# Preparation of CaCO₃ from CaCl₂ waste liquid and flue gas CO₂ based on absorption–mineralization process using water-soluble amines

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## ABSTRACT

The treatment of $CaCl_2$ waste liquid has become a common technical problem in the soda industry, and there is still no good solution. Meanwhile, the global is under intense pressure from drastic climate change, and $CO_2$ emission reduction is urgent. If the two waste are utilized, it will have multiple benefits, but there is little research on it. In this work, a novel route for comprehensively utilizing the flue gas $CO_2$ of power plant and the $CaCl_2$ waste liquid of ammonia-alkali plant was developed, in which $CaCl_2$ solution and flue gas $CO_2$ were transformed into $CaCO_3$ products based on an absorption–mineralization process using water-soluble amines. The technical feasibility with six amines was fully verified, and to further obtain the larger particle size $CaCO_3$ that facilitates industrial filtration, the effects of different operating conditions were investigated. Results showed that ethanolamine (MEA) is the optimal amine, with the mineralization rate is 97.2%. The $CaCO_3$ with the larger particle size is of 20-30 μm under the optimal condition.

**Keywords:** $CO_2$ mineralization, $CaCl_2$ waste liquid, water-soluble amine, calcium carbonate

## 1. INTRODUCTION

Soda ash occupies an important position in our national economy[1]. In China, the total output of soda was 28.73 Mt in 2021, half of which was produced by ammonia alkali method[2]. The ammonia alkali method has the low cost, pure product and simple process, but about 11 m³ of distiller waste, which contain mainly calcium chloride ($CaCl_2$, 90-120g/L) and unreacted sodium chloride (NaCl, 40-50g/L), is discharged while 1 ton of soda is produced in this way[3]. The $CaCl_2$ waste liquid in most cases is discharged directly to the nearest river, lake, or sea, damaging the environment seriously[4]. Scholars around the world have made massive efforts in the treatment of the $CaCl_2$ waste liquid. Wang et al.[5] reviewed the industrial application of ammonia alkali waste liquid, such as the preparation of engineering soil, cement, red brick and other building materials, but there are certain restrictions due to the present of chlorine. Some ammonia alkali plants inject $CaCl_2$ waste liquid back into the mine to generate $CaSO_4$ deposited at the bottom of the ore deposit, while increasing the NaCl content in brine, but this method is only applicable to $Na_2SO_4$ mines, and not a long-term solution[6]. In short, there is still no good treatment method for $CaCl_2$ waste liquid.
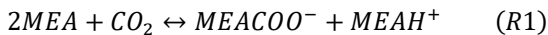
At the same time, the current climate changes drastically, and $CO_2$ emission reduction is urgent[7-9]. And 43% of the $CO_2$ emitted by human activities is used for power generation and energy supply[8]. Most ammonia-alkali plants are equipped the thermal power plants, where flue gas $CO_2$ is discharged into the atmosphere directly after desulfurization and denitrification, aggravating Greenhouse Effect.

If the $CaCl_2$ waste liquid of ammonia alkali plant and the flue gas $CO_2$ of the thermal power plant can be comprehensively used to obtain more valuable products, it will be of great significance.

Sun et al. [10] investigated the method of simultaneously absorbing $CO_2$ and $NH_3$ in a rotary filled bed to synthesize nano-$CaCO_3$. Li [11] and Dong [12] et al. proposed a reactive extraction-crystallization process using N235-isoamyl alcohol as the extraction to treat $CaCl_2$ waste liquid, in which $CaCl_2$ solution was transformed into $CaCO_3$ and HCl. The trioctylamine hydrochloride in the oil phase was regenerated by thermal desorption. However, the problem is oil-soluble

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amine viscosity, and lots of diluents need to be added during both mineralization and thermal desorption to enhance heat and mass transfer, and then these diluents need to be separated subsequently, but the separation is difficult and the energy consumption is high. At the same time, due to the poor absorption of $CO_2$ by oil-soluble amines, the conversion of $CO_2$ to $HCO_3^-$ is more difficult, and the conversion rate of Ca is low.

