Indirect Carbonation by a Two-Step Leaching Process Using Ammonium Chloride and Acetic Acid

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Indirect carbonation as an efficient CO_2 sequestration strategy has received extensive attention in recent years. This study proposes a two-step leaching indirect carbonation process using NH_4Cl and CH_3COOH in order to combine the advantages of the two leaching agents to obtain a better experimental outcome. The experimental results show that NH_4Cl has a high pH buffering capacity, which can increase the pH of the mixed leachate to an alkaline level. Among the 21 groups of mixed leachate, 17 were alkaline (pH > 7). The mixed leachate has a high Ca^{2+} ions carbonation rate under low CH_3COOH concentration conditions, and the carbonation rate of steel slag with a particle size of < 38 μm can reach 60% when the CH_3COOH concentration is 0.1 M. SEM imaging showed that the $CaCO_3$ formed by the reaction exists in a hexagonal calcite crystal form.

INTRODUCTION

The dramatic increase in the concentration of CO_2 in the atmosphere has caused scientists to act. Forty years ago, in 1980, the concentration of CO_2 in the atmosphere was 337 ppm; however, the number has now increased to 419 ppm,[1] an increase of 24.3%. As a promising CO_2 sequestration measure, carbon capture and storage (CO_2 capture and storage, CCS) technology has received increasing attention in recent years. CCS technology includes three parts: CO_2 capture, CO_2 utilization, and CO_2 storage.[2] It uses certain technical means (such as chemical absorption, membrane separation, and adsorbent adsorption) to capture CO_2 from combustion or gasification processes.[3] The captured CO_2 is then used in the food and beverage industry, chemical production (such as urea, methanol, etc.), and mineral carbonation,[4] or it is pressurized (> 100 bar) to be transported to different geological structures or geologically-relevant locations, including deep seas, sea beds, oil and gas fields, saline-alkali aquifers, and other places, for long-term storage.[5] The use of CCS technology is considered an important approach for the reduction of the concentration of CO_2 in the atmosphere,[4] and thus it also plays a very important role in alleviating the ecological and environmental problems caused by the greenhouse effect.

Mineral carbonation is an important method of storage in CCS technology; that is, alkaline earth metal ions (mainly Ca^{2+} ions) within minerals react with CO_2 to form thermodynamically stable carbonate, thereby achieving CO_2 sequestration.[6] The processes of mineral carbonation are classified as direct carbonation or indirect carbonation according to their technical route. Direct carbonation refers to a process in which mineral feed stock and CO_2 react to form carbonate through a one-step reaction. Indirect carbonation includes two steps, a leaching step and a precipitation step; that is, the alkaline earth metal elements in the minerals are extracted with chemical reagents, and then CO_2 is introduced into the leachate to react, producing pure carbonate.[7] Indirect carbonation has greater advantages than direct carbonation because, firstly, the pH environment required for the leaching reaction and the carbonation reaction is different. An acidic environment is conducive to the leaching reaction, and an alkaline environment is beneficial for the carbonation reaction.[6] Indirect carbonation separates the two steps so that they can be carried out in

their respective, suitable pH environments; thus, a higher leaching rate and carbonation rate can be obtained.[8] Secondly, carbonate generated by direct carbonation will deposit onto the surface of mineral particles,[9] hindering further leaching of the alkaline earth metal ions, while the leaching reaction of indirect carbonation does not involve the deposition of carbonate, thus avoiding the reduction of the leaching rate. Finally, indirect carbonation can obtain pure carbonate, which can lead to considerable economic benefits.[10,11]

Steel slag is a byproduct of the steelmaking process, and is often used as a feed stock for mineral carbonation due to its special physical and chemical properties. Steel slag has a relatively high content of CaO (30–60%),[12–14] which allows for the provision of more alkaline earth metal elements for the carbonation reaction. At the same time, due to the presence of free CaO, steel slag tends to be alkaline,[15,16] which is quite advantageous for the carbonation reaction because CO_3^{2-} ions are often formed in an alkaline environment.[17] In addition, the iron and steel industries that produce steel slag also generate a large amount of CO_2, which allows the steel slag to be used as a feed stock of mineral carbonation for nearby carbon sequestration,[6] reducing transportation costs.

CH_3COOH and NH_4Cl are commonly used in the leaching reaction of indirect carbonation to extract Ca^{2+} ions from steel slag.[10,18–28] As an acid, CH_3COOH is more acidic than NH_4Cl, so its leaching rate for Ca^{2+} ions is higher. However, the strong acidity also causes the pH of the leachate to be low, which makes the subsequent carbonation reaction difficult because it is hard for CO_2 to dissolve in a low pH environment and produce CO_3^{2-} ions. After the leaching reaction, the leachate contains CH_3COO^- ions. In the carbonation reaction, the introduction of CO_2 will produce H^+ ions and CO_3^{2-} ions in the aqueous phase, and Ca^{2+} ions will react with CO_3^{2-} ions to produce $CaCO_3$. Because CH_3COOH is a weak acid, the CH_3COO^- ions will combine with H^+ ions to produce CH_3COOH again. With the continuous introduction of CO_2, the amount of CH_3COOH will gradually increase. CH_3COOH will dissolve $CaCO_3$ and make the reacted Ca^{2+} ions dissolve back into the aqueous phase, which leads to a decrease in the carbonation rate.[7] Eloneva et al.[21] leached Ca^{2+} ions from steel slag with 1 M CH_3COOH, and then carbonated the leachate. In the case of no alkali addition, the carbonation rate of 3% was obtained in the experiment. Bilen et al.[20] conducted carbonation reaction of 0.7 M CH_3COOH leachate, and their experimental results showed that the precipitation reaction would not occur without the addition of NaOH. For NH_4Cl, its acidity comes from the H^+ ions produced by the hydrolysis of the NH_4^+ ions, thus it is slightly lower than that of CH_3COOH, and its ability to leach Ca^{2+} ions is also weak. During the leaching reaction, H^+ ions are constantly consumed, which

makes the equilibrium of the hydrolysis reaction shift to the right. After the leaching reaction, $NH_3 \cdot H_2O$ is present in the leachate, so it is alkaline. During the carbonation reaction of the NH_4Cl leachate, the H^+ ions produced by the introduction of CO_2 consume $NH_3 \cdot H_2O$ to produce NH_4^+ ions, which will hydrolyze to produce $NH_3 \cdot H_2O$. Therefore, in the initial stage of the reaction, the NH_4^+/$NH_3 \cdot H_2O$ pH buffer system formed in the aqueous phase will keep the pH of the aqueous phase stable for a long time, and this high pH environment is conducive to the carbonation reaction. Therefore, a higher carbonation rate of Ca^{2+} ions can be obtained from the leachate of NH_4Cl. Eloneva et al.[27] performed a carbonation precipitation reaction on different concentrations of ammonium salt leachate of steel slag, and the results showed that the carbonation rate of Ca^{2+} ions was 50–70%. Lee et al.[29] carried out the carbonation reaction of 2 M NH_4Cl leachate and obtained a carbonation rate of 60% under the optimal experimental conditions.

