

# Electronic Supplementary Material

## Formation of CaCO<sub>3</sub> hollow microspheres in carbonated distiller waste from Solvay soda ash plants

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### 1. Pitzer model

To calculate the activity coefficient of ions in the reaction system, the Pitzer electrolyte thermodynamic calculations (Harvie-Wear equations) were used:

$$\begin{aligned} \sum_i m_i(\phi - 1) = & 2 \left[ -(A^\phi I^3)/(1 + 1.2I^2) + \sum_{c=1}^{N_c} \sum_{a=1}^{N_a} m_c m_a (B_{ca}^\phi + ZC_{ca}) \right. \\ & + \sum_{c=1}^{N_c-1} \sum_{c'=c+1}^{N_c} m_c m_{c'} (\phi_{cc'}^\phi + \sum_{a=1}^{N_a} m_a \psi_{cc'a}) \\ & + \sum_{a=1}^{N_a-1} \sum_{a'=a+1}^{N_a} m_a m_{a'} \left( \phi_{cc'}^\phi + \sum_{a=1}^{N_a} m_a \psi_{cc'a} \right) + \sum_{n=1}^{N_n} \sum_{a=1}^{N_a} m_n m_a \lambda_{nc} \\ & \left. + \sum_{n=1}^{N_n} \sum_{c=1}^{N_c} m_n m_c \lambda_{nc} \right] \end{aligned} \quad S(1)$$

$$\begin{aligned} \ln \gamma_M = & z_M^2 F + \sum_{a=1}^{N_a} m_a (2B_{Ma} + ZC_{cX}) + \sum_{a=1}^{N_a} m_a \left( 2\phi_{Mc} + \sum_{a=1}^{N_a} m_a \psi_{Mca} \right) \\ & + \sum_{a=1}^{N_a-1} \sum_{a'=a+1}^{N_a} m_a m_{a'} \psi_{aa'M} + |z_M| \sum_{c=1}^{N_c} \sum_{a=1}^{N_a} m_c m_a C_{ca} + \sum_{n=1}^{N_n} m_a (2\lambda_{nM}) \end{aligned} \quad S(2)$$

$$\begin{aligned} \ln \gamma_X = & z_X^2 F + \sum_{c=1}^{N_c} m_c (2B_{cX} + ZC_{cX}) + \sum_{a=1}^{N_a} m_a \left( 2\phi_{Xa} + \sum_{c=1}^{N_c} m_c \psi_{Xac} \right) \\ & + \sum_{c=1}^{N_c-1} \sum_{c'=c+1}^{N_c} m_c m_{c'} \psi_{cc'M} + |z_M| \sum_{c=1}^{N_c} \sum_{a=1}^{N_a} m_c m_a C_{ca} + \sum_{n=1}^{N_n} m_a (2\lambda_{nX}) \end{aligned} \quad S(3)$$

$$\ln \gamma_N = \sum_{c=1}^{N_c} m_c (2\lambda_{nc}) + \sum_{a=1}^{N_a} m_a (2\lambda_{na}) \quad \text{S(4)}$$

$M, c, c'$ : cations;  $X, a, a'$ : anions;  $N_c, N_a, N_n$ : the number of types of anions, cations, and neutral molecules, respectively;  $\gamma_M, Z_M, m_c$ : the activity coefficient, valence number and the molality concentration of the cation, respectively;  $\gamma_X, Z_X, m_a$ : the activity coefficient, valence number and the molality concentration of the anion, respectively;  $\gamma_n, m_n$ : the activity coefficient and molality concentration of the neutral molecule;  $\lambda_{nc}$ : the interaction coefficient between the neutral molecule and anion  $c$ ;  $\lambda_{na}$ : the interaction coefficient between the neutral molecule and cation  $a$ .

