RESEARCH ARTICLE

Research on Indirect Carbonation of Two-step Leaching for the Purpose of Utilizing the Alkalinity of Steel Slag

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Abstract

A process that utilizes high alkaline properties of steel slag to promote the carbonation reaction while saving acid and alkali consumption was proposed. The experimental results verified the feasibility of the indirect carbonation process involving acetic acid to carry out the carbonation reaction without the addition of alkali. It was concluded that steel slag has high alkalinity, and the alkaline components of steel slag can be preserved by two-step leaching to contribute to the carbonation reaction. The results show that under the condition of a liquid–solid ratio of 10, the pH of the mixed leachate obtained by leaching with 0.25–1 M acetic acid for steel slag with a particle size of < 38 μm were all above 11.7. At the same time, the calcium ions leaching ratio of the two-step method was also higher than that of the one-step method. In the case of liquid–solid ratio was 20 and acetic acid concentration was 0.25 M, the leaching ratio of calcium ions of one-step method was 28.84%, while the total leaching ratio of the two-step method was 32.18%, which increased by 11.61%. The results of X-ray diffraction analysis of the carbonation products of the two-step method show that the main component of the product was calcite and a small amount of aragonite, which indicates that the two-step method can carry out the carbonation reaction to produce calcium carbonate.
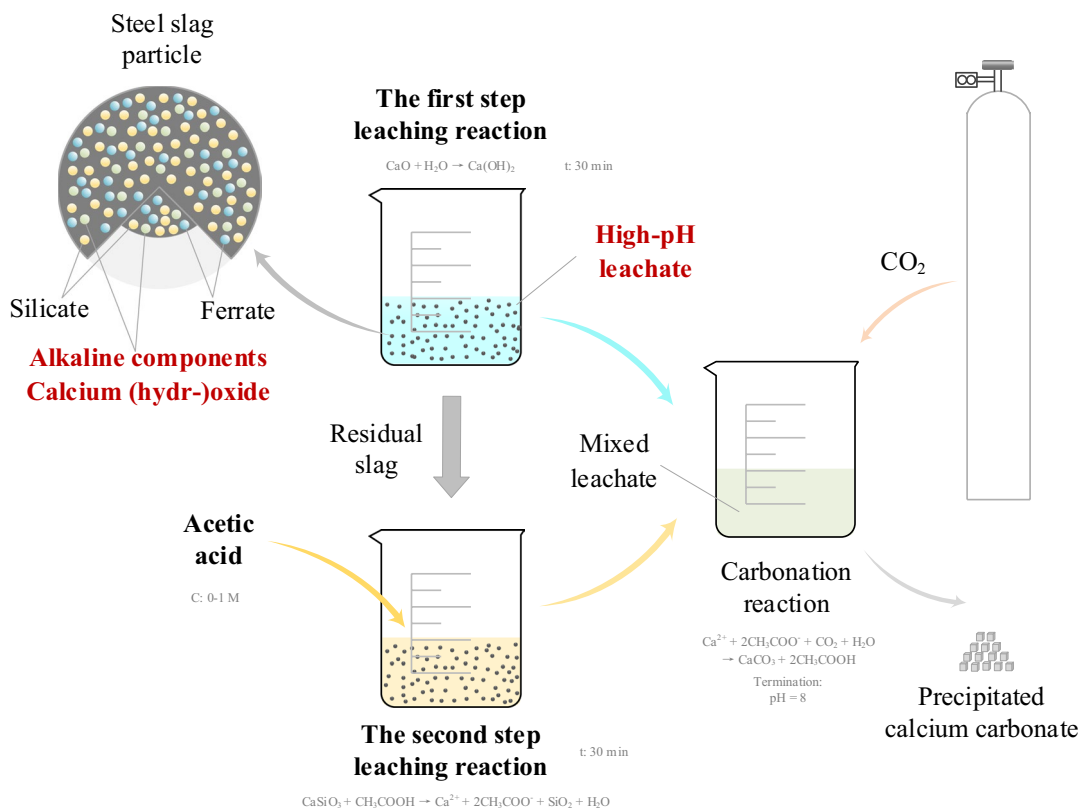

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Graphical Abstract

Introduction

The impact of the greenhouse effect caused by greenhouse gases on the global climate and environment has become increasingly obvious [1]. CO_2 is the main component of greenhouse gases, accounting for 65% [2]. In 2019, global CO_2 emissions reached 33.3 Gt [3], of which the iron and steel industry accounted for 6%–7% [4, 5]. As an energy-intensive industry, energy saving and emission reduction of the iron and steel industry is of great significance to reduce total CO_2 emissions. How to reduce CO_2 emissions is also an urgent issue for the iron and steel industry to achieve green and sustainable development. As a promising CO_2 sequestration technology, mineral carbonation has attracted increased attention in recent years. This technique simulates rock mineralization in nature to make minerals rich in alkaline earth metals react with CO_2 to form stable carbonates so as to achieve the purpose of CO_2 sequestration [6]. There are a considerable amount of alkaline earth metal minerals in the earth's crust, such as Wollastonite ($CaSiO_3$), serpentine ($Mg_3Si_2O_5(OH)_4$), and olivine ($(Mg,Fe)_2[SiO_4]$), which provides a sufficient source of feed stock for mineral

carbonation [4] [7]. At the same time, many industrial wastes such as iron and steel slags, red mud, coal fly ash, alkaline paper mill waste, and mining wastes can be used as ideal feed stock for mineral carbonation because of their special physical and chemical properties [8]. Mineral carbonation can permanently fix CO_2 in carbonate minerals without the risk of leakage [9, 10], so it is an ideal CO_2 sequestration measure.

Mineral carbonation can be divided into direct carbonation and indirect carbonation. The former is the carbonation of mineral feedstock and CO_2 in one step, while the latter consists of two steps: leaching reaction and precipitation reaction, that is, the alkaline earth metal ions (mainly Ca ions) in the feed stock are first extracted, and then after solid–liquid separation, CO_2 is passed into the filtrate for carbonation reaction [11]. Indirect carbonation has been widely studied due to its high CO_2 sequestration capacity and the ability to produce high value-added products such as precipitated calcium carbonate (PCC) [12–22]. At the same time, as a kind of calcium-rich industrial waste, steel slag is often used in indirect carbonation research because of its large quantity; most significantly, steel slag has high

alkalinity [23–25], which is preferred by mineral carbonation. For indirect carbonation, previous studies often used acidic chemical reagents to extract calcium ions in minerals. Acetic acid [12, 17, 26–30] and ammonium salt [13, 14, 20, 31, 32] are the most used Ca ion extractants. After the leaching reaction is completed, a low-pH calcium-rich leachate is obtained [33]. However, the low-pH environment is not conducive to the subsequent carbonation reaction, because the acidity of the solution prevents the dissolution of CO_2 in the aqueous phase to generate bicarbonate or carbonate ions [13, 34]. To carry out the carbonation reaction, the pH-swing method is proposed, that is, after the leaching reaction with acidic reagents, alkalis such as sodium hydroxide and aqueous ammonia were used to increase the pH of the leachate to facilitate carbonation [26, 35, 36]. The acid–alkali route inevitably causes excessive use of chemical reagents and increases the cost of the reaction. At the same time, it cannot reflect the high alkalinity of the steel slag, because the alkalinity will be neutralized by acidic chemical reagents in the leaching reaction. Therefore, for indirect carbonation, how to reduce the consumption of chemical reagents and how to make use of the high alkalinity of steel slag is a problem worthy of attention and consideration.

Based on this, a process that utilizes the high alkalinity of steel slag to promote the carbonation reaction while saving acid and alkali consumption was proposed. That is, the leaching reaction of indirect carbonation is divided into two steps. The first step is to carry out the leaching reaction with water as a solvent, so that the alkaline components in the steel slag are released into the water to obtain a highly alkaline primary leachate. Acid is then used for the second leaching reaction to obtain a low-pH secondary leachate. Subsequently, the primary leachate is added to the secondary leachate to obtain a mixed leachate with higher pH. Finally, CO_2 is passed into the mixed leachate for carbonation reaction. The two-step leaching reaction can transfer most of the alkalinity possessed by the free calcium oxide and calcium hydroxide in steel slag to water of the first leaching reaction. While preserving the alkalinity of steel slag, it also reduces the consumption of acid in the second leaching reaction by alkaline minerals. The saved acid can participate in the leaching reaction of other non-alkaline minerals, and
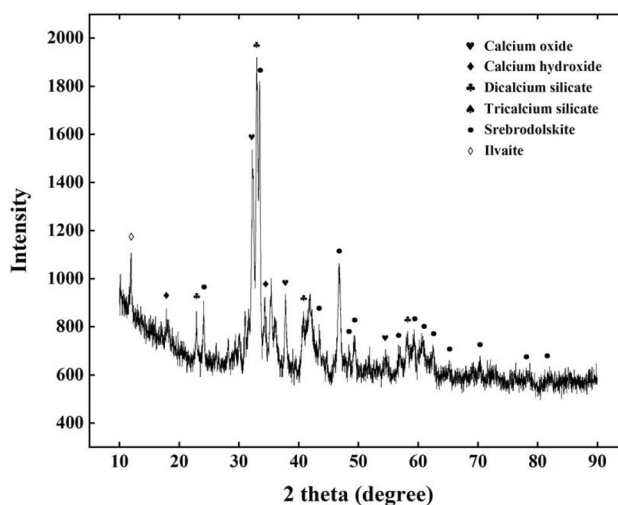

Fig. 1 XRD pattern of converter steel slag used in this experiment

the leaching ratio of the reaction is improved. At the same time, the consumption of alkali is also saved, because the preserved alkalinity of the steel slag can drive the increase of the pH of the leachate. Therefore, this new process is expected to solve the problem of excessive consumption of chemical reagents in the acid–alkali route and realize the green and sustainable development of the indirect carbonation process.