In view of the characteristics of the two leaching agents, this study proposes a combination of the two reagents to make use of their respective advantages, namely, the high Ca^{2+} ions leaching rate of CH_3COOH and the high Ca^{2+} ions carbonation rate of NH_4Cl, in order to obtain a better experimental outcome.

MATERIALS AND METHODS

Materials

The steel slag used in the experiment was collected from Masteel (Ma Anshan, China), and three groups of different particle sizes were obtained by crushing, grinding and screening: < 38 μm, 38–75 μm and 75–150 μm. The slag was dried overnight at 105°C to remove moisture, and then stored in sealed bottles for later use. The chemical composition of the three groups of steel slag with different particle sizes was analyzed by x-ray fluorescence, and the results are shown in Table I. The main chemical components of the steel slag are CaO, MgO, SiO_2, and Fe_2O_3. However, the chemical composition of the steel slag varied with the different particle sizes. The CaO content decreased with increasing steel slag particle size, while the Fe_2O_3 content increased with increasing steel slag particle size.

Glacial CH_3COOH (> 99.5 wt.%, AR) was purchased from Saen Chemical Technology (Shanghai), NH_4Cl was purchased from Shanghai Aladdin Biochemical Technology (> 99.8 wt.%, GR), and CO_2 gas (purity > 99%) was purchased from Beijing Plex Practical Gas.

Method

NH_4Cl and CH_3COOH were used for the step-by-step leaching experiment, and the experimental flowchart is shown in Fig. 1. In the first step, NH_4Cl solution was used to leach the Ca^{2+} ions in steel

Table I. Chemical composition of steel slag

Constituent (wt.%)	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]	45.34	4.35	1.31	11.41	30.31	2.19	1.27	0.85	0.25	2.42	0.30
Contents[b]	45.19	4.15	1.32	11.40	30.56	2.30	1.35	0.85	0.26	2.38	0.24
Contents[c]	43.74	4.26	1.35	11.40	31.86	2.29	1.37	0.85	0.26	2.43	0.19

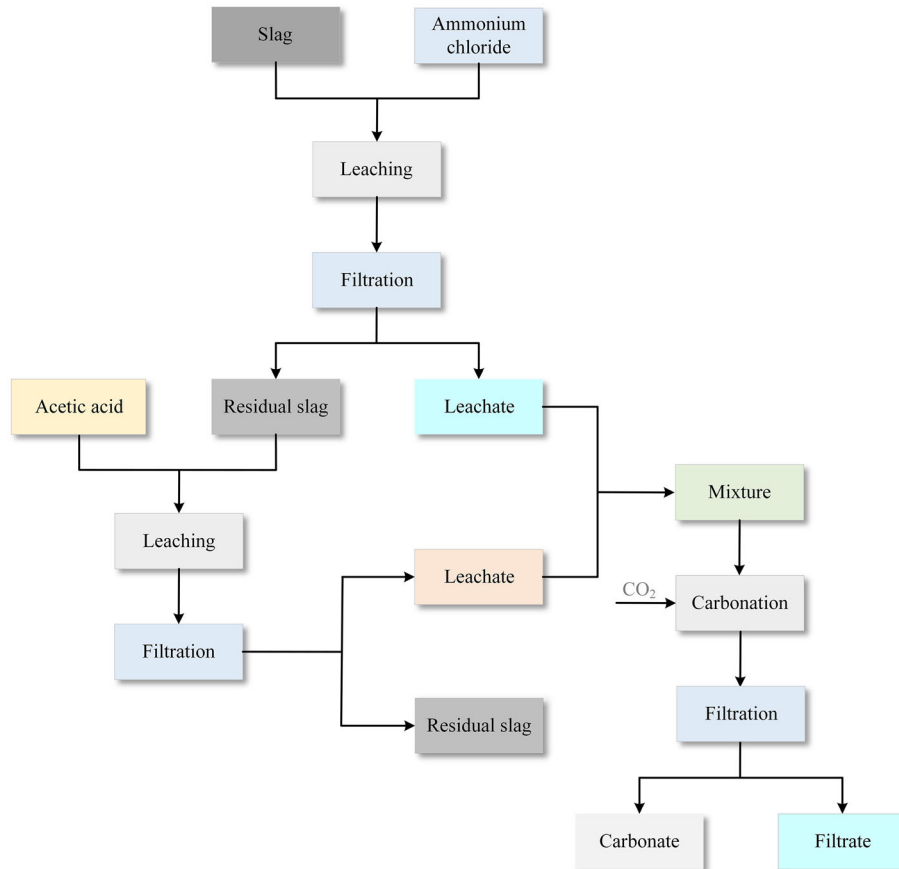[a]< 38 μm. [b]38–75 μm. [c]75–150 μm.

Fig. 1. Flow chart of experiment.

slag. After the leaching reaction, the slag obtained in the first step was filtered and reacted with CH$_3$COOH. Finally, the leachates obtained in the first and second steps were mixed, and CO$_2$ was introduced into the mixture for the carbonation reaction. In the experiment, 3 groups of steel slag with particle sizes of < 38 μm, 38–75 μm and 75–150 μm were selected. Seven groups of concentration ratios of NH$_4$Cl and CH$_3$COOH were selected: 2 M, 1.9/0.1 M, 1.8/0.2 M, 1.7/0.3 M, 1.6/0.4 M, 1.5/0.5 M, and 1.4/0.6 M. All the experiments were carried out at room temperature (25 °C).

The First Step of the Leaching Experiment

First, 100 mL of NH$_4$Cl solution with the required concentration was prepared with deionized water, and then the solution was added to a three-neck flask and placed in a water bath. The temperature of the water bath was set at 25°C, and a temperature electrode and pH electrode were inserted into the aqueous phase of the flask. The experiment was stirred by a magnetic rotor, with the rotation speed set at 500 rpm. Subsequently, 5 g of steel slag was weighed, and when the temperature and pH were stable, steel slag was added to the three-neck flask

to start the reaction. The reaction time was set to 30 min. After the reaction, the slurry was passed through a PTFE Millipore filter (0.45 μm pore size) to obtain the first leachate and filter residue. A small amount of filtrate was diluted to a certain concentration, and the concentration of Ca^{2+} ions was measured by inductively coupled plasma–atomic emission spectrometry (ICP-AES).

