O is insoluble in an aqueous solution, and it could be found in the leaching solution and solid phases. The Ca²⁺ concentrations in the leaching solution and solid phase were measured to calculate the calcium conversion ratios under various leaching conditions. The calcium conversion ratio x (%) was calculated by the equation (1):

$$x(\%) = \frac{C_{Ca^{2+}} \times V + m_{sp} \times w'_{Ca}}{m_{CS} \times w_{Ca}} \times 100$$
(1)

 CCa^{2+} is the concentration of calcium ions in the solution sampled at an interval time, V is the volume of the solution in the reactor, m_{sp} is the mass of leaching solid phase, w'_{Ca} is the mass fraction of Ca in the form of



Fig. 1. Schematic diagram of the leaching and micro-flotation process.

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Chemical composition of WCS.

1									
WCS	CaO	SiO ₂	Al_2O_3	SO_3	SrO	Na ₂ O	Fe ₂ O ₃	MgO	Others
Compositions/wt%	83.0	3.7	1.31	0.77	0.21	0.19	0.17	0.15	10.5

CaSO₄·2H₂O. m_{cs} represents the mass of WCS used in the experiment, w_{Ca} is the mass fractions of Ca in WCS.

2.4. Characterizations and measurements

WCS was firstly digested into solution phase by a microwave digestion instrument (Multiwave 3000, Anton Paar), and then the maximal Ca^{2+} content in aqueous solutions was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Thermal Fisher). The calcium ion concentration of the filtrate samples was determined by cation chromatograph with Dionex IonPac CS17 Analytical Column (4 \times 250 mm). The calcium content in the filter cake sample was determined via thermogravimetric analysis (TGA, Mettler), which was carried out in a nitrogen atmosphere at a heating rate of 10 °C/min. The scanning electron microscope (SEM, SU-8010, Hitachi) was used to characterize the microstructure of the solid samples. The crystalline phase was examined with X-ray diffraction (XRD, Analytical X-ray BV X'pert-MPD, Philips), at 40 kV and 25 mA in the range 20 from 5° to $90^\circ.$ The chemical structure of samples was identified with Fourier transform infrared spectroscopy (FTIR) (Tensor-27, Bruken) by KBr pellet method in the range of 4000–400 cm^{-1} at a resolution of 4 cm^{-1} .

2.5. Reaction kinetic model

The WCS leaching process with (NH₄)₂SO₄ solution involved the calcium ions leaching and the crystallization of CaSO4·2H2O with lower solubility, which was consistent with the assumptions of carbonation reaction. The surface coverage model was always used to simulate CO₂ carbonation including leaching-precipitation using different alkaline solid wastes (Chen et al., 2020; Liu et al., 2002; Shih et al., 1999). Fig. 2 depicted a schematic diagram of the leaching mechanism based on the surface coverage model. The hypothesis of the surface coverage model is that the reaction is controlled by chemical reaction on the particle surface and that the surface reaction only occurs on the reactive surface sites which are not covered by product. Besides, it is assumed that the surfaces of the reactant particles are uniform and all sites are equal. Subsequently, the monolayer product gradually covers the particle surface and the reacting surface area decreases with the deposition of solid product. In this study, the calcium hydroxide was first dissolved on the surface of WCS during the leaching process, and then the ionized calcium ions and sulfate ions quickly formed the calcium sulfate. Since the calcium sulfate is insoluble, the product island of calcium sulfate is gradually attached to the surface of the particles. According to this model, the leaching reaction reaches a maximum conversion when its reacting surface is fully covered by the product.

Therefore, the reaction rate of solid per unit total surface area (r_s) was mainly controlled by the formation and distribution of the product islands covered by the surface, and it could be expressed as (Liu et al., 2002; Pan et al., 2014; Shih et al., 1999):

$$r_s = k_s \cdot \Phi \tag{2}$$



Fig. 2. Schematic diagram of leaching mechanism of WCS in ammonium sulfate solution based on the surface coverage model.

Where, k_s (mol·min⁻¹m⁻²) was the apparent rate constant of the chemical reaction, which was a function of temperature, concentrations of reacting species, and Φ represented the proportion of active surface sites that were not covered by the product.