Materials and Methods

Materials

The converter steel slag used in this study was collected from Masteel (Maanshan, China). The slag was dried overnight at 105 °C to remove moisture, then the steel slag was ground and sieved to obtain three different particle sizes: < 38 μm; 38–75 μm; 75–150 μm. The chemical composition of steel slag was determined by X-Ray Fluorescence (XRF) analysis, and the result is shown in Table 1. The content of CaO in steel slag is high, which means that steel slag can provide more Ca ions for CO_2 sequestration. Meanwhile,

Table 1 Chemical composition of steel slag

Constituent	CaO	MgO	Al$_2$O$_3$	SiO$_2$	Fe$_2$O$_3$	MnO	TiO$_2$	V$_2$O$_5$	Cr$_2$O$_3$	P$_2$O$_5$	Others
Contents[a] (wt%)	45.34	4.35	1.31	11.41	30.31	2.19	1.27	0.85	0.25	2.42	0.3
Contents[b] (wt%)	45.19	4.15	1.32	11.40	30.56	2.30	1.35	0.85	0.26	2.38	0.24
Contents[c] (wt%)	43.74	4.26	1.35	11.40	31.86	2.29	1.37	0.85	0.26	2.43	0.19

[a] < 38 μm

[b] 38–75 μm

[c] 75–150 μm

we can find such a phenomenon from Table 1 that with the increase of the particle size of the steel slag, the content of CaO decreases, while the content of Fe_2O_3 increases. The X-ray diffraction (XRD) pattern of steel slag is shown in Fig. 1. The alkaline components of calcium oxide and calcium hydroxide can be found in this figure. At the same time, dicalcium silicate and tricalcium silicate are also common components in steel slag. In addition, there are many diffraction peaks of srebrodolskite in XRD pattern, which is caused by high iron content in steel slag.

The glacial acetic acid used in this experiment is analytical purity reagent (> 99.5 wt %) was purchased from Saen Chemical Technology (Shanghai) Co., Ltd. The CO_2 gas (purity > 99%) was purchased from Beijing Plex Practical Gas Co. Ltd.

Method

Deionized water was used as the solvent for the first step of leaching reaction, and acetic acid was used for the second step of leaching reaction. At the same time, three parameters which have great influence on the pH of leachate were selected: steel slag particle size, liquid–solid ratio, and acetic acid concentration; 48 groups of experiments were carried out to determine the best experimental conditions under which the alkalinity of steel slag can be effectively used to promote carbonation.

The experimental design is shown in Table 2. This experiment selects 3 variables: steel slag particle size (d, < 38; 38–75; 75–150 μm), liquid–solid ratio (L/S, 10; 20; 30; 50 mL/g), acetic acid concentration (C, 0; 0.25; 0.5; 1 M). A total of 48 sets of experiments were conducted to explore the suitable experimental conditions for steel slag alkalinity

to promote carbonation reaction and obtain ideal leaching ratio under different steel slag particle sizes.

The experimental flow chart is shown in Fig. 2. The steel slag was first subjected to the first leaching reaction in deionized water. After the reaction, a high-pH leachate and a primary residue slag were obtained. Then, the residual slag was reacted with acetic acid of different concentrations to obtain the second leachate and the residual slag. Subsequently, the second leachate was mixed with the first leachate, and if the pH of the mixed leachate was greater than 10, the mixed leachate was subjected to a precipitation reaction. The reason for setting such a pH range for the carbonation reaction is that the results of pre-experiment show that for the case of acetic acid as the extractant, when the pH of the leachate is less than 10, the carbonation reaction can hardly occur. At the same time, previous studies have also shown that a pH above 10 is more favorable for the carbonation reaction [33, 37].

The First Leaching Experiment

The schematic diagram of the leaching experimental set-up is shown in Fig. 3. Firstly, 100 mL deionized water was added to the three-necked flask placed in a water bath pot. The water bath temperature was set to 25 ℃. The temperature and pH were measured on-line by the temperature electrode and pH electrode inserted into the slurry. When the temperature and pH number are stabilized, a certain amount of steel slag was added to the reactor according to the set L/S ratio. Then the reaction begins, and the rotate speed of the experiment was set at 500 rpm. After 30 min, the reaction was finished and the slurry was vacuum filtered through a

Table 2 Experimental scheme design

NO.	d (μm)	L/S (mL/g)	C (M)	NO.	d (μm)	L/S (mL/g)	C (M)	NO.	d (μm)	L/S (mL/g)	C (M)
1	< 38	10	0	17	38–75	10	0	33	75–150	10	0
2	< 38	10	0.25	18	38–75	10	0.25	34	75–150	10	0.25
3	< 38	10	0.5	19	38–75	10	0.5	35	75–150	10	0.5
4	< 38	10	1	20	38–75	10	1	36	75–150	10	1
5	< 38	20	0	21	38–75	20	0	37	75–150	20	0
6	< 38	20	0.25	22	38–75	20	0.25	38	75–150	20	0.25
7	< 38	20	0.5	23	38–75	20	0.5	39	75–150	20	0.5
8	< 38	20	1	24	38–75	20	1	40	75–150	20	1
9	< 38	30	0	25	38–75	30	0	41	75–150	30	0
10	< 38	30	0.25	26	38–75	30	0.25	42	75–150	30	0.25
11	< 38	30	0.5	27	38–75	30	0.5	43	75–150	30	0.5
12	< 38	30	1	28	38–75	30	1	44	75–150	30	1
13	< 38	50	0	29	38–75	50	0	45	75–150	50	0
14	< 38	50	0.25	30	38–75	50	0.25	46	75–150	50	0.25
15	< 38	50	0.5	31	38–75	50	0.5	47	75–150	50	0.5
16	< 38	50	1	32	38–75	50	1	48	75–150	50	1

Fig. 2 Flow chart of indirect carbonation by two-step leaching
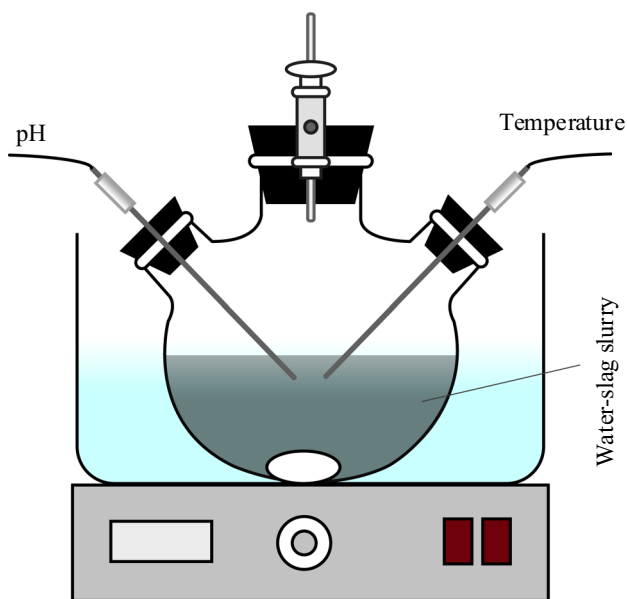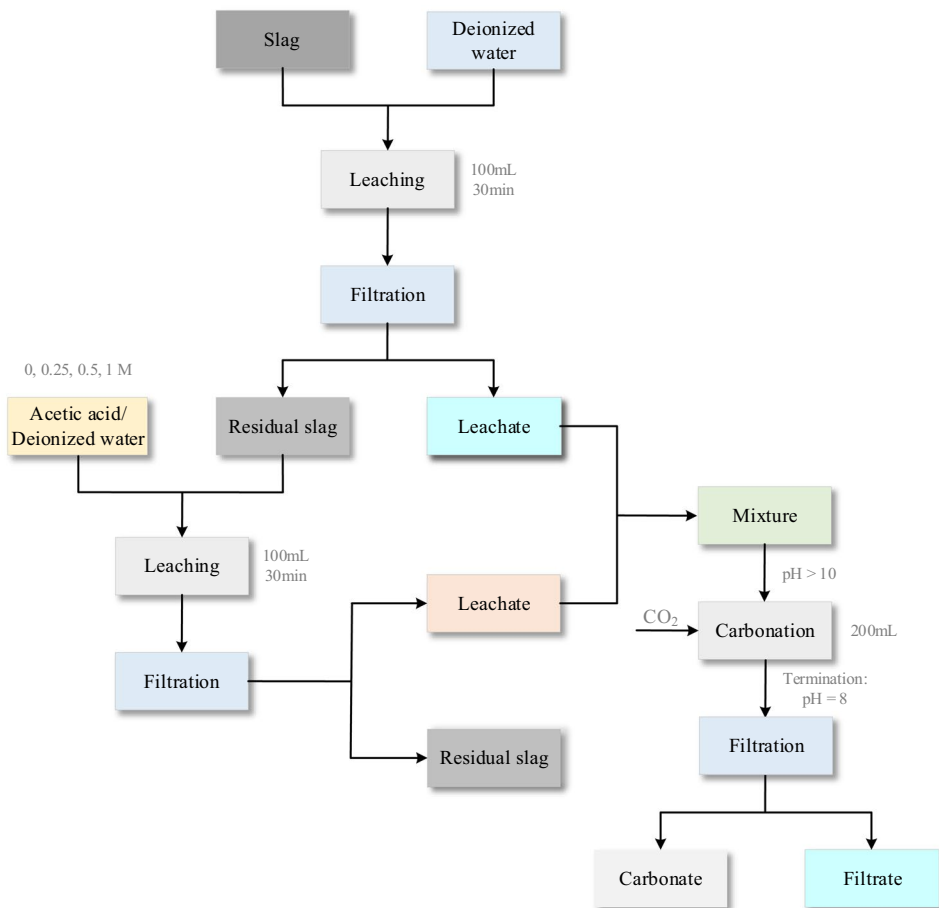
Fig. 3 Schematic diagram of experimental set-up

PTFE Millipore filter (0.45 μm pore size) to obtain the primary leachate with high pH and residue.