The leaching rate of the Ca^{2+} ions in the first leaching reaction ($\eta_{Ca,1}$) was calculated by Eq. 1:

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

where $C_{Ca,1}$ (mg/L) is the concentration of Ca^{2+} ions in the leachate obtained in the first leaching experiment, V (L) is the volume of the leachate, m_{slag} (g) is the mass of steel slag used in the experiment, x_{CaO} (%) is the mass fraction of CaO in the steel slag, MW_{CaO} (g/mol) is the molar mass of CaO and MW_{Ca} (g/mol) is the molar mass of Ca.

The Second Step of the Leaching Experiment

Deionized water was used to prepare 100 mL of CH_3COOH solution at the required concentration, and this was added to a three-necked flask and placed in a water bath. A temperature electrode and pH electrode were inserted into the CH_3COOH solution to measure the temperature and pH of the solution online, and the rotation speed was still set at 500 rpm. When the temperature and pH stabilized, the filter residue obtained in the first step was added to the flask to start the reaction. After 30 min, the reaction was finished, and the reaction slurry was filtered in the same above-mentioned way to obtain the second leachate and filter residue.

The leaching rate of Ca^{2+} ions in the second leaching reaction ($\eta_{Ca,2}$) is calculated by Eq. 2:

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

where $C_{Ca,2}$ (mg/L) is the concentration of Ca^{2+} ions in the leachate obtained by the second-step leaching experiment.

Carbonation Experiment

The leachate obtained from the two-step leaching reaction was mixed in a ratio of 1:1, and the mixed solution was added into a three-neck flask. A temperature electrode and pH electrode were inserted into the mixed leachate. After the temperature and pH were stabilized, CO_2 was introduced into the aqueous phase at a flow rate of 0.1 L/min for the carbonation reaction. The reaction time was set to 20 min. After the reaction, the carbonated slurry was filtered by a PTFE Millipore filter to obtain carbonated products and carbonated filtrate. A small amount of carbonated filtrate was diluted,

and the concentration of Ca^{2+} ions was detected by ICP-AES.

The Ca^{2+} ions carbonation rate (ξ_{Ca}) was obtained from Eq. 3:

$$\xi_{Ca} = \frac{0.5C_{Ca,1} + 0.5C_{Ca,2} - C_{Ca,3}}{0.5C_{Ca,1} + 0.5C_{Ca,2}} \quad (3)$$

where $C_{Ca,3}$ (mg/L) is the concentration of Ca^{2+} ions in the carbonated filtrate.

The experimental design is shown in Table II.

RESULTS AND DISCUSSION

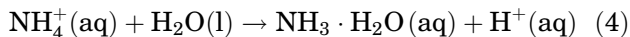### The pH of the Leaching Reaction

Steel Slag of < 38 μm

The pH variation during leaching process can be referred to in the online supplementary material, where Fig. S1a shows the pH variation of the steel slag leaching with different concentrations of NH_4Cl. The pH of the leachate quickly stabilizes within 2 min of the reaction. At the same time, there was little difference in the pH between the NH_4Cl leaching processes with different concentrations. After 30 min of reaction time, the pH was in the range of 8.69–8.89, which indicates that the NH_4Cl leachate is alkaline. In addition, the pH of the leachate does not completely increase with a decrease in the concentration of NH_4Cl. For example, the pH of 2 M NH_4Cl was 8.74 after leaching for 30 min, while the pH of the leachate of 1.9 M NH_4Cl was 8.69. However, overall, low-concentration NH_4Cl leaching resulted in a high-pH leachate. This is because NH_4Cl is a strong acid and a weak base salt, and because NH_4^+ ions will undergo a

Table II. Experimental scheme design

No.	d/μm	$C_{1,N}$/M	$C_{2,C}$/M
1	< 38	2.0	/
2	< 38	1.9	0.1
3	< 38	1.8	0.2
4	< 38	1.7	0.3
5	< 38	1.6	0.4
6	< 38	1.5	0.5
7	< 38	1.4	0.6
8	38–75	2.0	/
9	38–75	1.9	0.1
10	38–75	1.8	0.2
11	38–75	1.7	0.3
12	38–75	1.6	0.4
13	38–75	1.5	0.5
14	38–75	1.4	0.6
15	75–150	2.0	/
16	75–150	1.9	0.1
17	75–150	1.8	0.2
18	75–150	1.7	0.3
19	75–150	1.6	0.4
20	75–150	1.5	0.5
21	75–150	1.4	0.6

hydrolysis reaction to generate $NH_3 \cdot H_2O$, as shown in Eq. 4. The aqueous phases of NH_4^+ and $NH_3 \cdot H_2O$ coexist during the reaction to form a pH buffer system, so the pH variation is not clear.

$$NH_4^+(aq) + H_2O(l) \rightarrow NH_3 \cdot H_2O(aq) + H^+(aq) \quad (4)$$

The pH of the CH_3COOH leaching process is shown in Fig. S1b, from which it can be clearly seen that the pH of the leachate decreases with increasing CH_3COOH concentration, and the pH of leachates with slightly differing concentration values differ greatly. For example, when leaching with 0.1 M CH_3COOH, the pH of the leachate was 7.54 after 30 min of reaction time, while it was 6.21 at 0.2 M. At the same time, the time it took for the pH of the leachate to stabilize decreased with the increasing CH_3COOH concentration. The pH stabilized after 10 min at 0.1 M, and after 2 min at 0.6 M. This is because there are fewer H^+ ions that can be ionized under low-concentration CH_3COOH leaching conditions, so the reaction takes a long time to reach equilibrium. Under high-concentration CH_3COOH leaching conditions, the acid is more abundant than the slag, so the pH stabilizes faster.

The fitting of the pH variation curve of the leaching process found that the pH variation curves of the NH_4Cl and CH_3COOH leaching processes are in line with the curve $y = \frac{abx^{1-c}}{1+bx^{1-c}}$. That is, in the initial stage of the reaction, the pH increases rapidly with increasing time. After a certain period of time, the pH variation with time decreased, and in the last stage of the reaction, an increase in time did not lead to a variation in pH.