For a solid reactant consisting of single particles or if the conversion of the solid was low, the conversion ratio of the solid could be expressed as (Liu et al., 2002; Shih et al., 1999)

$$\frac{dX}{dt} = r_s \cdot s_g \cdot M = k_s \cdot \boldsymbol{\Phi} \cdot s_g \cdot M \tag{3}$$

Where, X was the reaction conversion, $S_g(\mathbf{m}^2 \cdot \mathbf{g}^{-1})$ was the initial specific surface area of the solid and M (g·mol⁻¹) was its molecular weight.

So, the rate of the variation of active surface sites (ϕ) that changed with time could be expressed as (Liu et al., 2002; Shih et al., 1999)

$$\frac{d\Phi}{dt} = r_s \cdot k_p \cdot \Phi^{n-1} \tag{4}$$

Where, Φ^{n-1} was a function representing the way of product deposition and k_p (m²·mole⁻¹) was a proportional constant, which reflected the fraction of the reactive surface and not covered by the reaction product. Eq. (4) could be integrated to get Φ as a function of time (Shih et al., 1999)

$$\Phi = [1 - (1 - n)k_1k_2t]^{\frac{1}{1 - n}}, n \neq 1$$
(5)

where,

$$k_1 = k_s s_g M, k_2 = k_p / s_a M \tag{6}$$

By substitution of Eq. (5) into Eq. (3), one could integrate Eq. (3) to obtain the relation between conversion and time (Shih et al., 1999)

$$X = \left[1 - \left[1 - (1 - n)k_1k_2t\right]^{(2-n)/(1-n)}\right] / (2 - n)k_2, \ 1 < n < 2$$
(7)

As shown in Eq. (7), k_1 and k_2 were the main kinetic parameters affecting the calcium conversion, corresponding to the changes of k_s and k_p , which were closely related to reaction parameters such as temperature, concentration and solid-solution ratio (S/L). Thus, the overall experiments investigated the effect of those conditions on the calcium leaching kinetic behaviour.

3. Results and discussion

3.1. Calcium leaching mechanism

The possible reactions involved in the calcium leaching in this system are as follows:

$$Ca(OH)_{2} + (NH_{4})_{2}SO_{4} \rightarrow CaSO_{4} \cdot 2H_{2}O\downarrow + 2NH_{3}\uparrow$$
(8)

$$CaO + (NH_4)_2SO_4 + H_2O \rightarrow CaSO_4 \cdot 2H_2O \downarrow + 2NH_3 \uparrow$$
(9)

$$CaCO_{3} + (NH4)_{2}SO_{4} + H_{2}O \rightarrow CaSO_{4} \cdot 2H_{2}O \downarrow + 2NH_{3}\uparrow + CO_{2}\uparrow$$
(10)

The $(NH_4)_2SO_4$ aqueous solution was acidic. Therefore, the reactions (8) and (9) were the major reactions in the leaching process. Ca ions in $(NH_4)_2SO_4$ solutions could easily combine with sulfate ions to form calcium sulfate, which has a lower solubility. Due to the lower solubility of calcium carbonate than that of CaSO₄·2H₂O, it was reasonable to propose Eq. (10) as a secondary dissolution reaction.

Generally, it was accepted that the fine particle size had more active sites and a higher surface area, which promoted the particle surface contact with reactants, resulting in better mass transfer and higher conversion ratio (Rao et al., 2015). To figure out the effect of the particle size distribution (PSD) on calcium conversion in this system, the WCS was sieved and divided into several size fractions using Tyler standard sieve, and the results were depicted in Fig. 3 Clearly, the reduction in particle size enhanced the calcium conversion ratio significantly. The



Fig. 3. Effect of particle size distribution on the calcium conversion.

calcium conversion ratio was increased sharply from 58 to 85% as the particle size decreased from 150-425 μ m to 75–150 μ m, and the purity of the leaching product (CaSO₄·2H₂O) also had the same changing tendency, which was nearly 90%. However, the calcium conversion ratio was increased indistinctively with a further decreased particle size as it was less than 150 μ m. The smaller the particle size, the larger reaction contact area between Ca(OH)₂ and (NH₄)₂SO₄, which makes the calcium leaching easier. From the kinetics point of view, ions can easily diffuse to the active calcium core through the liquid film and solid-liquid interface, and quickly form a dense product island to prevent the further reaction. This is why the calcium conversion ratio does not increase significantly when the particle size is further reduced to less than 150 μ m. Thus, the WCS with an optimum particle size of 75–150 μ m was adopted in the overall experiments.