A small amount of leachate was diluted to a certain number and the concentration of Ca ions was measured by inductively coupled plasma atomic emission spectrometry (ICP-AES). The Ca ions leaching ratio of the first leaching reaction ($\eta_{Ca,1}$) is obtained from Eq. 4, where $C_{Ca,1}$ (mg/L) is the Ca ions concentration of the first leachate, V (L) is the volume of the primary leachate, m_{slag} (g) is the mass of the steel slag used, x_{Ca} (%) is the mass fraction of Ca in the slag.

$$CaO + H_2O \rightarrow Ca(OH)_2 \tag{1}$$

$$Ca_2SiO_4 + 2H_2O \rightarrow 2Ca(OH)_2 + SiO_2 \tag{2}$$
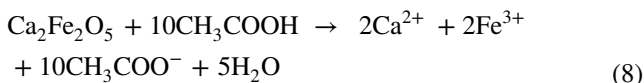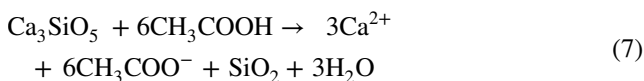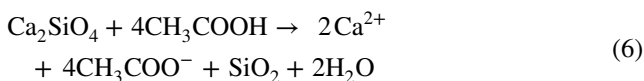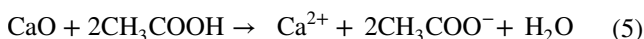
$$Ca_3SiO_5 + 3H_2O \rightarrow 3Ca(OH)_2 + SiO_2 \tag{3}$$

$$\eta_{Ca,1} = \frac{C_{Ca,1} \cdot V}{m_{slag} \cdot x_{Ca}} \times \frac{1}{1000} \tag{4}$$

The Second Leaching Experiment

Add 100 mL acetic acid of different concentrations into the reactor (The pK_a of acetic acid is 4.756 [38]). When the temperature and pH number are stabilized, the first residual slag was added to the reactor and the reaction was begin. The rotation speed was set to 500 rpm, and the reaction was stopped after 30 min. The reacted slurry was filtered in the same way to obtain the second leachate and residual slag. The Ca ions concentration of the second leachate was also measured by ICP-AES.

The second leaching ratio ($\eta_{Ca,2}$) is calculated by Eq. 9, where $C_{Ca,2}$ (mg/L) is the Ca ions concentration of the second leachate.

$$CaO + 2CH_3COOH \rightarrow Ca^{2+} + 2CH_3COO^- + H_2O \quad (5)$$

$$Ca_2SiO_4 + 4CH_3COOH \rightarrow 2Ca^{2+} \\ + 4CH_3COO^- + SiO_2 + 2H_2O \quad (6)$$

$$Ca_3SiO_5 + 6CH_3COOH \rightarrow 3Ca^{2+} \\ + 6CH_3COO^- + SiO_2 + 3H_2O \quad (7)$$

$$Ca_2Fe_2O_5 + 10CH_3COOH \rightarrow 2Ca^{2+} + 2Fe^{3+} \\ + 10CH_3COO^- + 5H_2O \quad (8)$$

$$\eta_{Ca,2} = \frac{C_{Ca,2} \cdot V}{m_{slag} \cdot x_{Ca}} \times \frac{1}{1000} \quad (9)$$

Carbonation Experiment

The first leachate was mixed with the second leachate, and the pH of the mixed leachate was measured. If the pH was greater than 10, the carbonation reaction will be carried out. In the carbonation reaction stage, the mixed leachate was added to the three-necked flask placed in a water bath pot. Temperature and pH electrodes are inserted from the two necks of the flask, and after the temperature and pH are stabilized, CO_2 was introduced at a flow rate of 0.1 L/min from another neck of the flask, and the reaction started. The speed was also set to 500 rpm, and the reaction was stopped when the pH of the solution was 8. The carbonated slurry was filtered to obtain a filtrate and a white precipitate. ICP-AES was also used to measure the Ca ions concentration of the carbonated filtrate.

The carbonation conversion rate of calcium ions (ξ_{Ca}) is obtained from Eq. 11, where $C_{Ca,3}$ is the Ca ions concentration of the carbonated filtrate. Because the primary leachate and the second leachate are mixed in the same amount, the concentration of Ca ions in the mixed leachate is $0.5C_{Ca,1} + 0.5C_{Ca,2}$.

$$Ca^{2+} + 2CH_3COO^- + CO_2 + H_2O \rightarrow CaCO_3 \downarrow + 2CH_3COOH \quad (10)$$
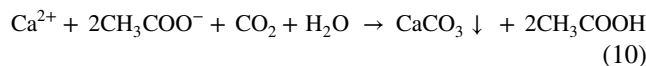
$$\xi_{Ca} = \frac{0.5C_{Ca,1} + 0.5C_{Ca,2} - C_{Ca,3}}{0.5C_{Ca,1} + 0.5C_{Ca,2}} \quad (11)$$

Results and Discussions

pH of Leachate

Since the pH of the leachate is an important indicator that determines the progress of the carbonation reaction, it is necessary to understand the pH changes of each step of the leaching reaction. In this experiment, the high alkalinity of the steel slag is released into the aqueous solution through the first leaching reaction. f-CaO and $Ca(OH)_2$, which participate in the leaching reaction and cause the pH of the leachate to rise, also avoid the consumption of acid in the second leaching reaction. Therefore, the amount of acid used is reduced.

<38 μm Particle Size Slag

The pH data of the steel slag leachate with a particle size of < 38 μm are shown in Fig. 4. For the first and second leaching reactions in deionized water, the pH was basically stabilized within 2 min, which indicates that the leaching of Ca ions proceeds rapidly in the first 2 min of the reaction. During this time, the alkaline components involved in the reaction are the phases of f-CaO and $Ca(OH)_2$ [39]. In the secondary leaching reaction of C = 0.25 M and C = 0.5 M, the pH slowly reached equilibrium after 3–10 min of reaction, which indicated that in addition to f-CaO and $Ca(OH)_2$, there are (aluminum) calcium silicate and calcium ferrite phases involved in the reaction. Due to the slow destruction of these mineral phase structures by acetic acid, the pH reaches equilibrium slowly. The pH of the leachate with 1 M acetic acid under the condition of L/S = 20, 30, and 50 quickly reaches equilibrium within 1 min. This is because the amount of acetic acid is far more than the amount of Ca in the slag. The relatively high acid concentration accelerates the leaching reaction, so the pH quickly reaches equilibrium within 1 min. However, under the condition of L/S = 10 of the same acetic acid concentration, the pH of the leachate reached equilibrium within 3 min. This is because under this condition, the amount of acetic acid is basically the same as the amount of Ca ions in the slag, which makes the leaching reaction rate at this time slightly slower than that of other L/S ratio conditions. The fitting curve of pH data is also shown in
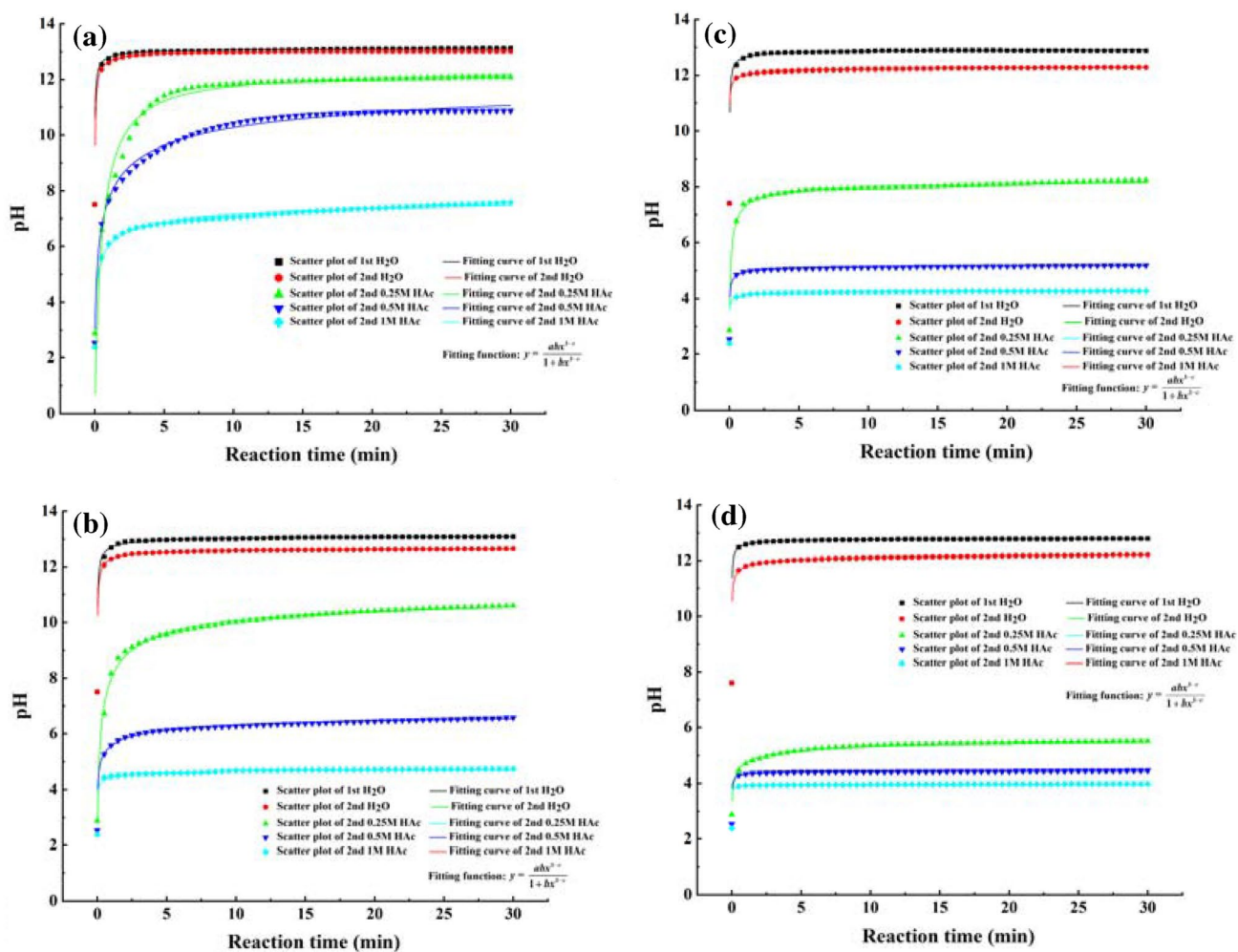
Fig. 4 pH of leachate with the particle size of < 38 μm. **a**: L/S $= 10$; **b**: L/S $= 20$; **c**: L/S $= 30$; **d**: L/S $= 50$

Fig. 4. The pH data are well fitted to the function curve of $y = \frac{abx^{1-c}}{1+bx^{1-c}}$. It can be generally included from the function that, at the beginning of the reaction, pH increases rapidly with the increase of time. After a period of time, the increase of time has little effect on the pH change, which is in good agreement with the pH scatter diagram.