The pH of the mixed leachate of < 38 μm steel slag is shown in Fig. 2. Except for the 1.4/0.6 M group, the pH values of the mixed leachates are all greater than 8, which is alkaline. At the same time, the pH values of the mixed leachate of the 2 M, 1.9/0.1 M, 1.8/0.2 M, 1.7/0.3 M, and 1.6/0.4 M groups are all greater than 8.5. It should be pointed out that
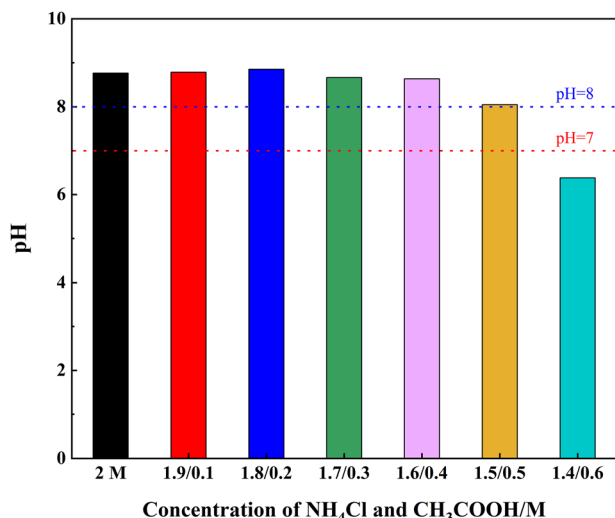

Fig. 2. pH of < 38 μm steel slag mixed leachate.

the pH values of the mixed leachate of the 1.7/0.3 M and 1.6/0.4 M groups were 5.36 and 4.98, respectively, which were relatively acidic, while the pH values of the mixed leachate were 8.66 and 8.63, respectively, indicating that the NH_4Cl had a significant effect on raising the pH of the CH_3COOH leachate. For the 1.4/0.6 M group, the pH of the mixed extract was lower, at only 5.44. This is because the pH of the 0.6 M CH_3COOH leachate is 4.51, which is low, and the amount of NH_4Cl is further reduced, which results in an insufficient alkalinity for the CH_3COOH leachate; therefore, the pH of the mixed leachate is low.

Steel Slag of 38–75 μm

The pH variations in the 38–75 μm steel slag leached in NH_4Cl and CH_3COOH are shown in Fig. S2a and b, respectively. The pH of the NH_4Cl leachate at the end of the reaction was not much different from that of the < 38 μm group, which indicated that the particle size had little effect on the pH of the NH_4Cl leachate. This phenomenon, and the insignificant effect of NH_4Cl concentration on the pH of the leachate in the previous section, suggest that the NH_4Cl leachate is not sensitive to changes in the experimental parameters due to the presence of the $NH_4^+/NH_3 \cdot H_2O$ buffer system. However, for the CH_3COOH leachate, the pH of the 38–75 μm group was significantly lower than that of the < 38 μm group. For the 0.1 M CH_3COOH leaching, the pH of the leachate of the < 38 μm group was 7.54, while the pH of the 38–75 μm group was 6.37, representing a decrease of 1.17 units. The pH of the leachate under other concentration conditions also decreased to different degrees. This shows that NH_4Cl and CH_3COOH are two reagents with different properties. NH_4Cl is a strong acid and a weak base salt that generates H^+ ions through the hydrolysis reaction of NH_4^+ ions, while CH_3COOH is a weak acid that releases H^+ ions through an incomplete electrolysis reaction, as shown in Eq. (5), which leads to the difference in pH of their respective leachates.

$$CH_3COOH(aq) \rightarrow CH_3COO^-(aq) + H^+(aq) \quad (5)$$

The pH variations of the 38–75 μm steel slag mixed leachate are shown in Fig. 3. The pH values of the mixed solutions of the 2 M, 1.9/0.1 M, 1.8/0.2 M, and 1.7/0.3 M groups were greater than 8, the pH values of the mixed solutions of the 1.6/0.4 M and 1.5/0.5 M groups were between 7 and 8, and the pH of the 1.4/0.6 M group was less than 7 (6.38). Compared with the < 38 μm group, the pH of the mixture in the 38–75 μm group decreased to a certain extent, but the decrease was not significant. This is also due to the buffering effect of the NH_4Cl leachate.

Steel Slag of 75–150 μm

The pH variations of the 75–150 μm steel slag leached in NH_4Cl and CH_3COOH are shown in
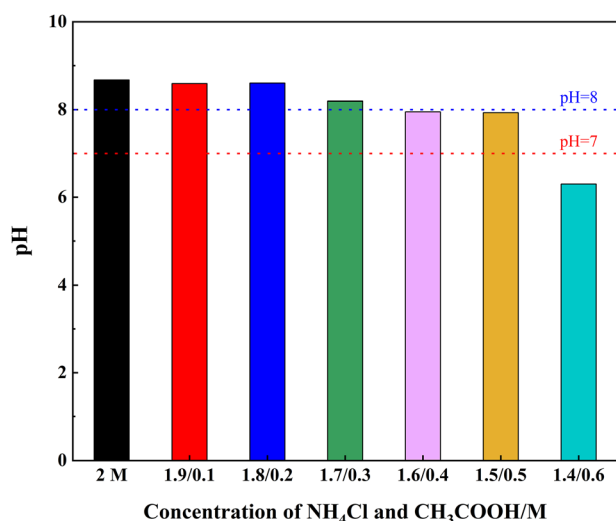
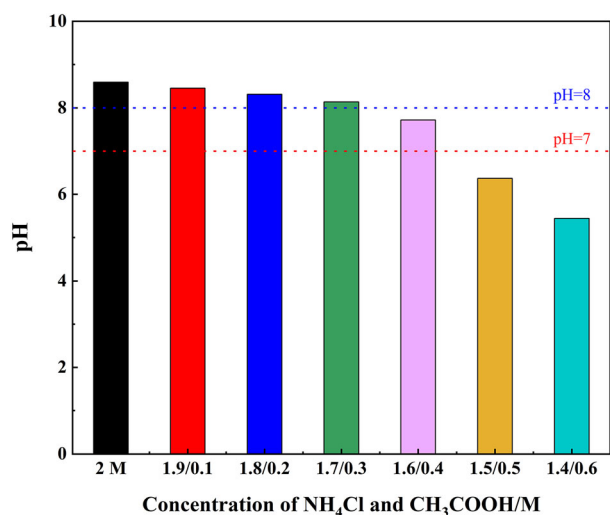Fig. 3. pH of 38–75 μm steel slag mixed leachate.

Fig. 4. pH of 75–150 μm steel slag mixed leachate.

Fig. S3. The pH of the NH$_4$Cl leachate was in the range of 8.57–8.74, which was not significantly lower than the results of the first two groups. For the CH$_3$COOH leaching experiment, the pH of the leachate is in the range of 4.39–5.98, and the difference between its pH and the pH of the previous group of particle sizes is smaller than that of the former two groups, which shows that an increase in particle size has a weaker effect on the reaction, and that the relationship between the particle size and the effect on the reaction is not linear.