3.2. Kinetic analysis

The leaching process from WCS was a multi-phase solid-liquid-solid reaction, and the reaction kinetic could be described by the surface coverage model. The parameter n from Eq. (7) was set between 1.0–2.0 under various conditions, and finally the best value of 1.6 was obtained with the R² value of 0.99, $x = \{1-[1-(-0.6) k_1k_2t]^{(-2/3)}\}/((0.4k_2))$ was plotted with respect to the leaching time. When the product island formed around the surface of calcium component, the diffusion through the product island would be the rate-limited step, preventing further calcium leaching, finally reaching a maximum conversion (Pan et al., 2014). Therefore, in addition to the k_s value, the k_p value was another important kinetic parameter.

Fig. 4 (a-c) presented the model fitting results of WCS leaching under different conditions. Obviously, all the calcium conversion ratio increased monotonically with increasing reaction time, and the reaction was nearly complete after 15 min. The surface coverage model is agreed well with the experimental data, with R^2 values ranging from 0.97 to 0.99. It is indicated that the WCS leaching kinetics behavior is basically consistent with the surface coverage model assumptions. The ionic reaction is the initial rate-limiting step for calcium leaching and eventually switches to the product islands diffusion-control mechanism along with CaSO₄·2H₂O crystallization. The reaction product of CaSO₄·2H₂O is insoluble and formed irregular islands on the surface of the particles, which have a significant effect on the conversion ratio.

As we all known, high temperature can bring a better reactivity and increase the energy for atomic and molecular collisions. The data in Fig. 4 showed that as the temperature increased from 25 °C to 80 °C, the calcium conversion ratio approached 90%. Furthermore, when compared to room temperature (25 °C), the higher reaction temperature could significantly enhance the calcium leaching reaction rate. In this study, the formation of insoluble CaSO₄·2H₂O in (NH₄)₂SO₄ solution system was exothermic, and increased temperature was beneficial to kinetics. However, it can be seen in Fig. 4a that calcium leaching is not particularly sensitive to temperature compared to the effects of other parameters. This might due to the rapid aggregation of product islands (CaSO₄·2H₂O) formed by the vigorous reaction under high temperature (60-80 °C) and preventing (NH₄)₂SO₄ from reaching the reactive zone (Zhong et al., 2020). Generally, the k_s value at higher temperatures was more significant than that of lower temperature, indicating a more rapid leaching rate with a higher temperature. However, the insignificant improvement of k_s value with increasing temperature from 60 to 80 °C in Fig. 4a suggested that higher reaction temperature might result in more



Fig. 4. Comparison of model predictions and experimental data under different conditions (a) temperature, (b) (NH₄)₂SO₄ concentration, (c) S/L ratio.

products being attached on the surface of reactant particles, decreasing the proportion of active surface sites, which was confirmed by the changes of k_p values. The lower k_p value meant a number of products were deposited on the particle surface, preventing further leaching of active calcium components inside the particle.

The concentration and type of ammonium salt solution affected calcium leaching efficiency (Jo et al., 2014). Fig. 4b depicted that, as the (NH₄)₂SO₄ concentration varied from 1.0 to 2.0 mol/L, the calcium conversion ratio rose from 57.94% to 90.72%. However, the calcium conversion significantly reduced with that increased beyond 2.0 mol/L. According to Eqs. (8)-(10), the leaching of calcium was a liquid-solid reaction and the calcium conversion ratio was dependent on leaching kinetics (Cui et al., 2015). The high concentration of (NH₄)₂SO₄ increased the mole ratio of NH_4^+/Ca^{2+} , contributing to improving the mass transfer coefficient and diffusivity, as well as providing the greater driving force to overcome the mass transfer resistance of (NH₄)₂SO₄ diffusion from solution to a solid phase, which was beneficial to improve calcium leaching rate (Huang et al., 2017; Liu et al., 2014). However, a higher concentration might also cause a violent reaction, resulting in the accumulation of many product islands (CaSO₄·2H₂O), thus hindering the reaction eventually. As shown in Fig. 4b, with the increase of the initial $(NH_4)_2SO_4$ concentration from 1.0 to 2.0 mol/L, the k_s value increased, indicating the increase of (NH₄)₂SO₄ concentration accelerated the calcium leaching and the formation of CaSO₄·2H₂O. However, as the (NH₄)₂SO₄ concentration was further increased, a certain amount of CaSO₄·2H₂O quickly accumulated around the reactant, resulting in the inert component hindered ions diffusion after the formation of the product island. This was the reason why k_p at 2.5 mol/L was smaller than 2.0 mol/L.