In the first leaching reaction, the pH of the leachate can reach 13.13, 13.09, 12.87, and 12.79, respectively, when the L/S ratio was 10, 20, 30, and 50, respectively. In the second leaching reaction, under the condition of C $= 0$ M (without the participation of acetic acid), the pH of the leachate at L/S $= 10$ was 13.00, which is only 0.13 units lower than that of the first leachate. The steel slag still has high alkalinity after the first leaching reaction under this L/S ratio. In the subsequent secondary leaching reaction of acetic acid with different concentrations, the pH of the leachate of the L/S $= 10$ group at 0.25 M, 0.5 M,

and 1 M were 12.08, 10.87, and 7.58, respectively, which still had high pH. The pH of the secondary leachate of the L/S $= 20$ group under the condition of C $= 0$ M was 12.65, a decrease of 0.44 pH units. Compared with the L/S $= 10$ group, the amount of pH drops slightly increased. Therefore, the pH of the secondary leachate of this group at C $= 0.25$ M, 0.5 M, and 1 M decreased significantly compared with the L/S $= 10$ group, which were 10.61, 6.58, and 4.73, respectively. For the L/S $= 30$ and 50 groups, the higher L/S ratio means less slag involved in the reaction, which makes the pH buffer ability far inferior to the L/S $= 10$ and 20 groups. The pH of the secondary leachate was mostly between 4 and 5.5.

The pH of the mixed leachate of steel slag with a particle size of < 38 μm is shown in Fig. 5. The mixed leachate at L/S $= 10$ was 13.03, 12.67, 12.44, and 11.75, respectively, which shows that the steel slag used under this L/S ratio
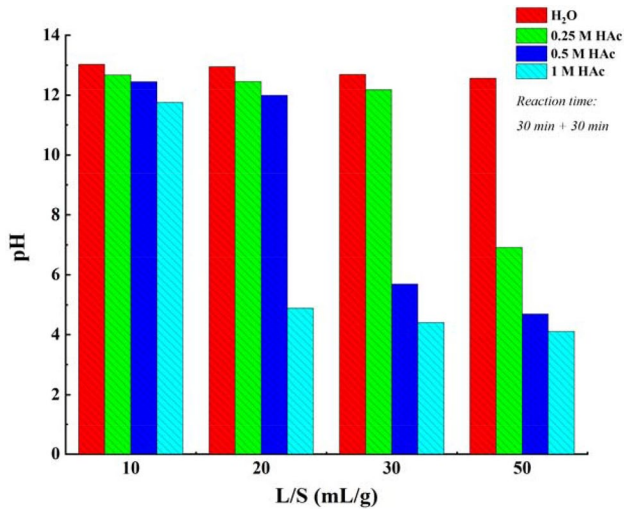
Fig. 5 pH of mixed leachate with the particle size of < 38 μm

can provide sufficient alkalinity for carbonation reaction, and the mixed leachate at all concentrations can carry out carbonation reaction. Under the condition of L/S = 20, the pH of the mixed leachate of C = 0 M, 0.25 M, and 0.5 M were all above 12, and the carbonation reaction can be carried out. The pH of the mixed leachate of C = 1 M was 4.89, which is obtained by mixing the first leaching leachate with a pH of 13.09 and the second leachate with a pH of 4.73. This is because acetic acid is a weak acid, and when mixed with the first leachate, the remaining acetic acid in the second leachate will further ionize the hydrogen ion to neutralize the pH of the first leachate, making the pH of the mixed leachate at a low level [40]. Under the condition of L/S = 30, only the pH of the mixed leachate of C = 0 M and 0.25 M were higher than 10. For a L/S ratio of 50, only the C = 0 M group can undergo carbonation reaction. As the L/S ratio increases, the amount of slag used in the leaching reaction decreases, and sufficient alkalinity cannot be provided to buffer the acidic environment of the second leachate.
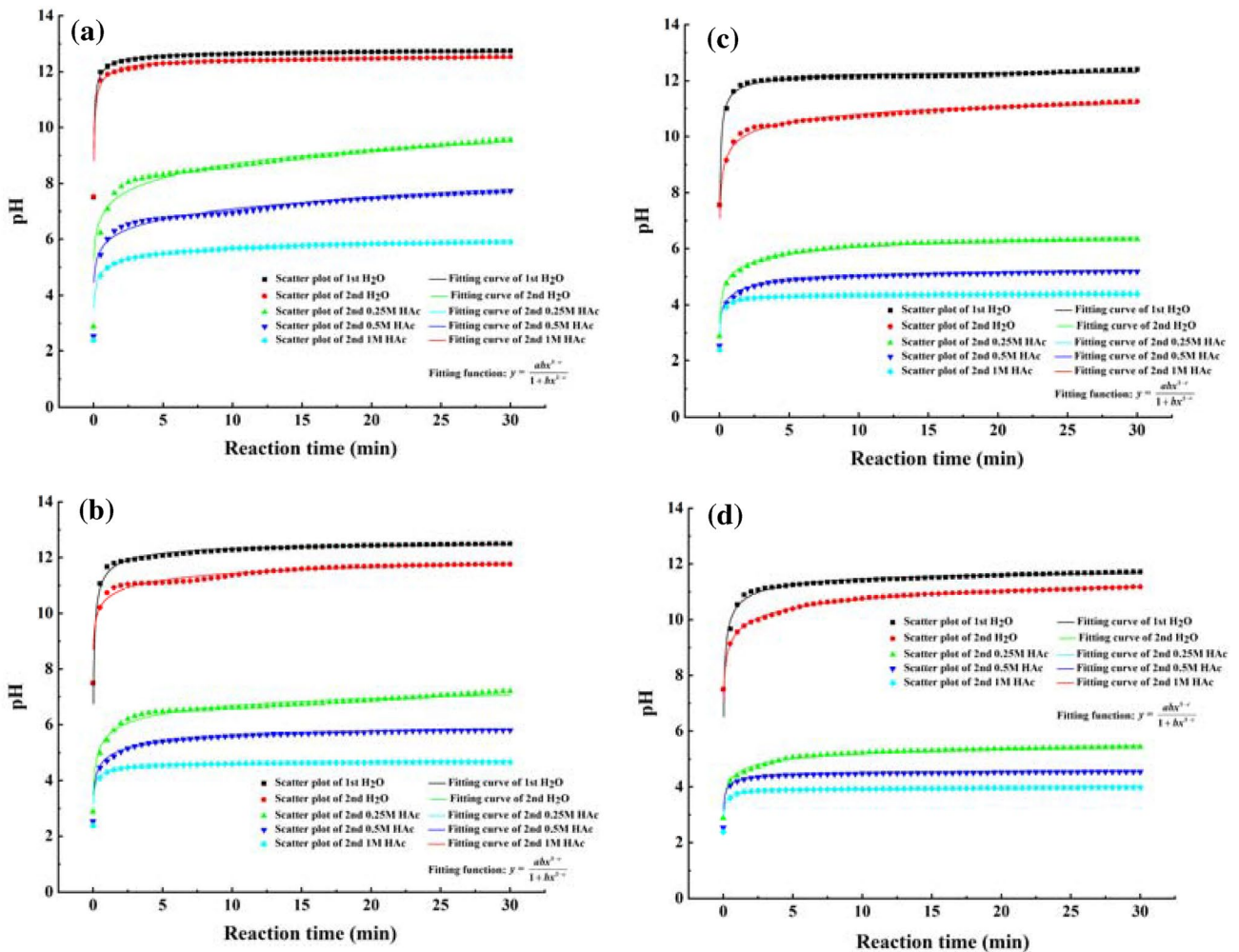

Fig. 6 pH of leachate with the particle size of 38–75 μm. **a**: L/S = 10; **b**: L/S = 20; **c**: L/S = 30; **d**: L/S = 50
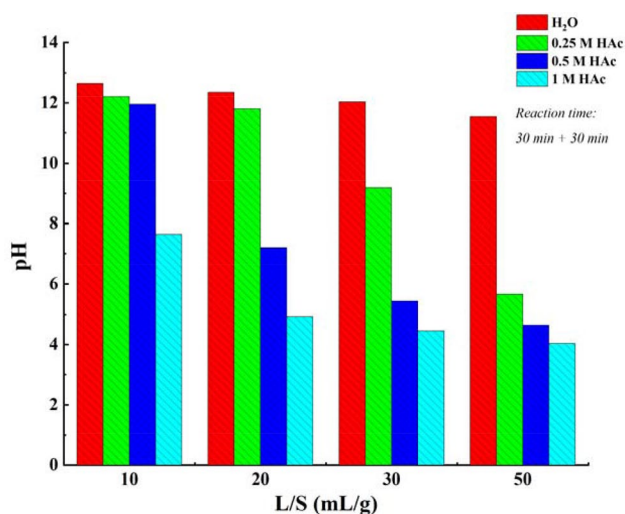
Fig. 7 pH of mixed leachate with the particle size of 38–75 μm

38–75 μm Particle Size Slag

The pH data of the steel slag leachate with a particle size of 38–75 μm are shown in Fig. 6. Under the same experimental conditions, the pH stabilization time of the 38–75 μm steel slag leachate is slightly increased compared to the < 38 μm group. This is because the increase in the particle size of the steel slag reduces its surface area in contact with the solvent, and the large particle size increases the diffusion path of Ca ions inside the steel slag matrix, resulting in a slowdown in leaching reaction rate.