The pH of the 75–150 μm steel slag mixed leachate is shown in Fig. 4. The pH of the 1.5/0.5 M group dropped below 7 (6.37), the pH of 1.6/0.4 M dropped between 7 and 8 (7.72), and the pH of the other four groups was still greater than 8. It can be seen that the greater the amount of CH$_3$COOH, the greater the drop in pH of the mixed solution.

Ca^{2+} Ions Leaching Rate

The changes in the Ca^{2+} ions leaching rate of the three groups of steel slags with different concentrations of NH$_4$Cl and CH$_3$COOH are shown in Fig. 5. The leaching rate of Ca^{2+} ions decreases with decreasing NH$_4$Cl concentration and increases with increasing CH$_3$COOH concentration. At the same time, as with the pH results, changes in the concentration of NH$_4$Cl have little effect on the leaching rate of the Ca^{2+} ions, while changes in the concentration of CH$_3$COOH have a more obvious effect on the leaching rate of the ions. For the < 38 μm particle size group, as can be seen from Fig. 5a, the leaching rate of the NH$_4$Cl in the 1.8/0.2 M group was 4.25% lower than that of the 1.9/0.1 M group, while the leaching rate of the CH$_3$COOH increased by 99.60%. At the same time, the Ca^{2+} ions leaching rate of the NH$_4$Cl is relatively low. When leaching with 2 M NH$_4$Cl, the leaching rates of the three particle size groups of steel slag were 38.65%, 28.77%, and 24.15%, while the leaching rates when leaching with 0.6 M CH$_3$COOH were 31.93%, 29.87%, and 26.45%, respectively. The leaching rates of 0.6 M CH$_3$COOH in the 38–75 μm group and the 75–150 μm group were even higher than that of 2 M NH$_4$Cl, which shows that the leaching ability of CH$_3$COOH is better than that of NH$_4$Cl.

When leaching with 2 M NH$_4$Cl, the leaching rate of the 38–75 μm group was reduced by 25.56% compared with the < 38 μm group, and the 75–150 μm group was reduced by 16.06% compared with the 38–75 μm group, which was similar to the variations in pH, indicating that the relationship between particle size and reaction effect is not linear. The larger the particle size, the smaller the inhibitory effect of increasing particle size on the reaction effect.

In addition, the Ca^{2+} ions leaching ability of CH$_3$COOH for large particles of steel slag is better than that of NH$_4$Cl. It can be seen from Fig. 5 that, as the particle size increases, the difference between the leaching rates of CH$_3$COOH and NH$_4$Cl gradually decreases. At the concentration of 1.9/0.1 M, the differences in the leaching rates of CH$_3$COOH and NH$_4$Cl in the three groups of particle sizes were 27.47%, 19.02%, and 14.04%, respectively. For the < 38 μm group, the Ca^{2+} ions leaching rate of all the concentrations of NH$_4$Cl was higher than that of CH$_3$COOH, while in the 38–75 μm group, the leaching rate of CH$_3$COOH in the 1.4/0.6 M group exceeded that of NH$_4$Cl. For the 75–150 μm group, there are 1.5/0.5 M and 1.4/0.6 M groups of CH$_3$COOH with higher leaching rates than NH$_4$Cl. This also shows that the leaching ability of CH$_3$COOH is better than that of NH$_4$Cl, because the specific surface area of large-sized steel slag is small, and the diffusion path of Ca^{2+} ions from the slag matrix to the surface is longer. Therefore, the leaching reaction of Ca^{2+} ions does not proceed
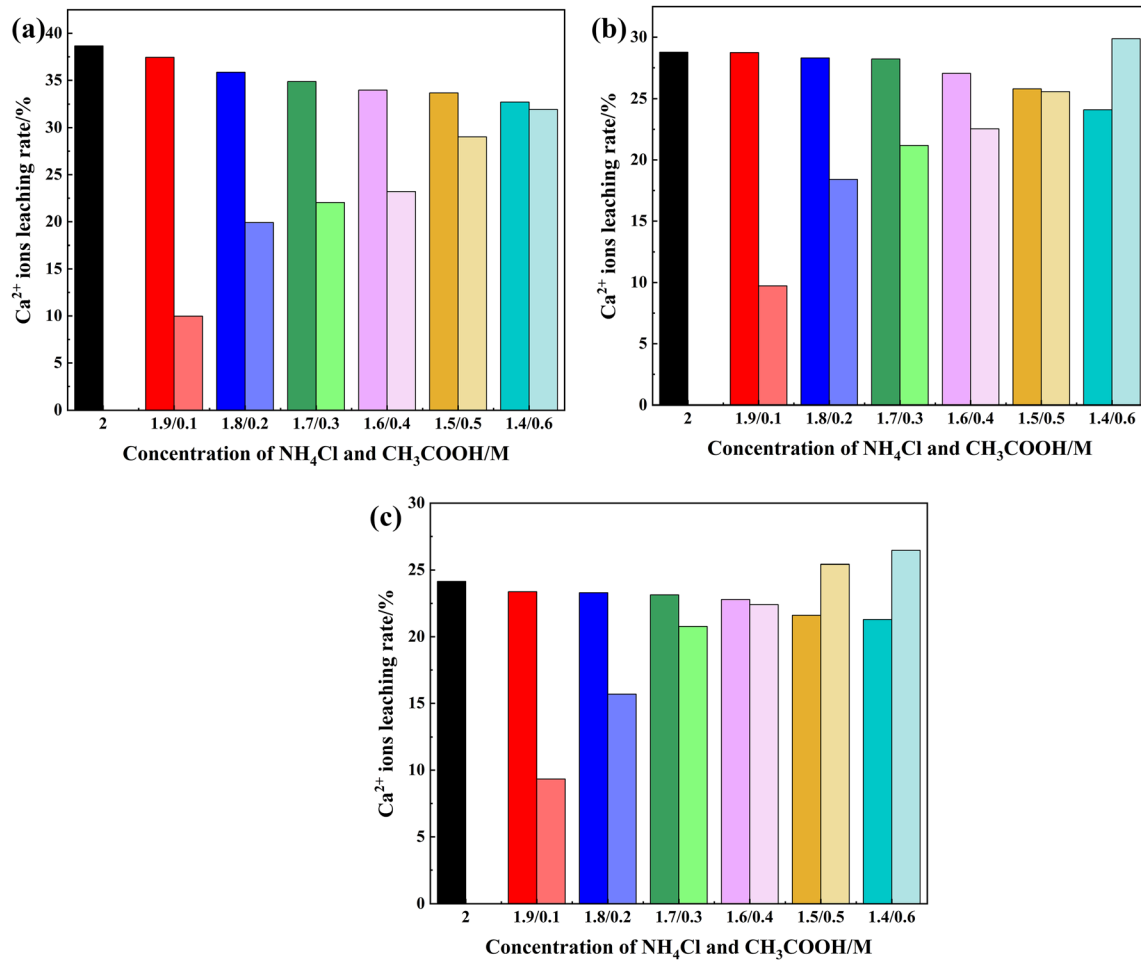
Fig. 5. Ca^{2+} ions leaching rates of three groups of particle size steel slag: (a) < 38 μm; (b) 38–75 μm; (c) 75–150 μm.