Fig. 4c demonstrated that both reaction rate and calcium conversion ratio decreased as S/L increased, which was consistent with the changing of k_s and k_p values. Researches (Kavci et al., 2014; Rao et al., 2015; Zhao et al., 2015) showed that the difference of S/L represented the difference of solid-liquid diffusional resistance, the further increase of solid dosage would not only decrease the mole ratio of NH₄⁺/Ca²⁺ but also increase the viscosity of slurry and diffusional mass transfer resistance. In addition, the rate of product deposition on reactant surface ($k_s \cdot k_p$) (Pan et al., 2014) was directly related to calcium leaching steady-state. It could be seen in Table 2, the $k_s \cdot k_p$ was higher with an S/L of 10.5%, indicating that leaching would be faster to reach steady-state with a lower dosage of WCS. Therefore, calcium leaching could be accelerated via reducing the S/L at a certain (NH₄)₂SO₄ concentration.

According to the model assumption, the reaction was occurred on the surface of solid particle, and there was a mass transfer between the solid-liquid interface. The active surface site of calcium component will be gradually covered by the product ($CaSO_4 \cdot 2H_2O$) during the leaching reaction. To further analyze the kinetics mechanisms, the micrographs of the final solid product at different leaching time are obtained under

Table 2

Model parameters with operating conditions for surface coverage model.

the condition of 40 $^\circ C$ with the (NH₄)₂SO₄ concentration of 2.0 mol/L (Fig. 5).

The results show that the reaction occurs on the particle surface, where the CaSO₄·2H₂O crystal phase is generated. As shown in Fig. 5a, the unreacted single particle presents a relatively smooth morphology, while after 5 min (Fig. 5b), exhibiting new characteristic crystal phase (lath-like crystals, length up to 10 μ m) on the surface of particle. Subsequently, the proportion of active surface sites gradually decreases and large amount lath-like crystals assemble on the particle surface (Fig. 5c & d). It was indicated that most of the calcium component has been reacted, as evidenced from the fact that the CaSO₄·2H₂O crystals almost completely cover and this phenomenon is in good agreement with the findings reported in the literature (Fernández Bertos et al., 2004; Pan et al., 2013).

3.3. Activation of leaching

Based on the above kinetic analysis, product islands played a negative role in the calcium leaching process, which could be accelerated via reducing a ratio of S/L. Besides, our previous study (T. T. Wang et al., 2021) also showed that product island affected the ion leaching behavior in the liquid layer and it could be re-activated by rehydration. Therefore, to avoid excessive $(NH_4)_2SO_4$ consumption, it was necessary to explore a higher calcium conversion at a relatively high solid-to-liquid ratio. Herein, the feasibility of calcium leaching enhancement by readjusting S/L was investigated in Fig. 6. Results showed that with an S/L ratio of 15%, the calcium conversion finally reached a relatively low level of ~65% within 15 min. It was noted that calcium conversion was increased to ~90% by re-addition of solution (initial S/L ratio of 10.5%). This verified that calcium leaching in $(NH_4)_2SO_4$ system could be reinforced by readjusting S/L after reaching equilibrium.

3.4. Characterization of the precipitates

The precipitated crystalline phase was examined by XRD analysis. The XRD patterns of the reaction products after leaching for 1, 5, 15, and 30 min under the condition of 40 °C with 2.0 mol/L (NH₄)₂SO₄ concentration were shown in Fig. 7, providing strong evidence for the crystalline phase evolution. As we all known, the diffraction peaks at around $2\theta = 34.1^{\circ}$, 18.0° , 50.8° , and 47.1° were corresponded to the (101), (001), (110), and (102) reflections of Ca(OH)₂, respectively, whereas those at $2\theta = 20.7^{\circ}$, 11.6° , 29.1° , 31.1° , and 33.4° were corresponded to the (-121), (020), (-141), (121), and (051) reflections of CaSO₄·2H₂O, respectively. As the leaching proceeded, the diffraction peaks of Ca(OH)₂ disappeared and were replaced with the characteristic diffraction peaks of gypsum (CaSO₄·2H₂O). After 1 min, the CaSO₄·2H₂O diffraction peaks appeared gradually, indicating that Ca