Water-soluble amines include alcohol amines with short carbon chains, amino acid salts, and polyamines. The diluents is not necessary in mineralization due to its low viscosity, and the system are all in aqueous solution, which is conducive to absorbing $CO_2$ into $CO_3^{2-}$, then precipitating with $Ca^{2+}$ to obtain $CaCO_3$. According to existing studies[13,14], the mechanism of $CO_2$ absorption by primary secondary amine and tertiary amine is different. For the primary and secondary amine, like ethanolamine (MEA), follows the zwitterion mechanism. According to reaction 1, carbamate ($MEACOO^-$) and protonated amine ($MEAH^+$) are formed as the main products of $CO_2$ absorption. Additionally, a part of generated $MEACOO^-$ can further react with water and produce bicarbonate ($HCO_3^-$) in the solution (reaction 2). For the tertiary amine, such as the most common tertiary amine, N-methyldiethanolamine (MDEA), $HCO_3^-$ is the main $CO_2$-containing species produced as shown in reaction 3.

$$2MEA + CO_2 \leftrightarrow MEACOO^- + MEAH^+ \qquad (R1)$$

$$MEACOO^- + H_2O \leftrightarrow MEA + HCO_3^- \qquad (R2)$$

$$MDEA + CO_2 \leftrightarrow MDEAH^+ + HCO_3^- \qquad (R3)$$

At present, water-soluble amines are mostly used for the capture of $CO_2$[15-17], which absorb $CO_2$ at low temperature and desorb at high temperature, but the study about further mineralization with $CaCl_2$ to obtain

$CO_2$ in the $CaCl_2$ system instead of oil-soluble amines with water-soluble amines is possible.

Therefore, in this work, a novel $CO_2$ absorption-mineralization process by water-soluble amines in the $CaCl_2$ system was proposed. The $CaCl_2$ waste liquid and flue gas $CO_2$ were utilized comprehensively to achieve the reduction emission of $CaCl_2$ and $CO_2$. At present study, the feasibility of the process was fully verified by using six water-soluble amines. And the production of $CaCO_3$ to replace limestone for calcination. To further obtain the large particle size $CaCO_3$ that is conducive to industrial filtration, the influence of various operating conditions on the particle size and morphology of $CaCO_3$ were studied, and the knowledge gaps in this area were filled to a certain extent.

## 2. MATERIAL AND METHODS

### 2.1 Materials

Anhydrous $CaCl_2$ (≥96.0%, Shanghai Ling Feng Chemical Reagent Co., Ltd.) was employed in this study. Six water-soluble amines (AR): ethanolamine (MEA), N-methyldiethanolamine (MDEA), triethanolamine (TEA), 2-Amino-2-methyl-1-propanol (AMP), sodium glycinate (GlyNa), and piperazine (PZ) were purchased from Shanghai Macklin Biochemical Co., ltd., China. $CO_2$ gas (99.5%) and $N_2$ gas (99.5%) were from Air Liquide (Shanghai) Gas Co., Ltd., used to proportionally mix to simulate flue gas $CO_2$ with a concentration of 15%.

### 2.2 $CO_2$ Absorption−Mineralization Experiment

$CO_2$-saturated amine solutions were prepared in the experimental setup in Fig. 2. A gas mixture of 15% $CO_2$ and 85% $N_2$ was introduced into a 500 mL three-necked
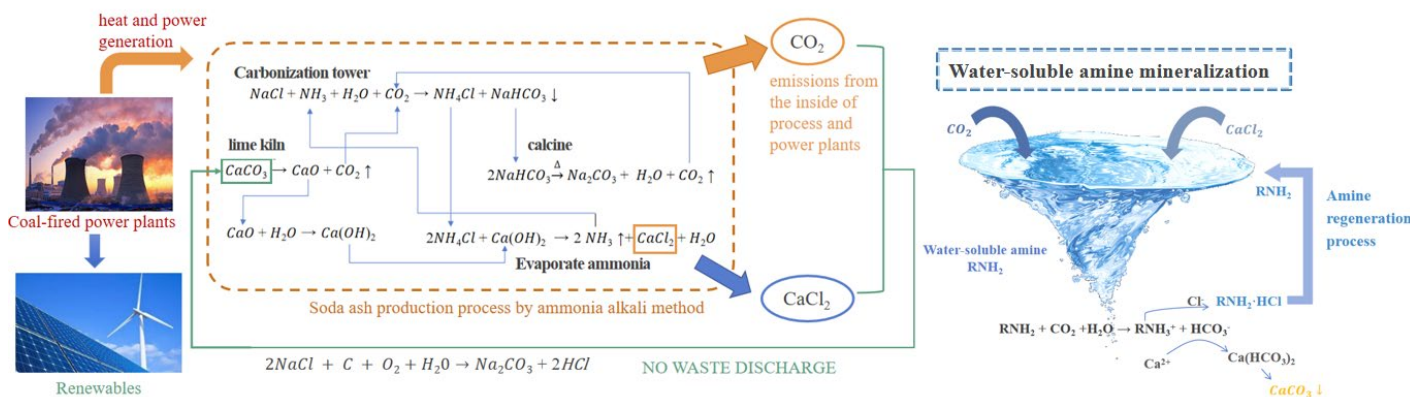