easily, and the forward reaction necessitates more acidic conditions. The difference in the leaching rate between CH$_3$COOH and NH$_4$Cl decreases with increasing particle size, which indicates that the acidity of CH$_3$COOH is stronger than that of NH$_4$Cl, and its leaching ability for Ca^{2+} ions is also stronger.

The pH of the Carbonation Reaction

The pH variations during the carbonation reaction of the three groups of steel slag mixed leachate are shown in Fig. 6. Most of the pH variations result in a step shape; in the initial stage of the reaction (3–10 min), the pH drops slowly. Afterward, the pH goes through a rapid decline (approximately 90 s) to a lower level. Finally, the pH drops slowly until it stabilizes.

During the experiment, it was found that, in the initial stage of the reaction, the introduction of CO$_2$ did not cause white precipitation in the leachate. White precipitation began to appear in the solution at about 3 min of reaction, and there was obvious white precipitation in the aqueous phase at approximately 4 min. This is because CO$_2$ needs to be dissolved in the aqueous phase to form carbonic acid

after it's introduced. At the initial stage of the reaction, there are few CO$_3^{2-}$ ions produced by carbonic acid electrolysis, and the concentration product Q of Ca^{2+} ions and CO$_3^{2-}$ ions is less than the solubility product Ksp of CaCO$_3$; therefore, no CaCO$_3$ is produced. The dissolution of CO$_2$ at the beginning of the reaction is the limiting link of the reaction, so the pH of the aqueous phase decreases slowly. As the amount of dissolved CO$_2$ increases, the amount of carbonic acid in the aqueous phase also increases. At this time, carbonic acid continuously ionizes H$^+$ ions, HCO$_3^-$ ions, and CO$_3^{2-}$ ions, so that the pH of the aqueous phase drops rapidly. When the Ca^{2+} ions in the aqueous phase are consumed in large quantities and have a lower concentration, the concentration product Q of Ca^{2+} ions and CO$_3^{2-}$ ions also decreases. At this time, the carbonation reaction progresses slowly, and the amount of CO$_3^{2-}$ ions required for the reaction also decreases. Therefore, the ionization reaction of H$_2$CO$_3$ tends to balance, so the pH drops slowly until it stabilizes.

The above phenomenon occurs when the pH of the mixed solution is greater than 8. For the case of pH < 8, as in the experiments of 1.4/0.6 M in the
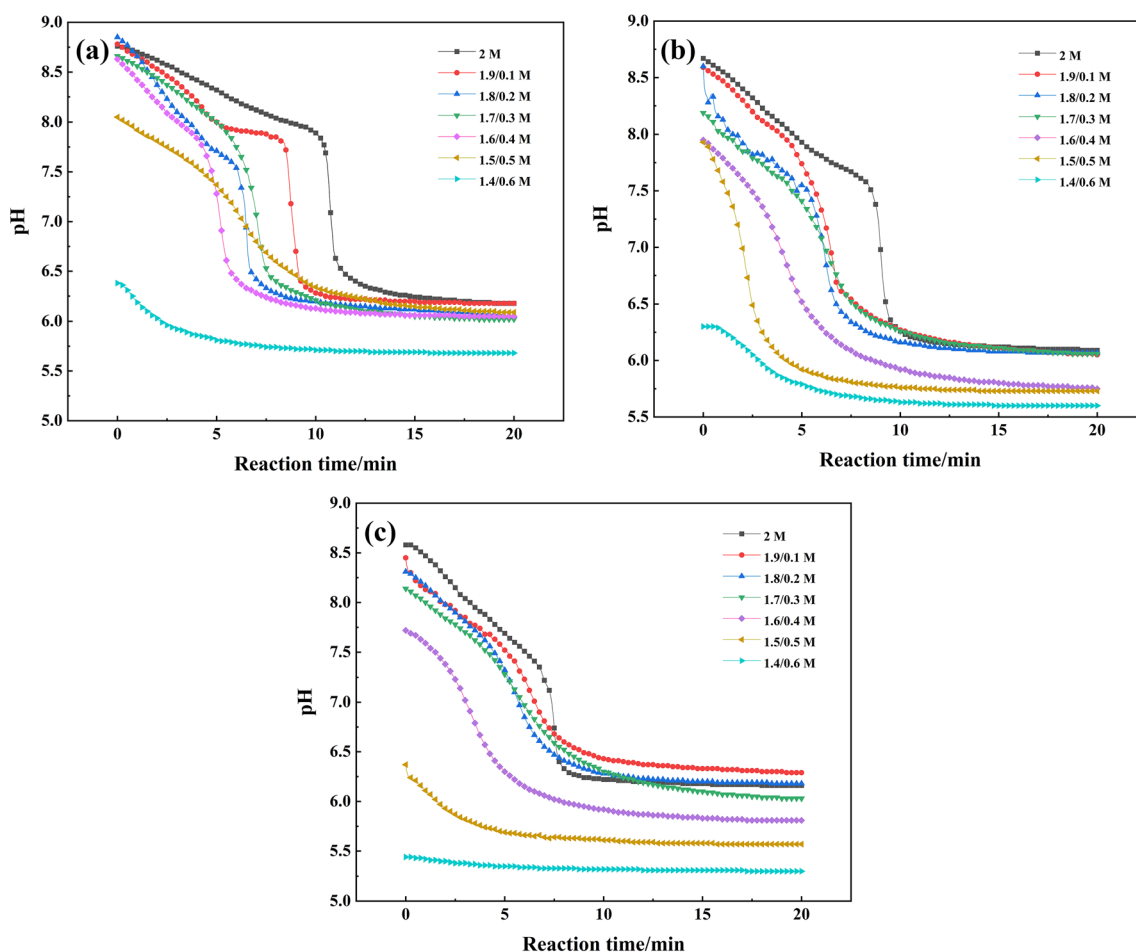
Fig. 6. The pH variations during the carbonation reaction of the three particle size groups of steel slag leachates: (a) < 38 μm; (b) 38–75 μm; (c) 75–150 μm.