Conditions			Kinetic parameters			
Temperature °C	S/L ^a (%)	SA ^b (mol/L)	$k_{ m s} imes 10^{-3} { m mol\cdot min^{-1}m^{-2}}$	$k_{ m p} imes 10^3 \ { m m}^2 \cdot { m mole}^{-1}$	$k_{\rm s} \cdot k_{\rm p}$ min ⁻¹	R ²
25	10.5	2.0	0.13541	0.72346	0.09796	0.993
40	10.5	2.0	0.36024	0.74424	0.26811	0.995
60	10.5	2.0	0.53722	0.75493	0.40556	0.998
80	10.5	2.0	0.53375	0.72322	0.38602	0.996
60	17.5	2.0	0.1808	0.29917	0.05409	0.995
60	15.0	2.0	0.28701	0.51923	0.14902	0.977
60	12.5	2.0	0.33275	0.68027	0.22636	0.994
60	10.5	2.5	0.25396	0.68132	0.17303	0.972
60	10.5	1.5	0.26903	0.71397	0.19208	0.996
60	10.5	1.0	0.11606	0.65638	0.07618	0.991

^a Solid-solution ratio.

^b Ammonium sulfate solution concentration.



Fig. 5. SEM analysis of (a) WCS; (b) leaching 5min; (c) & (d) leaching 15min.



Fig. 6. Kinetic optimization experiment by readjusting S/L.

 $(OH)_2$ was partially transformed to $CaSO_4 \cdot 2H_2O$. When the reaction time exceeded 30 min, the pure $CaSO_4 \cdot 2H_2O$ peaks were observed, indicating that $Ca(OH)_2$ was completely transformed to $CaSO_4 \cdot 2H_2O$.

3.5. Purification and recovery of CaSO₄·2H₂O

Based on the above analysis, the calcium component in carbide slag was leached into a new crystalline phase (CaSO₄·2H₂O). Notably, the impurities in carbide slag were also coexisted in the precipitate of CaSO₄·2H₂O. Here, to avoid affecting the further high-value utilization of CaSO₄·2H₂O, the flotation method was employed to finally remove the impurities and the influence of dosage on the separation performance were presented in Fig. 8. It could be seen that the purity and whiteness of CaSO₄·2H₂O were synchronously increased with the increase of collector (OBS) dosage (Fig. 8a). About 94% purity and over 90% whiteness of CaSO₄·2H₂O was obtained when OBS dosage was up



Fig. 7. XRD patterns of the precipitate at different reaction time.

to 0.3 kg/t, indicating that collector prepared by oleate and alkylbenzene sulfonate had a good collecting performance. However, when the content of OBS exceeds 0.3 kg/t, the purity and whiteness of CaSO₄·2H₂O began to decrease, which might result from the entrainment of impurities together with CaSO₄·2H₂O. Thus, considering the yield of CaSO₄·2H₂O, corresponding inhibitor (SS) was needed to assist the flotation. Fig. 8b illustrated that the whiteness of CaSO₄·2H₂O increased from 80% to 91% when inhibitor (SS) dosage increased to 4 kg/t; correspondingly, the CaSO₄·2H₂O purity was increased from 89% to 93.5%. Nevertheless, when the inhibitor (SS) dosage exceeded 4 kg/t, both whiteness and purity of CaSO₄·2H₂O were decreased, which might be resulted from the antifoaming effect of SS.

In order to further visually observe that if there was the impurity layer on $CaSO_4.2H_2O$ surfaces, SEM equipped with EDS was used to directly find the microstructural characteristics and elemental compositions. It could be seen in Fig. 9a, the surface of the $CaSO_4.2H_2O$ was covered with a large number of fine mineral particles, while little of small particles were observed on the surface in Fig. 9b. Meanwhile, the EDS analysis results also showed that main elements in two samples were Ca, S, Al, O, C, and Si elements. While Ca, O, and S elements



Fig. 8. Effect of OBS and SS dosage on the flotation performance (a) OBS (b) SS.