Fig. 1. Schematic diagram of the proposed absorption−mineralization cyclic process using water-soluble amines for comprehensive utilization of $CaCl_2$ waste liquid and flue gas $CO_2$ in ammonia alkali plant

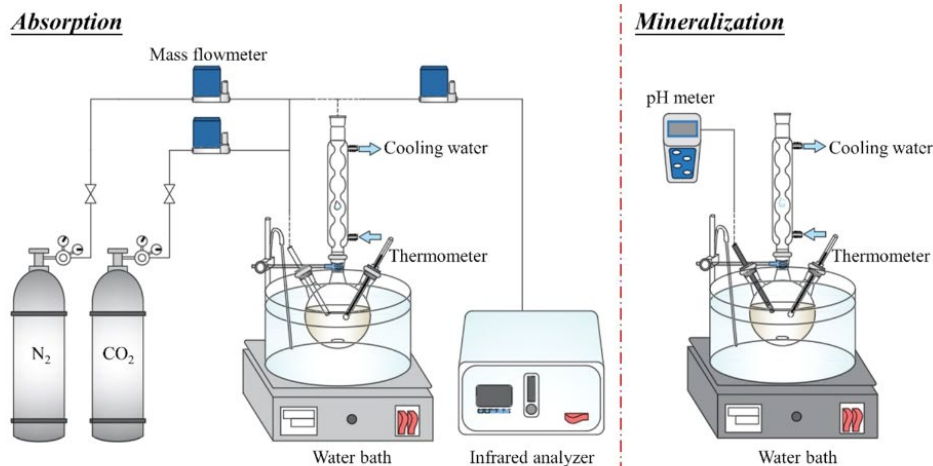$CaCO_3$ is rarely. Inspired by the above ideas, to mineralize

Fig. 2. Experimental setup of $CO_2$ absorption and mineralization.

flask filled with 2 mol/L solution of each amine. The gas flow was controlled using a mass flowmeter, and the absorption temperature was maintained using a water bath at 40 °C. The temperature of the cooling water was controlled at 10 °C. The $CO_2$ concentration of the outlet gas was measured using an infrared analyzer. The gas mixture continued to bubble to the solution until the infrared analyzer indicated that the $CO_2$ concentration remained constant. Then the 50 ml $CaCl_2$ solution with a concentration of 10wt%, which is close to the concentration of $CaCl_2$ waste liquid in ammonia alkali plant, were mixed with 100 mL of saturated amine solutions in a 500 mL jacket beaker. The pressure remained constant, and the temperature was controlled using a water bath at 25 ℃ throughout the experiment. Once the reaction was complete, the suspension was filtered, and the precipitate was washed several times with ethanol and ethanol, then dried at 110 ℃, then weighed, and used for SEM and XRD characterization. The mineralization rate $\alpha$ was calculated using eqs 1 .

$$\alpha = \frac{m_{CaCO_3} * 110.984}{m_{CaCl_2} * 100.087} \qquad (1)$$

where $m_{CaCO_3}$ and $m_{CaCl_2}$ represents the quality of $CaCO_3$ obtained after drying and $CaCl_2$ added at the beginning; 110.984 and 100.087 are the molar masses of $CaCl_2$ and $CaCO_3$, respectively.