< 38 μm group and the 1.6/0.4 M, 1.5/0.5 M, and 1.4/0.6 M in the other two particle size groups, the pH first drops rapidly and then stabilizes. This is due to the higher concentration of CH_3COOH in these groups of experiments, which resulted in more CH_3COO^- ions in the leachate. When CO_2 is introduced into the aqueous phase, CH_3COO^- will combine with the H^+ ions ionized by H_2CO_3 to generate CH_3COOH, which accelerates the ionization of H_2CO_3 and makes the pH drop rapidly. At the same time, the low pH makes it hard to generate CO_3^{2-} ions, so the carbonation reaction proceeds with difficulty, and there is little white precipitate in the aqueous phase. When the combination of CH_3COO^- ions and H^+ ions reaches equilibrium, the ionization reaction of H_2CO_3 also tends to equilibrium, so the pH slowly stabilizes.

Ca^{2+} Ions Carbonation Rate

The Ca^{2+} ions carbonation rate of the three groups of steel slag leachates is shown in Fig. 7. For the < 38 μm group, when leaching with 2 M NH_4Cl, the Ca^{2+} ions carbonation rate was 76.54%. As the concentration of CH_3COOH increases and the

concentration of NH_4Cl decreases, the carbonation rate gradually decreases. The carbonation rate of the 1.9/0.1 M group was 60%, while that of the 1.4/0.6 M group was only 3.05%, and almost no carbonation reaction occurred. The trend in the carbonation rate is not consistent with the trend in the pH of the mixed leachate. Regarding the pH of the mixture, it can be seen from Fig. 2 that, except for the 1.5/0.5 M and 1.4/0.6 M groups, the pH values of the other 5 mixtures were all above 8.6, with no obvious fluctuations. However, the carbonation rate decreased considerably. The carbonation rate of the 1.6/0.4 M group was 23.62%, which was 69.14% lower than that of the 2 M group. This is because, as the concentration of CH_3COOH increases, the amount of CH_3COO^- ions in the leachate also increases. CH_3COO^- ions will combine with the H^+ ions ionized by H_2CO_3 to form CH_3COOH, thus making it difficult for the carbonation reaction to occur. This result shows that the ionic system of the leachate has a significant effect on the carbonation rate, and that its effect is much greater than that of pH. Therefore, in order to control the precipitation reaction during indirect carbonation, attention should be given not only to
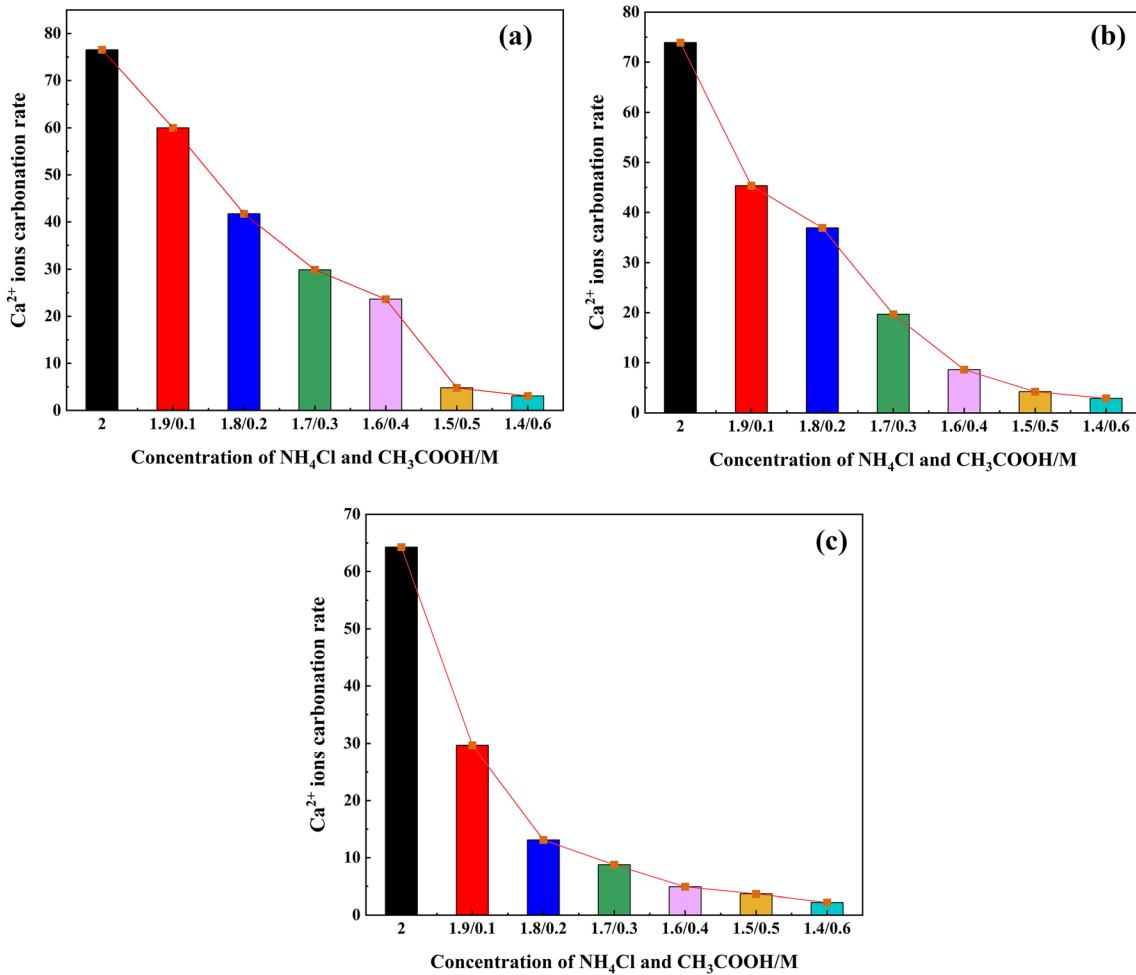
Fig. 7. Ca^{2+} ions carbonation rate of three groups of particle size steel slag: (a) < 38 μm; (b) 38–75 μm; (c) 75–150 μm.

the pH of the leachate but also to the ionic system of the leachate. Under the same pH condition, the carbonation rate of the leachate of different ionic systems will also have considerable differences.