Fig. 9. SEM-EDS analysis of the float production (a) before flotation (b) after flotation.

represented CaSO₄·2H₂O, the Al, O, C, and Si elements were constituent elements for impurities. After flotation, the fine slime on the surface of particles was significantly removed, and the surface of CaSO₄·2H₂O crystals was smooth, which indicated that the flotation method could effectively remove impurity minerals and improve the purity and whiteness of CaSO₄·2H₂O (Sun et al., 2018; J. Wang et al., 2020).

4. Conclusions

In this paper, we systematically researched the influences of critical process parameters on the calcium leaching from waste carbide slag. The results show that nearly 90% of calcium in WCS was converted into $CaSO_4.2H_2O$ in about 15 min at condition of 40 °C, 2.0 mol/L $(NH_4)_2SO_4$, and S/L ratio of 10.5%. Furthermore, the leaching kinetics indicated that the ionic reaction was the initial rate-limiting step for calcium leaching and eventually switched to the product islands diffusion-control mechanism along with $CaSO_4.2H_2O$ crystallization. Consequently, calcium leaching could be accelerated by reducing the solid-solution ratio at a certain $(NH_4)_2SO_4$ concentration. The study provides a potential application to recover the calcium from the industrial by-product of waste carbide slag and gypsum under the ambient conditions.

CRediT authorship contribution statement

Wenxiu Li: Investigation, Formal analysis, Conceptualization, Methodology, Software, Data curation, Writing – original draft, Writing – review & editing. Tao Wang: Project administration, Supervision, Visualization, Writing – review & editing. Yuhang Yang: Resources. Mengxiang Fang: Resources, Writing – review & editing. Xiang Gao: Resources, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix B. Supplementary data

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References

- Bao, W., Zhao, H., Li, H., Li, S., Lin, W., 2017. Process simulation of mineral carbonation of phosphogypsum with ammonia under increased CO2 pressure. J. CO2 Util. 17, 125–136.
- Chen, D., van de Ven, T.G.M., 2016. Flocculation kinetics of precipitated calcium carbonate induced by electrosterically stabilized nanocrystalline cellulose. Colloids Surfaces A Physicochem. Eng. Asp. 504, 11–17. https://doi.org/10.1016/j. colsurfa.2016.05.023.
- Chen, T.L., Jiang, W., Shen, A.L., Chen, Y.H., Pan, S.Y., Chiang, P.C., 2020. CO2 mineralization and utilization using various calcium-containing wastewater and refining slag via a high-gravity carbonation process. Ind. Eng. Chem. Res. 59, 7140–7150. https://doi.org/10.1021/acs.iecr.9b05410.
- Cui, L., Guo, Y., Wang, X., Du, Z., Cheng, F., 2015. Dissolution kinetics of aluminum and iron from coal mining waste by hydrochloric acid. Chin. J. Chem. Eng. 23, 590–596. https://doi.org/10.1016/j.cjche.2014.05.017.