The pH of the leachate of the first leaching reaction under different L/S ratio conditions were 12.74, 12.50, 12.39, and 11.72, respectively. As the L/S ratio increases, the pH of the leachate keeps decreasing. The pH of the mixed leachate of the 38–75 μm group is shown in Fig. 7. Under the condition of a L/S ratio of 10, the pH of the mixed leachate of the C = 0 M, 0.25 M, and 0.5 M groups are 12.64, 12.21, and
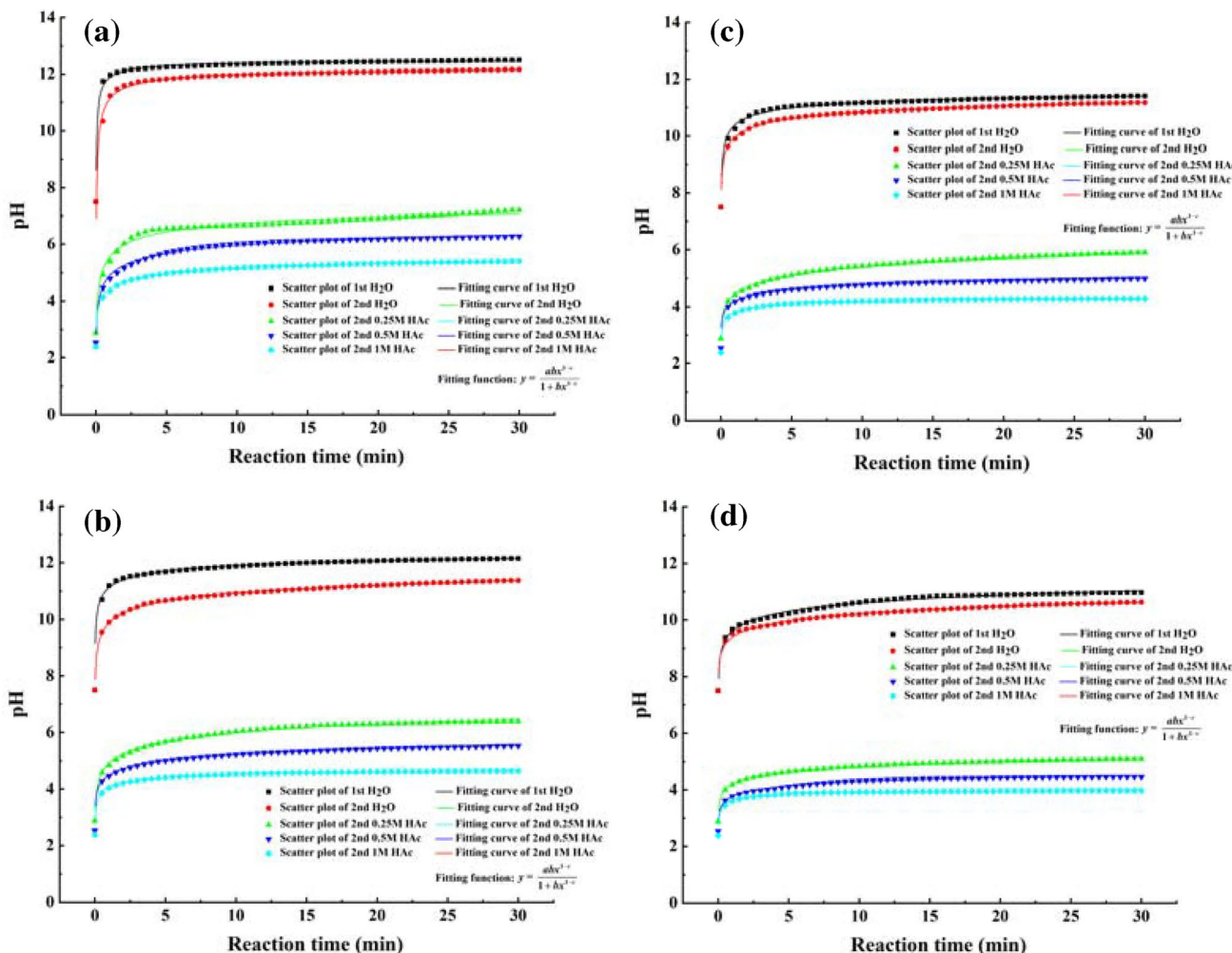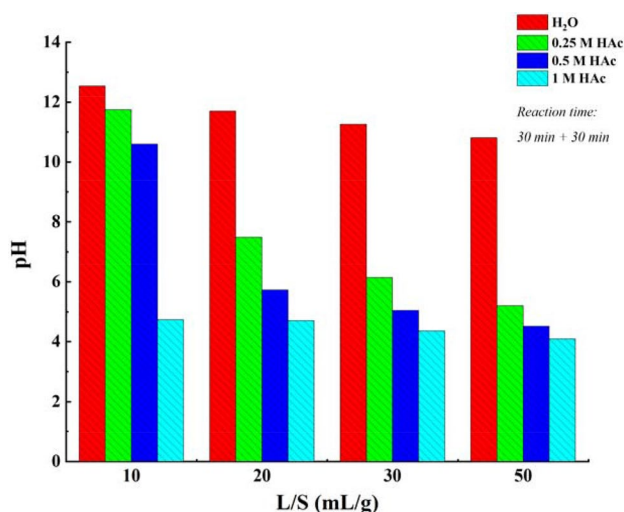

Fig. 8 pH of leachate with the particle size of 75–150 μm. **a**: L/S = 10; **b**: L/S = 20; **c**: L/S = 30; **d**: L/S = 50

Fig. 9 pH of mixed leachate with the particle size of 75–150 μm

11.95, respectively. However, the pH of the mixed leachate of the C = 1 M group was 7.64, and the carbonation reaction could not be carried out. For the L/S = 20 condition, there are C = 0 M and 0.25 M of the mixed leachate pH greater than 10, and for the L/S = 30 and 50 conditions, only C = 0 M of the mixed leachate pH meets the carbonation conditions.

75–150 μm Particle Size Slag

The pH data of the 75–150 μm steel slag leachate are shown in Fig. 8. It takes more longer for the pH of the leachate to stabilize, and the pH of the leachate for the first leaching reaction under different L/S ratio conditions were 12.50, 12.15, 11.41, and 10.97, respectively. The pH of the first leachate under the conditions of L/S ratio of 30 and 50 were slightly lower. This is because (1) steel slag with large particle size has lower CaO content, so it can provide less f-CaO and $Ca(OH)_2$ [20, 41, 42]; (2) steel slag with large particle size is not conducive to the leaching of Ca ions inside the steel slag particles. The pH of the mixed leachate of 75–150 μm group is shown in Fig. 9. Only C = 0 M, 0.25 M, and 0.5 M groups at the L/S ratio of 10 and C = 0 M group at the L/S ratio of 20, 30, and 50 can carry out carbonation reaction. This indicates that steel slag with a particle size of 75–150 μm can provide less alkalinity and has a weaker contribution to the carbonation reaction.

Ca Ions Leaching Ratio

In this experiment, deionized water was used as solvent in the first step of leaching reaction to transfer the alkalinity

of steel slag to water. However, the leaching ratio of Ca ions by water is low. Therefore, acetic acid was used in the second leaching reaction to extract more Ca ions. The leaching ratio of calcium ions under different conditions is shown in Fig. 10. The influence of three different variables on the leaching ratio of calcium ions can be intuitively observed.

The Effect of Particle Size on the Leaching Ratio of Ca Ions

Figure 10a–c shows the leaching ratio of steel slag with particle sizes of < 38 μm, 38–75 μm, and 75–150 μm, respectively. For the first leaching reaction, the leaching ratios of Ca ions under the three particle sizes are 9.07, 8.13, and 7.40, respectively. When using deionized water for leaching in the second step, the leaching ratio of Ca ions was greatly reduced compared with the first leaching reaction. The maximum leaching ratio of the three groups of steel slags were only 3.90, 2.87, and 1.85%. It can be inferred that most active calcium-containing minerals (f-CaO, $Ca(OH)_2$) have participated in the reaction and released alkalinity in the first leaching reaction. The decrease in the leaching ratio of Ca ions with the particle size also corresponds to the decrease in the pH, as discussed in Sect. pH of Leachate. The above data all show that as the grain size of steel slag increases, the leaching ratio of Ca ions gradually decreases. This is because (1) the increase of the particle size means the reduction of the specific surface area of the steel slag, which greatly reduces the area of the slag exposed to the liquid phase; (2) the increase in particle size increases the diffusion path of Ca ions inside the slag particles, which is not conducive to the leaching of Ca ions.

The effect of particle size on the leaching ratio of Ca ions is more significant when using deionized water as the solvent. In the first leaching reaction, the Ca ions leaching ratio of steel slag with a particle size of < 38 μm were 20.84–47.28% higher than that of steel slag with a particle size of 75–150 μm, and in the second leaching reaction, this change was 109.30–114.10%. However, in the second step of leaching reaction with the participation of acetic acid, the effect of steel slag particle size on the leaching ratio of Ca ions is not very significant. Under the conditions of C = 0.25 M, 0.5 M, and 1 M, the Ca ions leaching ratio of steel slag with a particle size of < 38 μm increased by 2.7–11.56%, 2.41–12.50%, 3.52–19.70% compared with steel slag with a particle size of 75–150 μm, respectively. This is because in the first and second leaching reactions without the participation of acetic acid, the deionized water has a limited ability to dissolve steel slag particles. Most of the deionized water dissolves the active calcium-containing minerals (f-CaO, $Ca(OH)_2$) on the surface of the particles, and the dissolution capacity of calcium-containing minerals inside steel slag particles is insufficient, so the leaching ratio

of calcium ions in this case depends greatly on the particle size. For the second step of leaching reaction involving acetic acid, because acetic acid can destroy the lattice structure of the calcium-containing mineral, the leaching reaction of Ca ions extends to the inside of the steel slag particles. Therefore, in this case, the leaching ratio of Ca ions has little dependence on the particle size.