### 2.3 Characterization

The crystal structure of the product was examined by XRD (D/MAX-B, Rigaku Co., Japan). Morphology of $CaCO_3$ microspheres was characterized by SEM (Quanta 250, FEI Co., US). Particle size distribution of $CaCO_3$ was determined by a Malvern particle size analyzer (Mastersizer 2000, Malvern Co., UK).

## 3. RESULTS AND DISCUSSION

### 3.1 Feasibility of water-soluble amines mineralization

To confirm the feasibility of the process, six widely studied water-soluble amines were used for mineralization. As shown in Table 1 and Fig. 3, $CaCO_3$ could be obtained with different water-soluble amines, and the mineralization rate is generally high, which is higher than the best cases of oil-soluble amines with about 75% .

Table 1 The mineralization results of six water-soluble amines.

| Category | Name | Mineralization rate/% | Particle size D50 /μm |
|---|---|---|---|
| Alcohol amine | MEA | 97.20% | 14 |
| | TEA | 82.40% | 24.2 |
| | AMP | 95.76% | 16 |
| | MDEA | 89.06% | 15.6 |
| Amino acid salts | GlyNa | 96.00% | 16.6 |
| Diamine | PZ | 87.40% | 9.65 |

Among all amines, ethanolamine (MEA) had the highest mineralization rate of 97.2%. In addition, MEA is the only water-soluble amine that has achieved industrial production, which is conducive to subsequent industrialization, therefore MEA is chosen as the optimal amine and mostly used in subsequent researches. The mechanism of mineralization is as reported in which water-soluble amines absorb $CO_2$ in solution to generate $HCO_3^-$ and proton amines, $HCO_3^-$ subsequently combines with $Ca^{2+}$ to obtain $CaCO_3$, and protonamines combine with $Cl^-$ to generate amine hydrochloride. Research on
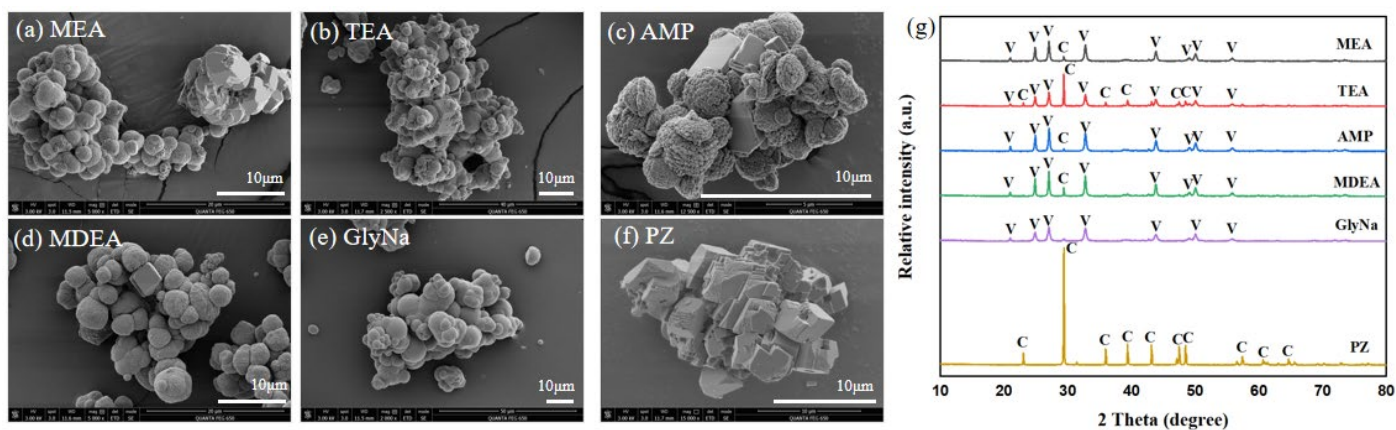
Fig. 3. SEM images (a-f) and XRD patterns (g) of $CaCO_3$ obtained from six water-soluble amines, C: calcite, V: vaterite. (Conditions: Amine overdose, $CO_2$ absorbed at 40 ℃ to saturation, $CaCl_2$ was added dropwise at 25 °C for mineralization.)
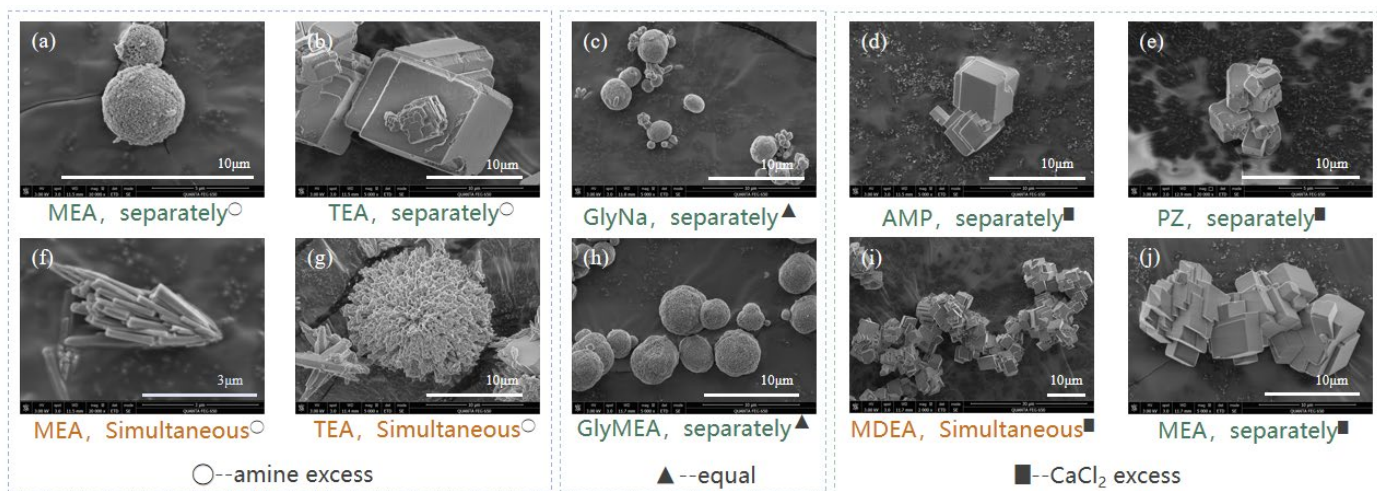