- Fernández Bertos, M., Simons, S.J.R., Hills, C.D., Carey, P.J., 2004. A review of accelerated carbonation technology in the treatment of cement-based materials and sequestration of CO2. J. Hazard Mater. 112, 193–205. https://doi.org/10.1016/j. jhazmat.2004.04.019.
- He, Z., Zhang, Z., Yu, J., Xu, Z., Chi, R., 2016. Process optimization of rare earth and aluminum leaching from weathered crust elution-deposited rare earth ore with compound ammonium salts. J. Rare Earths 34, 413–419. https://doi.org/10.1016/ S1002-0721(16)60042-X.
- Hu, J., Liu, W., Wang, L., Liu, Q., Chen, F., Yue, H., Liang, B., Lu, L., Wang, Y., Zhang, G., Li, C., 2017. Indirect mineral carbonation of blast furnace slag with (NH4)2SO4 as a recyclable extractant. J. Energy Chem. 26, 927–935. https://doi.org/10.1016/j. jechem.2017.06.009.
- Huang, C., Zong, J., Xu, J., Yan, F., 2017. Fabrication of tubular magnesium oxide nanocrystals via combining ammonium sulfate leaching and precipitation method and it's crystal growth behavior. Powder Technol. 320, 80–88. https://doi.org/ 10.1016/j.powtec.2017.07.035.
- Jimoh, O.A., Mahmed, N., Okoye, P.U., Ariffin, K.S., 2016. Utilization of milk of lime (MOL) originated from carbide lime waste and operating parameters optimization study for potential precipitated calcium carbonate (PCC) production. Environ. Earth Sci. 75, 1251.
- Jo, H., Park, S.H., Jang, Y.N., Chae, S.C., Lee, P.K., Jo, H.Y., 2014. Metal extraction and indirect mineral carbonation of waste cement material using ammonium salt solutions. Chem. Eng. J. 254, 313–323. https://doi.org/10.1016/j.cei.2014.05.129.
- Kavci, E., Çalban, T., Çolak, S., Kuşlu, S., 2014. Leaching kinetics of ulexite in sodium hydrogen sulphate solutions. J. Ind. Eng. Chem. 20, 2625–2631. https://doi.org/ 10.1016/j.jiec.2013.12.089.
- Li, W., Huang, Y., Wang, T., Fang, M., Li, Y., 2022. Preparation of calcium carbonate nanoparticles from waste carbide slag based on CO2 mineralization. J. Clean. Prod. 363, 132463 https://doi.org/10.1016/J.JCLEPRO.2022.132463.
- Li, Y., Su, M., Xie, X., Wu, S., Liu, C., 2015. CO2 capture performance of synthetic sorbent prepared from carbide slag and aluminum nitrate hydrate by combustion synthesis. Appl. Energy 145, 60–68.
- Liu, C., Shih, S., Lin, R., 2002. Kinetics of the reaction of Ca(OH)2/ash sorbent with SO2 at low temperatures. Chem. Eng. Sci. 57, 93–104.
- at low temperatures. Chem. Eng. Sci. 57, 93–104. Liu, W., Teng, L., Rohani, S., Qin, Z., Zhao, B., Xu, C.C., Ren, S., Liu, Q., Liang, B., 2021. CO2 mineral carbonation using industrial solid wastes: a review of recent developments. Chem. Eng. J. 416, 129093 https://doi.org/10.1016/j. cej.2021.129093.
- Liu, Z.X., Yin, Z.L., Xiong, S.F., Chen, Y.G., Chen, Q.Y., 2014. Leaching and kinetic modeling of calcareous bornite in ammonia ammonium sulfate solution with sodium persulfate. Hydrometallurgy 144–145, 86–90. https://doi.org/10.1016/j. hydromet.2014.01.011.
- Maroto-Valer, M.M., Fauth, D.J., Kuchta, M.E., Zhang, Y., Andrésen, J.M., 2005. Activation of magnesium rich minerals as carbonation feedstock materials for CO2