The Effect of L/S Ratio on the Leaching Ratio of Ca Ions

For the first leaching reaction, the leaching ratio of steel slag with a particle size of < 38 μm in deionized water was between 5.14 and 9.07%, and the leaching ratio increases with the increase of the L/S ratio. In the second step of the leaching reaction involving acetic acid, in the case of C = 0.25 M, under the condition of L/S = 10, the Ca ions leaching ratios of the three groups of particle sizes were 13.30, 13.12, and 12.95%, respectively. However, under the condition of a L/S = 50, their Ca ions leaching ratios were 52.47, 50.30, and 47.07%, which increased by 294.51, 283.38, and 263.47%, respectively. The increase of the L/S ratio has a great promotion effect on the leaching of Ca ions. This is because (1) the increase in the L/S ratio means that the amount of steel slag used in the experiment is reduced, and the acetic acid is sufficient relative to the calcium-containing minerals in the slag, which ensures that there are sufficient hydrogen ions to participate in the leaching reaction of Ca ions; (2) the increase of L/S ratio also ensures that there is sufficient aqueous phase in the reaction. Compared with the condition of low L/S ratio, the concentration of Ca ions in the aqueous phase under the condition of high L/S ratio is lower, which increases the Ca ions concentration gradient between the slag and aqueous phase, thus facilitating the diffusion of calcium ions from the slag matrix to the bulk solution. At the same time, it can also be seen from Fig. 10 that for the case of C = 1 M, when L/S = 20, the effect of the increase of L/S ratio on the leaching ratio of Ca ions slows down, and C = 0.5 M has a similar rule, but the law weakens slightly, from which we can infer that in the case of using a high concentration of acetic acid, 20 is a more rational L/S ratio condition.

The Effect of Acetic Acid Concentration on the Leaching Ratio of Ca Ions

The reason why acetic acid was chosen as the solvent in the second step of leaching reaction is because for indirect carbonation, acetic acid and ammonium chloride are two commonly used leaching agents. The acidity of acetic acid
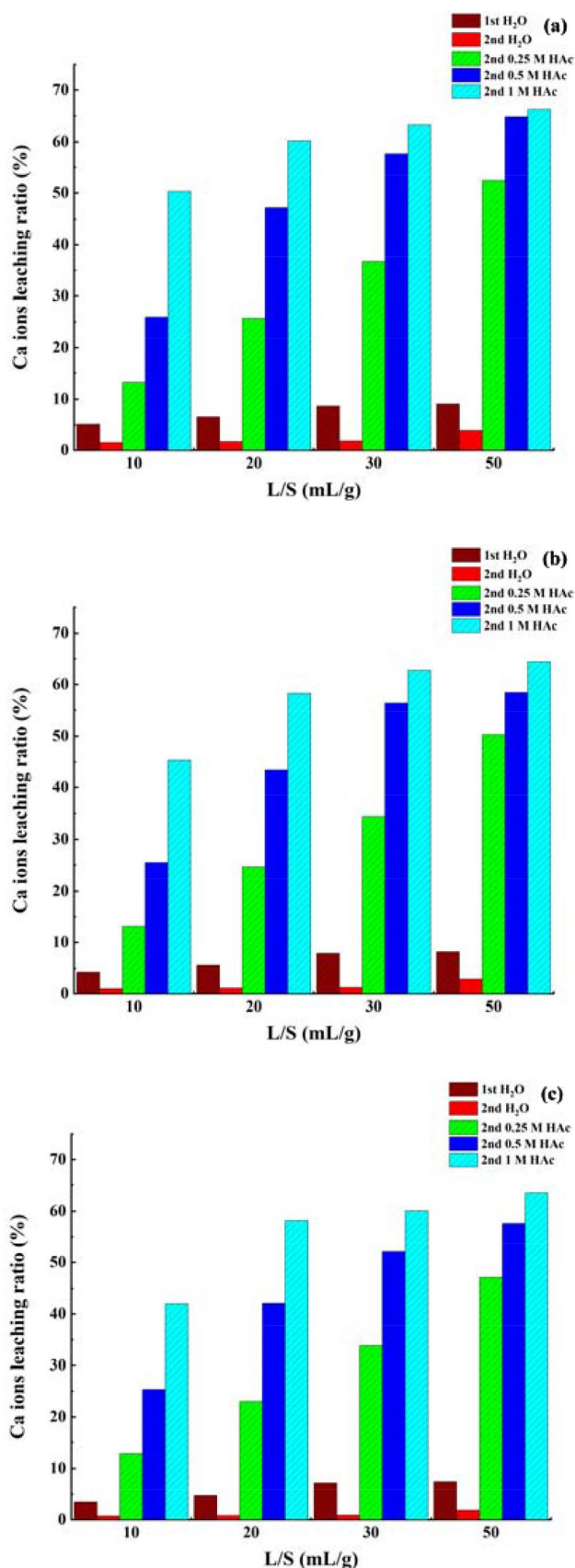
is stronger than that of ammonium chloride, so its leaching ratio of Ca ions is also higher. At the same time, due to the relatively high acidity of acetic acid, when it is used for the leaching of Ca ions in steel slag, the pH of the obtained leachate is low, which makes it difficult to carry out carbonation reaction without additional alkali addition. Considering that steel slag has high alkalinity, the alkalinity of steel slag itself was used as an alkali source to promote the carbonation reaction. The use of acetic acid in the second step of the leaching reaction can more clearly reflect the effect of the alkalinity of the steel slag on the pH and carbonation conversion rate of the mixed leaching solution.

The acetic acid concentration also has a significant effect on the leaching of Ca ions. It can be seen from Fig. 10 that as the concentration of acetic acid increases, the leaching ratio of calcium ions also increases. At the same time, the change of acetic acid concentration has a great influence on the leaching ratio of Ca ions under the condition of low L/S ratio, and the smaller the effect is with the increase of L/S ratio. For instance, for the case of L/S = 50, the leaching ratio of steel slag with three particle sizes at C = 1 M increased by 26.22, 28.09, and 34.80%, respectively, compared with that at C = 0.25 M, while for L/S = 10, the increase was 278.20, 245.50, and 224.48%, respectively. This is because as the L/S ratio increases, the amount of slag decreases, and the amount of acid increases compared with that of slag. This makes the lower concentration of acetic acid to leach Ca ions in the steel slag to a greater extent, therefore, there is little difference between the leaching ratio of Ca ions at low concentration and that of higher.

For the total Ca ions leaching ratio of the two-step method, when deionized water was used for leaching in the second step, steel slag with a particle size of < 38 μm achieved the largest Ca ions leaching ratio of 12.97%. When using 1 M acetic acid for leaching in the second step, the maximum leaching ratio of steel slag in the < 38 μm particle size group is 75.3%, and the maximum leaching ratios of the other two particle size groups are 72.56 and 70.85%, respectively, which shows the excellent Ca ions extraction ability of the two-step method.

Carbonation Conversion Rate

The purpose of the two-step leaching method is to utilize the alkalinity of the steel slag to promote the carbonation reaction. Therefore, the contribution of the alkalinity in the steel slag in the first leaching reaction will directly determine whether and to what extent the carbonation reaction can proceed. The Ca ions conversion rate of steel slag with different particle sizes is shown in Fig. 11. It can be seen from Fig. 11a that without the participation of acetic acid, the Ca ions conversion rate of the mixed solution can reach 85.98%–91.4%, and most of the Ca ions are involved in the
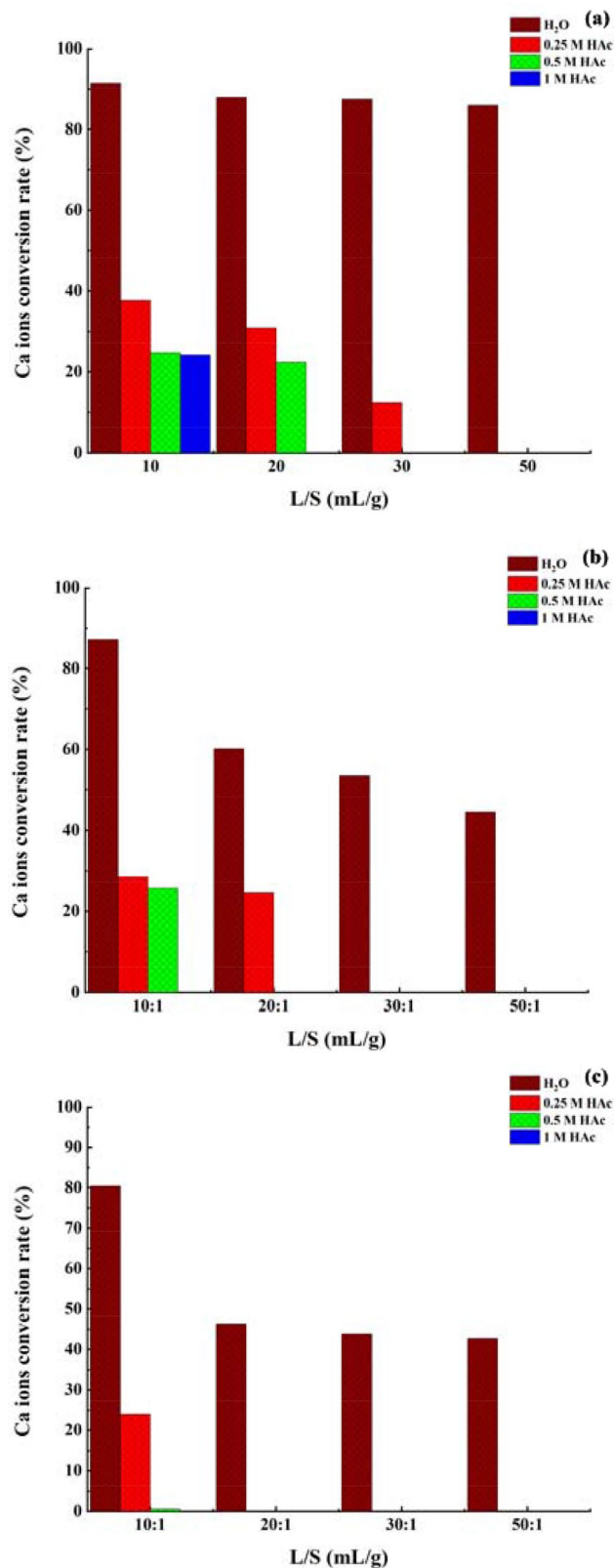

