The indirect mineral carbonation of industrial residues is one of the potential technologies for CO₂ sequestration. In this paper, the leaching and carbonation of electric arc furnace (EAF) slag under microwave irradiation was investigated. The experimental results show that the main reactive calcium-containing phase in the EAF slag carbonation process is calcium silicate, and the final leaching ratio of larger particles is lower than that of smaller particles due to the silica layer produced on the surface of the calcium silicate. The Drozdov equation with a self-impeding coefficient can describe EAF slag leaching kinetics under microwave irradiation. The explosive homogeneous nucleation phenomenon under microwave irradiation contributes to the thinning and narrowing of crystals. Microwave irradiation can inhibit the crystaltype transformation of vaterite.

With the modernization and industrialization of countries over the past centuries, large amounts of CO₂ emissions and industrial solid waste have caused severe pollution. Although the use of fossil fuels as the primary source of the world's energy results in high CO₂ emissions, their usage is inevitable in the foreseeable future due to the costs of other energy sources, societal pressures and the established infrastructure. To effectively reduce artificial CO₂ emissions, carbon capture and storage (CCS) is widely used. Mineral carbonation, a potentially important technology in CCS, has many advantages. For example, the process energy consumed by mineral carbonation is very low, and product of the process is stable in nature. Since the weathering reaction of silicate and CO₂ requires a large geological time scale, this reaction is not suitable for CO₂ sequestration on engineering time scales. Therefore, many solutions have been developed to improve the reaction rate and reduce the process cost, such as adopting a wide variety of materials, leaching agent and methods.

In the past three decades, natural minerals, such as orsterite, serpentine and wollastonite, have been used as mineral carbonation feedstocks. With the development of research, some industrial wastes, such as metallurgy slag, fly ashes, and building and mining waste, have been applied as feedstocks because these industrial wastes are more active and do not need to be exploited. Moreover, industrial wastes are usually close to CO₂ emission sites, so the transportation cost can be greatly decreased.

As the dry reaction is usually much slower than the wet reaction, the study of mineral carbonation focuses on wet reaction. In the case of aqueous mineral carbonation, leaching agents have attracted more attention because lower pH values are helpful for the leaching of alkaline earth elements but harmful for CO₂ fixation. Strong acids, such as hydrochloric acid, were first selected as leaching agents, and then weak acids were gradually used as leaching agents, based on thermodynamic considerations; however, impurity ions are the main drawback, and carbonate precipitation is difficult to generate without a pH increasing agent in some cases. Subsequently, ammonium salts have been studied as leaching agents due to their lower acidity. After the leaching reaction, the system pH scale of ammonium chloride solution ranges from 8.0–10.5, where only calcium ions exist, so pure calcium carbonate can be prepared without purification. Additionally, ammonium salts used as leaching agents can be recycled at the carbonation stage, so the process effectively reduces the cost and has attracted much attention. Nevertheless, the leaching ratio is far from satisfactory. However, many methods have also been proposed to improve the leaching ratio. Park and Fan found that the fluidization of serpentine slurry with 2 mm glass beads was most effective in refreshing the surface of the serpentine particles during the dissolution process. Finely ground and heat-activated serpentine derived from mining residues has also been studied for CO₂ capture and sequestration. Additionally, some unconventional methods, such as ultrasonic and microwave...
Results and Discussion

The mechanism of the leaching reaction. From the leaching ratio curves of the four size fractions in Fig. 1, the initial leaching ratio of calcium was much lower, and the final leaching ratio was also lower for larger particles. Although the leaching ratio tends to reach a balance as the reaction time increases for each particle,
size, small particles clearly tend to reach a balance more quickly. As the phases of EAF slag are complex and their leaching behaviors are different, comparing the changes in the main phases before and after the leaching reaction will be helpful in understanding the leaching mechanism. Preliminary SEM and XRD analysis indicated that the main phases in EAF slag are calcium silicate, calcium ferroaluminates and the RO phase, where the RO phase is a solid solution mainly containing iron and magnesium without calcium. Figure 2a,b shows typical metallographic SEM images of three-phase symbiosis. Figure 2b shows that calcium mainly exists in calcium silicate and calcium ferroaluminates. Typical metallographic microstructures of leached residues at 54–74 μm are shown in Fig. 2c–f. It can be seen that calcium is leached from silicate instead of ferroaluminates from leached residues at 2 min (Fig. 2c,d), and the calcium ferroaluminates still do not react when the leaching reaction reaches 120 min (Fig. 2e,f), so the main reactive calcium-containing phase in EAF slag is only calcium silicate.

Figure 3a shows the as-received slag, in which the calcium silicate surface is smooth and dense and the calcium content is high. In contrast, in the 2 min leached slag in Fig. 3b, there is a loose silica passivation layer produced on the surface of calcium silicate particles (97–150 μm), and in practice, the leaching reaction will be prevented as the passivation layer becomes thicker with increased leaching time.