sequestration. Fuel Process. Technol. 86, 1627–1645. https://doi.org/10.1016/j. fuproc.2005.01.017.

- Pan, S.Y., Chiang, P.C., Chen, Y.H., Tan, C.S., Chang, E.E., 2014. Kinetics of carbonation reaction of basic oxygen furnace slags in a rotating packed bed using the surface coverage model: maximization of carbonation conversion. Appl. Energy 113, 267–276. https://doi.org/10.1016/j.apenergy.2013.07.035.
- Pan, S.Y., Chiang, P.C., Chen, Y.H., Tan, C.S., Chang, E.E., 2013. Ex Situ CO2 capture by carbonation of steelmaking slag coupled with metalworking wastewater in a rotating packed bed. Environ. Sci. Technol. 47, 3308–3315. https://doi.org/10.1021/ es304975y.
- Rao, S., Yang, T., Zhang, D., Liu, W.F., Chen, L., Hao, Z., Xiao, Q., Wen, J.F., 2015. Leaching of low grade zinc oxide ores in NH4CI-NH3 solutions with nitrilotriacetic acid as complexing agents. Hydrometallurgy 158, 101–106. https://doi.org/ 10.1016/j.hydromet.2015.10.013.
- Said, A., Mattila, H.P., Järvinen, M., Zevenhoven, R., 2013. Production of precipitated calcium carbonate (PCC) from steelmaking slag for fixation of CO2. Appl. Energy 112, 765–771. https://doi.org/10.1016/j.apenergy.2012.12.042.
- Shih, S.M., Ho, C.S., Song, Y.S., Lin, J.P., 1999. Kinetics of the reaction of Ca(OH)2 with CO2 at low temperature. Ind. Eng. Chem. Res. 38, 1316–1322. https://doi.org/ 10.1021/ie980508z.
- Sun, L., Cao, Y., Liao, Y., Ma, Z., 2018. Interaction mechanism between molybdenite and kaolinite in gypsum solution using kerosene as the flotation collector. Minerals 8. https://doi.org/10.3390/min8070304.
- Teir, S., Kuusik, R., Fogelholm, C.J., Zevenhoven, R., 2007. Production of magnesium carbonates from serpentinite for long-term storage of CO2. Int. J. Miner. Process. 85, 1–15. https://doi.org/10.1016/j.minpro.2007.08.007.
- Thenepalli, T., Jun, A.Y., Han, C., Ramakrishna, C., Ahn, J.W., 2015. A strategy of precipitated calcium carbonate (CaCO3) fillers for enhancing the mechanical properties of polypropylene polymers. Kor. J. Chem. Eng. 32, 1009–1022. https:// doi.org/10.1007/s11814-015-0057-3.
- Wang, B., Pan, Z., Cheng, H., Zhang, Z., Cheng, F., 2021. A review of carbon dioxide sequestration by mineral carbonation of industrial byproduct gypsum. J. Clean. Prod. 302, 126930 https://doi.org/10.1016/j.jclepro.2021.126930.
- Wang, J., Dong, F., Wang, Zhaojia, Yang, F., Du, M., Fu, K., Wang, Zhen, 2020. A novel method for purification of phosphogypsum. Physicochem. Probl. Miner. Process. 56, 975–983. https://doi.org/10.37190/PPMP/127854.
- Wang, J., Huang, X., Wang, L., Wang, Q., Yan, Y., Zhao, N., Cui, D., Feng, Z., 2017. Kinetics study on the leaching of rare earth and aluminum from FCC catalyst waste slag using hydrochloric acid. Hydrometallurgy 171, 312–319. https://doi.org/ 10.1016/j.hydromet.2017.06.007.
- Wang, L., Liu, W., Hu, J., Liu, Q., Yue, H., Liang, B., Zhang, G., Luo, D., Xie, H., Li, C., 2018. Indirect mineral carbonation of titanium-bearing blast furnace slag coupled with recovery of TiO2 and Al2O3. Chin. J. Chem. Eng. 26, 583–592. https://doi.org/ 10.1016/j.cjche.2017.06.012.
- Wang, T., Huang, H., Hu, X., Fang, M., Luo, Z., Guo, R., 2017. Accelerated mineral carbonation curing of cement paste for CO2 sequestration and enhanced properties of blended calcium silicate. Chem. Eng. J. 323, 320–329. https://doi.org/10.1016/j. cej.2017.03.157.
- Wang, T., Yi, Z., Guo, R., Huang, H., Garcia, S., Maroto-Valer, M.M., 2021. Particle carbonation kinetics models and activation methods under mild environment: the case of calcium silicate. Chem. Eng. J. 423, 130157 https://doi.org/10.1016/j. cei.2021.130157.
- Wang, X., Maroto-Valer, M.M., 2011. Dissolution of serpentine using recyclable ammonium salts for CO2 mineral carbonation. Fuel 90, 1229–1237. https://doi.org/ 10.1002/cssc.201000441.
- Wang, Y., Ye, B., Hong, Z., Wang, Yonghao, Liu, M., 2020. Uniform calcite mircro/ nanorods preparation from carbide slag using recyclable citrate extractant. J. Clean. Prod. 253, 119930.
- Zhang, D., Li, S., Song, W., Lin, W., 2016. Cyclic CO2 capture performance of carbide slag. Energy Sources, Part A Recover. Util. Environ. Eff. 38, 577–582. https://doi. org/10.1080/15567036.2013.820234.
- Zhao, H., Li, H., Bao, W., Wang, C., Li, S., Lin, W., 2015. Experimental study of enhanced phosphogypsum carbonation with ammonia under increased CO2 pressure. J. CO2 Util. 11, 10–19. https://doi.org/10.1016/j.jcou.2014.11.004.
- Zhong, Y., Shi, T., Chen, Q., Yang, X., Xu, D., Zhang, Z., Wang, X., Zhong, B., 2020. Leaching calcium from phosphogypsum desulfurization slag by using ammonium chloride solution: thermodynamics and kinetics study. Chin. J. Chem. Eng. 28, 208–215. https://doi.org/10.1016/j.cjche.2019.08.006.