Fig. 11 Ca ions carbonation conversion rate of steel slag with different particle sizes. a: d < 38 μm; b: d = 38–75 μm; c: 75–150 μm

carbonation reaction. This is because the mixed leachate under this condition has a higher pH (12.56–13.03). For the case where acetic acid was involved, taking the condition of L/S = 10 as an example, the carbonation rates of the mixed leachates were 24.2%–37.6%. Compared with the situation without the participation of acetic acid, the carbonation rate decreased significantly, although their mixed leachate also had higher pH (11.75–12.67). This is because in the leaching reaction, acetic acid reacts with calcium-containing minerals to form calcium acetate. In the carbonation reaction, the Ca ions in the calcium acetate are converted into calcium carbonate, while acetate combines with hydrogen ions ionized by carbonic acid to convert into acetic acid. With the progress of the reaction, the pH of the mixed leachate decreased and the amount of acetate converted to acetic acid increased, which would inhibit the carbonation of Ca ions. As a result, the carbonation rates with the participation of acetic acid were lower than that of without the participation of acetic acid. Thus, in addition to pH, the extent of carbonation is determined by substances that inhibit the carbonation. Under the condition of L/S = 20, the pH of the mixed leachate when 1 M acetic acid was used in the second leaching reaction was only 4.89, which is far lower than the conditions required for the carbonation reaction. Similarly, carbonation reaction could not be carried out in the conditions of C = 0.5 M and 1 M at the L/S = 30:1 and C = 0.25 M, 0.5 M, and 1 M at the L/S = 50:1. This is because as the L/S ratio increases,
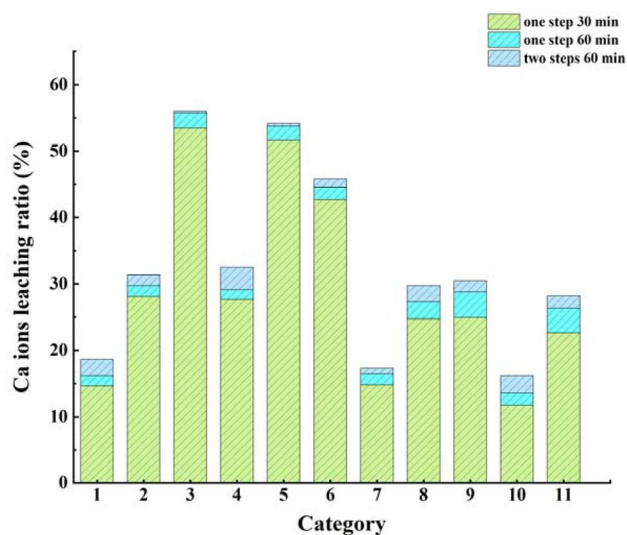
the decrease in the amount of slag leads to a decrease in the pH buffer ability, which results in a lower pH of the mixed solution. Therefore, although a high L/S ratio can obtain a higher Ca ions leaching ratio, it will lower the pH of the mixed solution and is not conducive to the subsequent carbonation reaction.

It can be seen from Fig. 11b that for the 38–75 μm group, without the participation of acetic acid, the carbonation rates were slightly lower than that of the < 38 μm group, because the pH of the mixed leachate were relatively low (11.54–12.64). With the participation of acetic acid, carbonation reaction could be carried out only in the conditions of C = 0.25 M and 0.5 M at the L/S = 10 and C = 0.25 M at the L/S = 20, and the carbonation conversion rates were in the range of 24.65%–28.53%. The result of Fig. 11c shows that only in the conditions of C = 0.25 M at the L/S = 10 carbonation reaction can be carried out. Without the participation of acetic acid, the carbonation rate of the mixed leachate was further reduced due to the lower pH of the mixed solution. The particle size of steel slag has a great impact on the Ca ions carbonation rate. On the one hand, the large-sized steel slag has relatively low CaO content and low alkaline mineral content. On the other hand, the large particle size also greatly limits the release of steel slag alkalinity, thereby affecting the carbonation rate of the reaction.

Although the carbonation rates with the participation of acetic acid were lower than that without the participation of
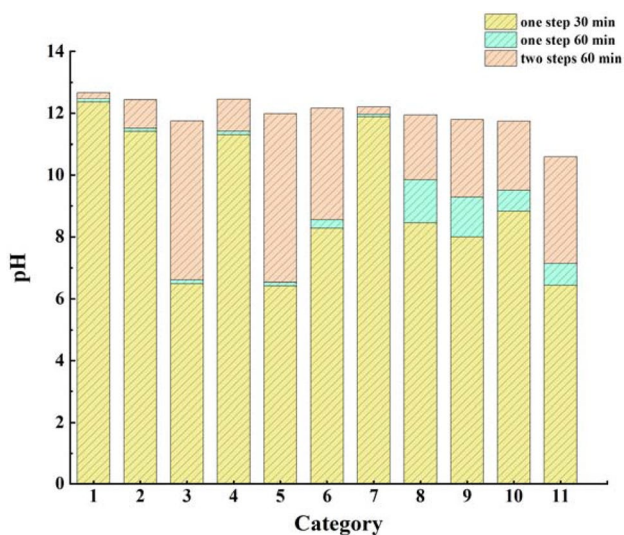
Fig. 12 The pH of the one-step and two-step leachates. 1: d < 38 μm, L/S = 10, C = 0.25 M; 2: d < 38 μm, L/S = 10, C = 0.5 M; 3: d < 38 μm, L/S = 10, C = 1 M; 4: d < 38 μm, L/S = 20, C = 0.25 M; 5: d < 38 μm, L/S = 20, C = 0.5 M; 6: d < 38 μm, L/S = 30, C = 0.25 M; 7: d = 38–75 μm, L/S = 10, C = 0.25 M; 8: d = 38–75 μm, L/S = 10, C = 0.5 M; 9: d = 38–75 μm, L/S = 20, C = 0.25 M; 10: d = 75–150 μm, L/S = 10, C = 0.25 M; 11: d = 75–150 μm, L/S = 10, C = 0.5 M

Fig. 13 Ca ions leaching ratio of one-step and two-step leaching reactions. 1: d < 38 μm, L/S = 10, C = 0.25 M; 2: d < 38 μm, L/S = 10, C = 0.5 M; 3: d < 38 μm, L/S = 10, C = 1 M; 4: d < 38 μm, L/S = 20, C = 0.25 M; 5: d < 38 μm, L/S = 20, C = 0.5 M; 6: d < 38 μm, L/S = 30, C = 0.25 M; 7: d = 38–75 μm, L/S = 10, C = 0.25 M; 8: d = 38–75 μm, L/S = 10, C = 0.5 M; 9: d = 38–75 μm, L/S = 20, C = 0.25 M; 10: d = 75–150 μm, L/S = 10, C = 0.25 M; 11: d = 75–150 μm, L/S = 10, C = 0.5 M

acetic acid, this indicates that the experimental route of indirect carbonation of steel slag using acetic acid without the additional of alkali addition is feasible. Steel slag as a kind of industrial waste with high alkalinity, the effective use of its alkalinity to promote the carbonation reaction has a very positive practical significance to save the chemical consumption and reduce the cost of mineral carbonation process.

Control Experiment

In the above two-step experiment, we have determined the experimental conditions that can carry out the carbonation reaction with the participation of acetic acid, a total of 11 groups. To determine whether the one-step leachate obtained under these experimental conditions can undergo carbonation reaction, we set up the control experiments. The reaction time of the control group was set to 30 min and 60 min. Because the total leaching reaction time of the two-step method was 60 min, while the reaction time with the participation of acetic acid was 30 min, therefore, we studied the situation of the one-step method after 30 min and 60 min, respectively.

The pH of the one-step leaching experiment is shown in Fig. 12. No matter the reaction time is 30 min or 60 min, there are only 4 groups in which the leachate of the one-step leaching reaction can undergo carbonation reaction (pH > 10). That is to say, 7 groups of experiments cannot carry out carbonation reaction when using one-step method but can do so when using two-step method. As a result, the effect of the two-step method on improving the pH of the leachate was verified. For the leaching experiment of steel slag with a particle size of < 38 μm, under the conditions of L/S = 10 and C = 0.25 M, the pH of the one-step leachate was close to the pH of the two-step mixed leachate. For the two experimental conditions of L/S = 10:1, C = 0.5 M and L/S = 20:1, C = 0.25 M, the pH of the one-step leachate were about 1 pH unit lower than the pH of the two-step

leachate. For the three experimental conditions of L/S = 10, C = 1 M; L/S = 20, C = 0.5 M and; L/S = 30, C = 0.25 M, the pH of the one-step leachate has a significant drop compared with the pH of the two-step mixed leachate, and the drop ranges between 3.6 and 5.5. The same situation appeared in the leaching experiment of steel slag with a particle size of 38–75 μm and 75–150 μm. With the increase of L/S ratio and acetic acid concentration, the decrease of pH of one-step leachate were larger than that of two-step method.