According to the leaching curve in Fig. 1, the leaching ratio of calcium increases quickly in the beginning and tends to reach a balance later, which clearly indicates a resistance phenomenon throughout the whole process. Putting the data from Fig. 1 into the kinetic model of the Drozdov equation with a self-impeding coefficient as below, the results from Fig. 4 show that ln[1/(1 – x)]/t−1 and x/t have a strong linear correlation with a correlation coefficient of more than 0.999. This result indicates that the Drozdov equation with a self-impeding coefficient can describe EAF slag leaching kinetics under microwave irradiation.

\[
\frac{1}{t} \ln \frac{1}{1 - x} - \frac{\beta^2}{t} = K_m
\]
where \( t \) is the leaching time, min; \( x \) is the leaching ratio, \%; \( \beta \) is the self-impeding coefficient; and \( K_m \) is the reaction ratio constant.

**Carbonation under microwave irradiation.** Figure 5 shows the calcium carbonate reaction in a water bath and under microwave irradiation. The reaction ratio was only 66% at 12 °C in the water bath, and the reaction ratio accelerated with increasing temperature. The reaction time was reduced to 50 min due to the rate of diffusion, and the reaction accelerated when the temperature reached 50 °C. However, the reaction curve did not change much as the temperature increased to 65 °C, probably because evaporating ammonia affects the dissolution of CO2. Furthermore, microwave irradiation improves the reaction rate; however, the solution boils in 30 min, and the reaction stops when the microwave power reaches 360 W. Interestingly, in contrast to the experiments in a water bath, the reaction ratio under microwave irradiation is very low at the initial stage and then increases rapidly until reaching the end of the reaction. The phenomenon of explosive homogeneous nucleation contributes to the thinning and narrowing of crystals.

The particle size of the produced calcium carbonate was analyzed after the carbonation reaction, as shown in Fig. 6. In a water bath, the particle size increases with increasing temperature, and the distribution range becomes broadened. However, the change in particle size is small under microwave irradiation, and the particle size of the produced calcium carbonate is considerably smaller and more narrow than that obtained in a water bath (except at 12 °C), which agrees with the phenomenon of explosive homogeneous nucleation in Fig. 5. In addition, there are two peaks in Fig. 6, which is the same as in a report about the carbonation of calcium hydroxide slurry31. The smaller peak is the primary crystals with a particle size of 0.4–2.5 \( \mu \)m, and the larger peak is the agglomeration of many initial crystallites, as indicated by the typical SEM image (Fig. 7).

As shown in Fig. 8, there was only vaterite at 12, 25 and 35 °C in the water bath, which is consistent with the report that vaterite is produced in ammonium chloride-ammonia32,33. However, the calcium carbonate crystals gradually converted into aragonite and calcite as the temperature increased to 50 and 65 °C, which indicates that temperature has a strong influence on the morphology of calcium carbonate and that the temperature should remain beneath a threshold for the preparation of pure calcium carbonate products. This conclusion is similar to the results of Tom Van Gerven's study18, which considered the preparation of high-quality precipitated calcium.
carbonate using a blast furnace (BF). Moreover, it can be seen from Fig. 9 that vaterite, aragonite and calcite have been produced at temperature of 65°C, and then the produced calcium carbonate gradually turn into calcite crystal with the increase of reaction time. In contrast, all the calcium carbonate crystals prepared under different powers of microwave irradiation were vaterite, although the solution temperature was relatively high (about 50°C) during half of the reaction time for a microwave power of 270 W (Fig. 5), which is a powerful statement that microwave irradiation can inhibit the crystalty petrans formation of vaterite.

Figure 5. The calcium carbonate reaction ratio and heating curve of the solution with time.

Figure 6. The effect of temperature and microwave power on particle size.

Figure 7. Typical SEM image of calcium carbonate produced by reaction under microwave irradiation.
Conclusions
The main reactive calcium-containing phase is calcium silicate in the EAF slag carbonation process, and the final leaching ratio of larger particles is lower than that of smaller particles due to the silica layer produced on the surface of calcium silicate. The Drozdov equation with a self-impeding coefficient can describe EAF slag leaching kinetics under microwave irradiation. The explosive homogeneous nucleation phenomenon under microwave irradiation contributes to the thinning and narrowing of crystals. Microwave irradiation can inhibit the crystal-type transformation of vaterite.

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Figure 8. X-ray diffraction patterns of calcium carbonate.

Figure 9. X-ray diffraction patterns of calcium carbonate with different time at 65° C.
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Author Contributions
Guojun Ma and Cheng Peng conceptualized this work, and Zhibo Tong and Gang Yang carried out all the experiments and analyses. Zhibo Tong and Dan Zhou took the lead in drafting the article. All authors have contributed to discussions and interpretation of the results.

Additional Information
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