Fig. 4. SEM images of $CaCO_3$ obtained by different feeding methods and different aimes. (Separately means the amine solution absorbs $CO_2$ to saturation and then mineralizes with $CaCl_2$ solution; simultaneous means absorption and mineralization take place simultaneously; In both cases, the solution is added directly rather than dropwise )

the regeneration of amine hydrochloride to amine is already underway, and the results will be reported in a follow-up period.

The SEM and XRD images in Fig. 3 show that, the different water-soluble amines have different effects with $CaCO_3$, and the crystal form, morphology and particle size of $CaCO_3$ from different amines are different. Such as using GlyNa as water-amines, the $CaCO_3$ obtained is generally with uniform spherical shapes as shown in Fig. 3(e), Fig. 4(c) and Fig. 4(h), and the crystal form is vaterite as shown in Fig. 3(g). It may because amine acid's preferential binding of acidic residues to metal ions in inhibition of vaterite dissolution[21].

After fully confirming the feasibility of the route, considering that the $CaCO_3$ we obtained is used to replace limestone in the alkali process for calcination, and the synthetic $CaCO_3$ is powder $CaCO_3$ (usually the particle size is 2-10μm), the particle size is too small for filtration, and it is difficult to replace the calcination of large pieces of limestone. Therefore, in the follow-up research stage, different operating conditions were investigated to obtain the largest possible particle size $CaCO_3$. At the same time, the influence of different operating conditions on the process of $CaCO_3$ synthesis is studied, which provides experimental reference for further research.