The carbonation rate of the 38–75 μm group was lower than that of the < 38 μm group. Under the condition of 1.6/0.4 M, the pH values of the leachate of the < 38 μm group and the 38–75 μm group were 8.63 and 7.95, and the carbonation rates were 23.62% and 8.59%, respectively, which indicates that the particle size has a greater impact on the pH of the leachate. At the same time, the pH has a significant effect on the carbonation rate. When the pH drops by 0.68 units, the carbonation rate drops by 63.63%. In addition, the pH of the 1.6/0.4 M group of the 38–75 μm group was lower than that of the 1.5/0.5 M of the < 38 μm group (8.05), but its carbonation rate was higher than that groups (4.79%), which also shows that the effect of the leachate ionic system on the carbonation rate is greater than the effect of pH. When the concentration of CH_3COOH in the 1.5/0.5 M group is higher, the amount of CH_3COO^- ions in the leachate is greater, and the inhibitory effect of CH_3COO^- ions

on the carbonation reaction is more significant, so its carbonation rate is lower. The carbonation rate of the 75–150 μm group was further reduced, and the carbonation rate of the four groups was lower than 10%, including the 1.7/0.3 M group with a pH of 8.14. This is because the large particle size makes the reaction less complete, the amount of CH_3COOH that does not participate in the reaction is greater, and its inhibitory effect on the carbonation reaction is more obvious. The carbonation rate under the condition of 1.9/0.1 M concentration was 29.67%, which was 50.55% lower than in the <38 μm group (60%).

Figure 8 shows the x-ray diffraction pattern of the carbonation product. It can be seen that the reaction product is mainly calcite, which indicates the formation of $CaCO_3$. Figure 9 shows the scanning electron microscopy morphology of the $CaCO_3$ formed by the precipitation reaction. The $CaCO_3$ exists in a hexagonal calcite crystal form, with a crystal grain size of approximately 2.5–5 μm. The crystal grains are agglomerated, and the size of the agglomerates is approximately 18–24 μm. The formation of $CaCO_3$ show that the carbonation reaction
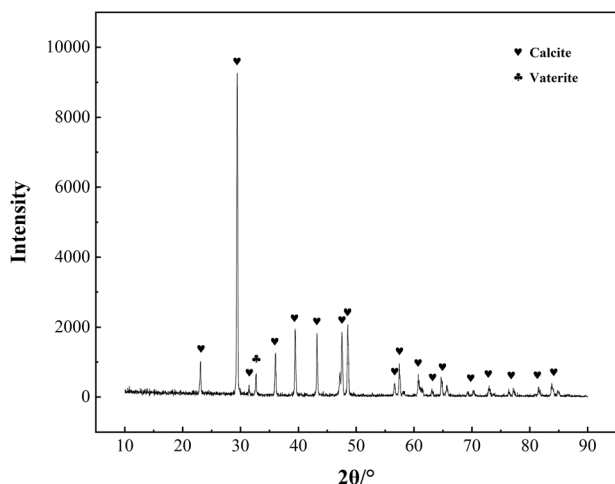
Fig. 8. XRD pattern of carbonation product (< 38 μm, 1.8/0.2 M).
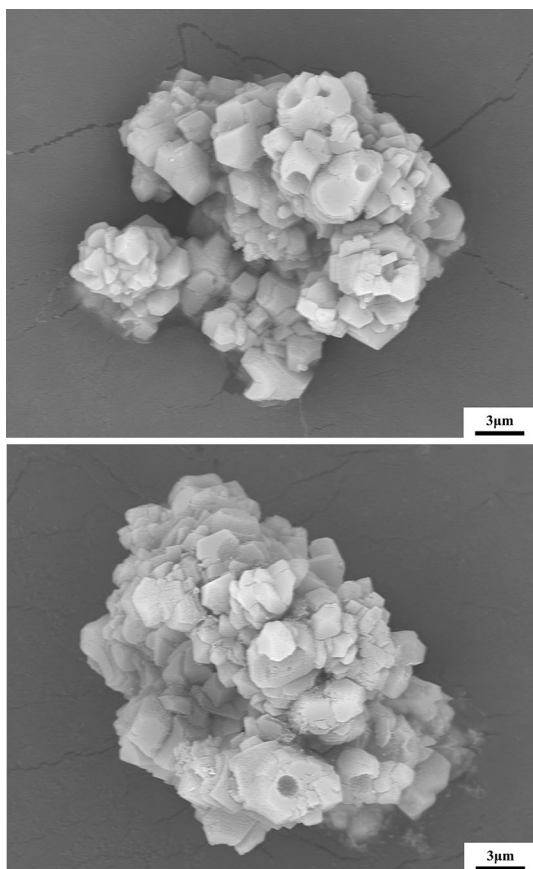

Fig. 9. SEM morphology of the carbonation product (< 38 μm, 1.8/0.2 M).

can take place in the case of multistep leaching using NH_4Cl and CH_3COOH without the addition of alkali.

CONCLUSION

This study explored the experimental effects of the indirect carbonation reaction of two-step leaching using NH_4Cl and CH_3COOH. Among the 21

groups of mixed leachate, 17 groups had an alkaline pH (pH > 7), while the pH of the CH_3COOH leachate was acidic except for the 0.1 M group of < 38 μm particle size. This indicates that the NH_4Cl leachate has a strong pH buffering capacity and can effectively increase the pH of the mixed leachate, which is favorable for the subsequent precipitation reaction. The pH variations of the mixed leachate are similar to the pH variations of the NH_4Cl leachate; that is, the fluctuation is not large, and it is mostly contained between 8 and 9. The mixed leachate of NH_4Cl and CH_3COOH has a higher Ca^{2+} ions carbonation rate, because the NH_4Cl leachate drives an increase in the pH of the mixed leachate, creating a suitable alkaline environment for the precipitation reaction. However, the trend in the carbonation rate is not completely consistent with the trend in pH; that is, as the concentration of CH_3COOH increases, the carbonation rate undergoes a greater decrease. This result shows that the ionic system of the leachate has a significant effect on the carbonation rate, and that its effect is much greater than that of the pH.

This study shows that a two-step leaching reaction that uses NH_4Cl and CH_3COOH can combine the advantages of the two leaching agents to obtain a higher pH leachate and a higher Ca^{2+} ions leaching rate. In view of the fact that the Ca^{2+} ions carbonation rate is greatly affected by the increase of CH_3COOH concentration, we will explore in future research how to increase the Ca^{2+} ions carbonation rate of the leachate with high pH and high CH_3COOH concentration to take further advantage of this two-step method.

CONFLICT OF INTEREST

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

SUPPLEMENTARY INFORMATION

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