The Ca ions leaching ratio is shown in Fig. 13. The leaching ratios of the one-step leaching experiment were less than the total Ca ions leaching ratio of the two-step method after 30 min of reaction. This is because the alkaline components are dissolved in water during the first leaching reaction, which avoids the consumption of acetic acid in the second leaching reaction, so that acetic acid can react with other calcium-containing components to extract more Ca ions. Extending the reaction time to 60 min, the Ca ions leaching ratios of the one-step method were still lower than that of the two-step method. It is worth noting that when the reaction time of one-step reaction was 60 min, the exposure time of the steel slag to acetic acid was 60 min, while the exposure time of the two-step method was only 30 min, but the Ca ions leaching ratios of the two-step method were higher than that of the one-step method. The promoting effect of releasing the alkaline components of steel slag in water in advance in the two-step method on the leaching of Ca ions is greater than that of prolonging the exposure time of steel slag in acetic acid in one-step method. It can also be seen from Fig. 13 that with the increase of the particle size of steel slag, the ratio of the leaching ratio of Ca ions at 30 min to that at 60 min decreases. This is because the diffusion path of Ca ions in large-sized steel slag is larger than that in small-sized steel slag, so it takes a long time for the reaction to reach equilibrium.

As can be seen from Fig. 11, there are seven groups of experiments in which carbonation cannot be carried out when using one-step method but can be carried out in two-step method. The XRD patterns of carbonation products obtained by using the two-step method in these seven groups of experiments are shown in Fig. 14. The main phase of the carbonation product is calcite, and there is also a small amount of aragonite in the product under some experimental conditions. This confirms that the two-step method can carry out the carbonation reaction and produce $CaCO_3$ without the addition of alkali, and the alkalinity of the steel slag can indeed be utilized to promote the carbonation reaction. At the same time, the peak intensity of calcite is also different. Steel slag with a particle size of < 38 μm has the highest peak intensity of calcite among the carbonated products obtained under the conditions of L/S = 30 and C = 0.25 M, and the product under this condition has the highest content of $CaCO_3$. The peak intensity of calcite in the product
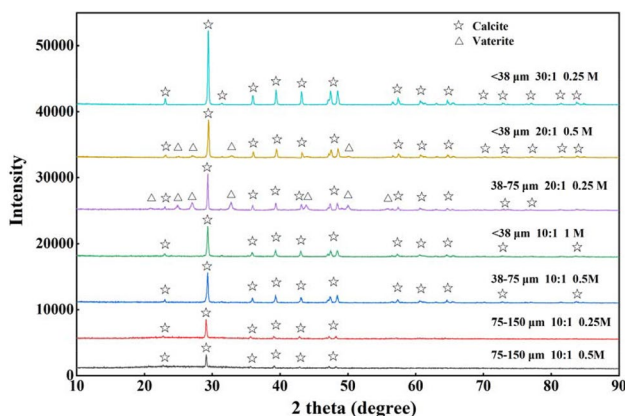

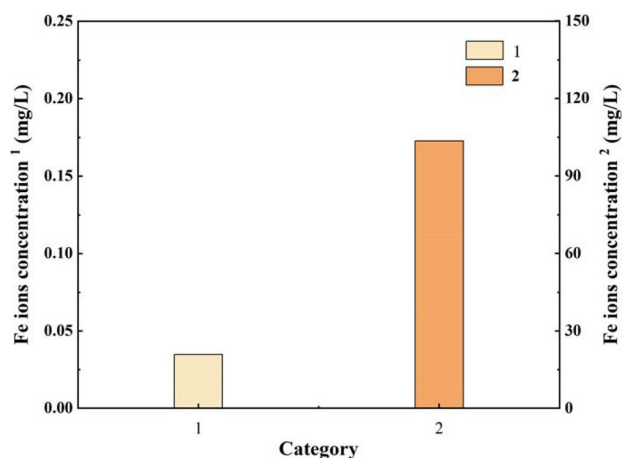**Fig. 14** XRD patterns of two-step carbonation products

obtained with the same particle size steel slag under the conditions of L/S = 20 and C = 0.5 M is the second, followed by steel slag with a particle size of 38–75 μm at L/S = 20 and C = 0.25 M. It can be generally seen from Fig. 14 that as the particle size of steel slag increases, the peak intensity of calcite in the obtained product gradually decreases. Meanwhile, the influence of acetic acid concentration on the peak intensity of calcite in the product is greater than that of L/S ratio. The decrease in pH of the leachate caused by high acetic acid concentration is less than the decrease in pH caused by high L/S ratio. Therefore, when using low-concentration acetic acid for leaching, a higher pH leachate is obtained, so that the content of $CaCO_3$ in the carbonated product is higher. Moreover, the influence of particle size on the peak intensity of calcite in the product is greater than that of acetic acid concentration. This is because steel slag with a small particle size is easier to release alkaline components in the water, and it reacts more completely with acetic acid to consume acid to a greater extent and increase the pH of the leachate. Therefore, the content of $CaCO_3$ is higher in the carbonation product obtained from the smaller particle size steel slag.

CO_2 Sequestration Capacity Analysis and Residual Slag Utilization Suggestions

Based on the above data, we have obtained the best carbonation condition for the two-step method, that is, d < 38 μm, L/S = 10, C = 1 M. Under this experimental condition, the total leaching ratio of Ca ions obtained by two-step leaching was 55.97%, and the pH of the mixed leachate was 11.75. The carbonation conversion rate of Ca ions in the leaching solution is 24.20%, and the carbonation conversion rate of

Ca ions in the steel slag is 13.55%. Calculated based on 1 kg of steel slag, the content of CaO is 44.91%, and the content of Ca ions is 32.08%. Therefore, 43.47 g of Ca ions in the steel slag participate in the carbonation reaction, which can fix 47.81 g of CO_2. However, under the same experimental condition, the pH of the leachate obtained by the one-step method at 30 min of reaction was 6.49, the reaction time was extended to 60 min, the pH of the leachate is 6.61, which were far lower than the pH of the two-step method. Carbonation experiment cannot be carried out in the one-step method under this experimental condition. Therefore, the two-step method has a net increase of 43.47 g for the CO_2 sequestration capacity when using 1 kg of steel slag. This reflects the significant promotion effect of the two-step method on the carbonation reaction.

The appropriately utilization of residual slag is an important factor affecting the sustainable development of indirect carbonation process. Raw steel slag faces the problem of difficult utilization, mainly because of the existence of free CaO which makes it possess bad volume stability. If it is used in building materials, there is a danger of volume expansion for a long time, which affects the quality and service life of building materials. In this study, most of the alkaline components of steel slag are released in water after the first step of leaching, and free calcium oxide is the main determinant of steel slag's alkalinity. In the second step of leaching reaction, the participation of acetic acid can completely eliminate free CaO in steel slag. Therefore, the problem of poor stability of steel slag can be solved, and it can be used as building materials, such as cement, concrete aggregate, and subgrade material. The wear resistance of steel slag due to its high iron content can improve the strength of building materials, which makes it have great advantages in building materials.

Dissolution Behavior of Iron

It is necessary to understand the dissolution behavior of iron in the leaching reaction due to high Fe_2O_3 content in steel slag. Taking the above optimal experimental conditions of two-step method as an example, as shown in Fig. 15, under the condition of d < 38 μm, L/S = 10, the concentration of Fe ions in the leachate obtained by the first step of leaching reaction with deionized water as the solvent was 0.035 mg/L. In the second step, the concentration of Fe was 103.6 mg/L when 1 M acetic acid is used. The leaching ratios of Fe ions in the two steps were 0.00017% and 0.49%, respectively. For the first step of leaching reaction, the presence of such a small amount of Fe ions in the leachate indicates that srebrodolkite hardly reacts with water. Despite the participation of 1 M acetic acid in the second leaching reaction, the leaching ratio of

Fig. 15 The concentration of Fe ion in the leachate. 1: the first step of leaching reaction with deionized water as solvent; 2: the second step of leaching reaction with 1 M acetic acid as solvent

Fe ions was still very low, which reflects that acetic acid is also difficult to react with srebrodolskite. Such a fact also indicates that srebrodolskite is not an effective calcium source contributing Ca ions, that is, Ca ions are mainly contributed by calcium oxide, calcium hydroxide, dicalcium silicate, and tricalcium silicate minerals.

Conclusions

A process that utilizes the high alkaline properties of steel slag to promote the carbonation reaction while saving acid and alkali consumption was proposed. The process using acetic acid leaching to carry out the carbonation reaction without the addition of alkali has proven to be feasible. The main conclusions of the research are as follows:

(1) Steel slag has high alkalinity. The pH of the leachate of steel slag with a particle size of < 38 μm under different L/S ratio conditions can reach 12.79–13.13, which can increase the pH of the mixed leachate to a higher level. At the same time, the pH of the two-step mixed leachate were also higher than that of the one-step leachate;

(2) When the particle size was less than 38 μm and the acetic acid concentration was 1 M, the maximum Ca ions leaching ratio by two-step method can reach 75.3%. At the same time, the total Ca ions leaching ratios of the two-step method were higher than that of the one-step method under the same experimental conditions (whether it was 30 min or 60 min), which shows that the two-step method is better than the one-step method for the extraction of Ca ions;

(3) The mixed leachate obtained from the two-step leaching experiment under 11 sets of conditions can undergo carbonation reaction. Under these 11 experimental conditions, 7 groups of the one-step leachate could not undergo carbonation reaction, which shows that the two-step leaching can improve the pH of the leachate and promote the carbonation reaction;

(4) The carbonation results show that without the participation of acetic acid, the carbonation rate of Ca ions was higher, and the maximum carbonation rate can reach 91.4%. As the concentration of acetic acid increases, the pH of the mixed leachate decreases and the carbonation rate also decreases;

(5) Under the best experimental condition of the two-step method with $d < 38$ μm, L/S = 10, C = 1 M, 13.5% of the Ca ions in the steel slag are converted to calcium carbonate. However, under the same experimental condition, the leachate obtained by the one-step method cannot undergo carbonation reaction, which shows that the two-step method has a 13.5% net increase in the carbonation conversion rate of Ca ions in the steel slag.

(6) The XRD analysis results of the carbonation products of the two-step leachate show that the main component of the product is calcite, and there is a small amount of aragonite in the product under some conditions, which indicates that the two-step leaching method can obtain calcium carbonate products without the addition of alkali.

Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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