## 3.2 Effect of feeding method

The $CaCO_3$ in the Fig. 4 were obtained by directly adding $CaCl_2$ to the absorbing $CO_2$ amine solution, and the particle size of the obtained $CaCO_3$ was 2-7μm, and in the Fig. 3 , $CaCO_3$ is obtained by adding $CaCl_2$ dropwise to the absorbing $CO_2$ amine solution, and the particles are agglomerated and the particle size changes larger, about 20μm. Based on this consideration, in order to
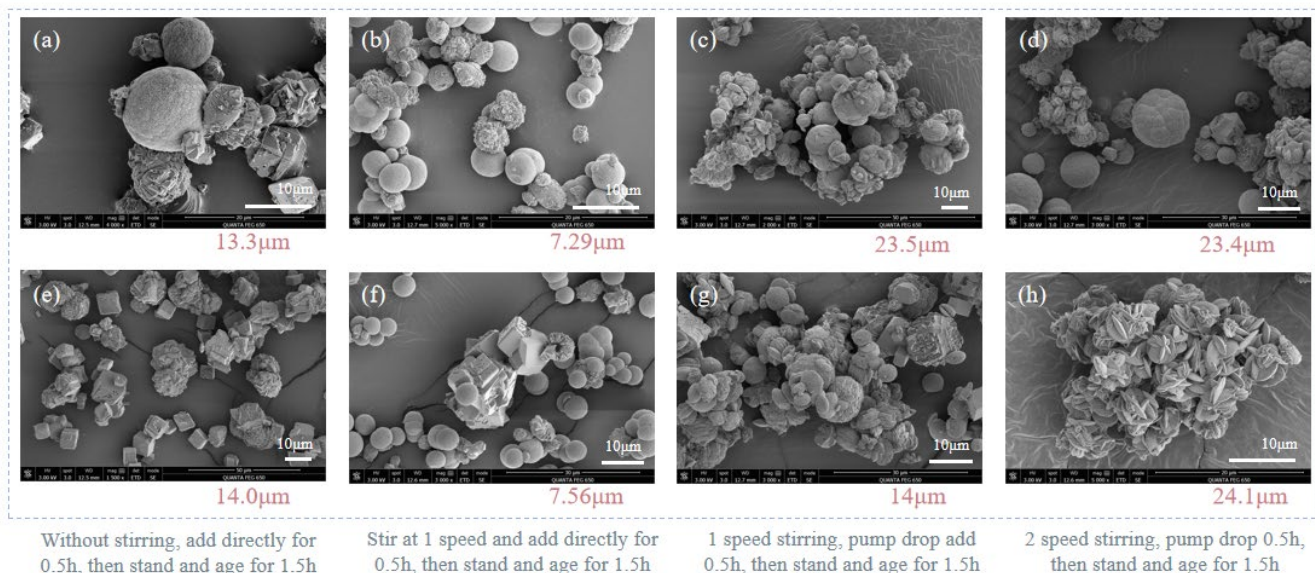
Fig. 5. SEM images of CaCO₃ obtained by different mineralization temperature, stirring rate, CaCl₂ drop acceleration rate.
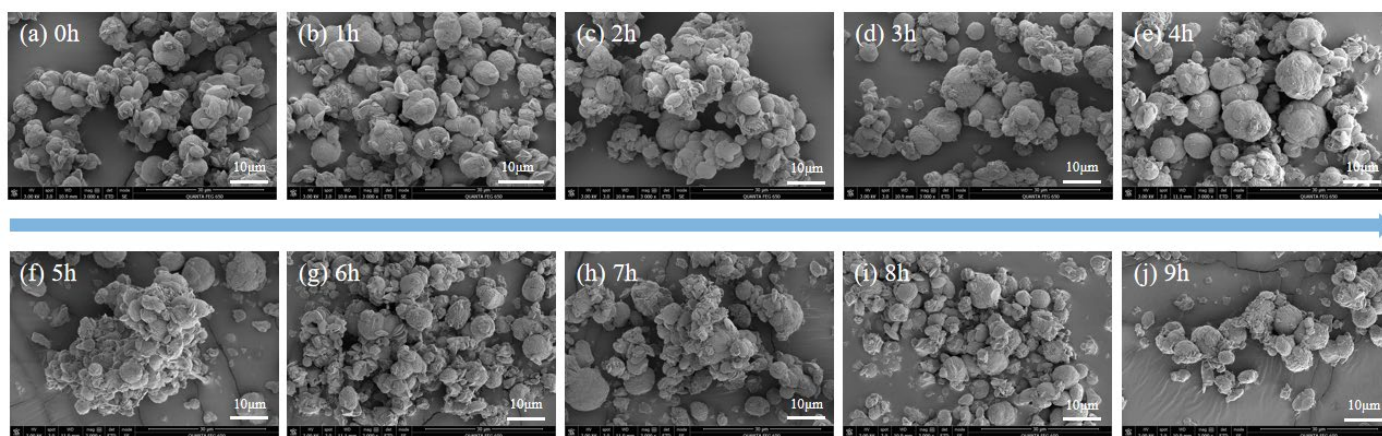(All under the condition of adding CaCl₂ to the MEA solution saturated with CO₂)



Fig. 6. SEM images of CaCO₃ obtained by different aging time.
(Under the condition of adding CaCl₂ to the MEA solution saturated with CO₂)

obtain large particle size $CaCO_3$, the method of dropwise addition can be considered. At the same time, it was found from Fig. 4 that if $CO_2$ and $CaCl_2$ were added to the amine solution at the same time, the $CaCO_3$ obtained was prone to multiple crystal forms, such as Fig. 4(g). In the case of high $CaCl_2$ concentration, calcite is easy to generate, such as (d), (e), (i) and (j) of Fig. 4. In other words, calcite is more likely to be formed when an amine solution is added to $CaCl_2$ solution. Conversely, unstable vaterite is more likely to be formed when $CaCl_2$ is dropped into an amine solution, but may be converted to more stable calcite subsequently.

### 3.3 Effect of mineralization temperature

Fig. 5 shows that with the increase of temperature, which from 40 °C to 50 °C, the crystal conversion of calcium carbonate is strengthened, and stable calcite is more likely to be generated. And compared with the Fig. 3(a) with a mineralization temperature of 25 °C, the particle size of calcium carbonate in Fig. 5(d) and 5(h) is larger, and all other conditions are consistent, indicating that the mineralization temperature has a certain positive effect on the particle size of synthetic $CaCO_3$.

### 3.4 Effect of stirring rate

Fig. 5 shows that enhanced stirring is not conducive to the conversion of vaterite to more stable calcite. From the Fig. 5(a) to (d) or 5(e) to (h), with the stirring of the mineralization process from scratch to gradually strengthened, the $CaCO_3$ particle size first decreases and then increases, and calcite gradually breaks up and transforms into vaterite, speculating that the reason may

be because in the case of disturbance, it is easier to generate unstable crystal forms.

### 3.5 Effect of $CaCl_2$ drop acceleration rate

Fig. 5(g) and 5(h) show that the slower the drop rate, the smaller particle size of petal-like calcium carbonate, and then petal-shaped small particle size calcium carbonate will transition towards vaterite, and then to calcite.

### 3.6 Effect of aging time

Fig. 6 represents that with the increase of aging time, first the vaterite continued to become more and larger, and then began to agglomerate more obviously at 2h, and then some individual particles in the aggregates grew, and at 4h, the particle size of a single spherical particle reached the maximum, about 15μm. After the cheroidite begins to break, the transition to calcite occurs, the particle size becomes smaller, the agglomeration becomes smaller, and the last 9h is about 5 μm irregular particles, and the hydrophilicity decreases. It can be seen that the aging time is not the longer the better, with the aging time, the calcium carbonate particle size shows a trend of first increasing and then decreasing, and when aging is about 2h, the agglomerate particle size reaches the maximum, about 20-30 μm.

## 4.  CONCLUSIONS

In this study, a new process to realize the comprehensive utilization of $CaCl_2$ waste liquid and flue gas $CO_2$ was proposed, and the feasibility of this process was fully verified by using six different water-soluble amines. Among all the amines, the mineralization effect of MEA is excellent, the mineralization rate can reach 97.2%. In addition, MEA is the only water-soluble amine that has been industrially produced up to now, which is easy to obtain, easy to industrialize the overall process, therefore MEA is selected as the optimal amine finally. In order to obtain the large particle size $CaCO_3$ which is more conducive to filtration, the effects of feeding method, mineralization temperature, stirring rate, drop addition rate of $CaCl_2$ and aging time on $CaCO_3$ crystallization were studied. Results showed that when the stirring rate was fast, $CaCl_2$ was added dropwise to the $CO_2$-saturated amine solution, and the aging time was about 2h, the $CaCO_3$ particle size was largest, about 20-30μm.

## DECLARATION OF INTEREST STATEMENT

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

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