$$F = -A^\phi \left[ \frac{I^{\frac{1}{2}}}{1 + 1.2I^{\frac{1}{2}}} + \frac{2}{1.2 \ln \left( 1 + 1.2I^{\frac{1}{2}} \right)} \right] + \sum_{c=1}^{N_c} \sum_{a=1}^{N_a} m_c m_a B'_{ca} \quad \text{S(5)}$$

$$+ \sum_{c=1}^{N_{c-1}} \sum_{c'=c+1}^{N_c} m_c m_{c'} \phi_{cc'} + \sum_{a=1}^{N_{a-1}} \sum_{a'=a+1}^{N_a} m_a m_{a'} \phi_{aa'}$$

$$C_{MX} = C_{MX}^\phi / (2|Z_M Z_X|^{\frac{1}{2}}) \quad \text{S(6)}$$

$$Z = \sum_{i=1} |z_i| m_i \quad \text{S(7)}$$

$A^\phi$ : the Debye-Hückel coefficient of permeability coefficient;  $\Psi$ : the acting force parameter of different kinds of ions (2 anions and 1 cation or 2 cations and 1 anion);  $B$  and  $B^\phi$ : the second virial coefficient;  $B'$ : the derivative of  $B$  with respect to ionic strength:

$$B_{CA}^\phi = \beta_{CA}^{(0)} + \beta_{CA}^{(1)} \exp\left(-\alpha_1 I^{\frac{1}{2}}\right) + \beta_{CA}^{(2)} \exp\left(-\alpha_2 I^{\frac{1}{2}}\right) \quad \text{S(8)}$$

$$B_{CA} = \beta_{CA}^{(0)} + \beta_{CA}^{(1)} g\left(\alpha_1 I^{\frac{1}{2}}\right) + \beta_{CA}^{(2)} g\left(\alpha_2 I^{\frac{1}{2}}\right) \quad \text{S(9)}$$

$$B'_{CA} = \frac{\left[ \beta_{CA}^{(0)} + \beta_{CA}^{(1)} g'\left(\alpha_1 I^{\frac{1}{2}}\right) + \beta_{CA}^{(2)} g'\left(\alpha_2 I^{\frac{1}{2}}\right) \right]}{I} \quad \text{S(10)}$$

Where the function  $g$  and  $g'$  are:

$$g(x) = \frac{2[1 - (1+x)\exp(-x)]}{x^2} \quad \text{S(11)}$$

$$g'(x) = -\frac{2\left[1 - \left(1+x + \frac{x^2}{2}\right)\exp(-x)\right]}{x^2} \quad \text{S(12)}$$

$\beta_{CA}^{(0)}, \beta_{CA}^{(1)}, \beta_{CA}^{(2)}$ : characteristic parameters of electrolyte CA;

$\phi_{ij}^{\phi}$ ,  $\phi_{ij}$ , and  $\phi'_{ij}$ : the second virial coefficient:

$$\phi_{ij}^{\phi} = \theta_{ij} + {}^E\theta_{ij} + I^E\theta'_{ij} \quad \text{S(13)}$$

$$\phi_{ij} = \theta_{ij} + {}^E\theta_{ij} \quad \text{S(14)}$$

$$\phi'_{ij} = {}^E\theta'_{ij} \quad \text{S(15)}$$

$\theta_{ij}$ : Pitzer action parameters for two cations or two anions;

${}^E\theta_{ij}$  and  ${}^E\theta'_{ij}$ : the asymmetric higher-order action terms;

$${}^E\theta_{ij} = \left(\frac{Z_i Z_j}{4I}\right) \left[ J(x_{ij}) - \frac{J(x_{ii})}{2} - \frac{J(x_{jj})}{2} \right] \quad \text{S(16)}$$

$${}^E\theta'_{ij} = \left(\frac{{}^E\theta_{ij}}{I}\right) + \left(\frac{Z_i Z_j}{8I^2}\right) \left[ x_{ij} J'(x_{ij}) - x_{ii} \frac{J'(x_{ii})}{2} - x_{jj} \frac{J'(x_{jj})}{2} \right] \quad \text{S(17)}$$

$$x_{ij} = 6Z_i Z_j A \phi I^{\frac{1}{2}} \quad \text{S(18)}$$

$J(x)$ : the group integral of the potential energy of a short-range interaction between ions;

$J'(x)$ : first order differential quotient of  $J(x)$ ;

To calculate accurately,  $J$  is fitted into the following functions:

$$J(x) = x[4 + C_1 x^{C_2} \exp(-C_3 x^{C_4})]^{-1} \quad \text{S(19)}$$

$$J'(x) = [4 + C_1 x^{C_2} \exp(-C_3 x^{C_4})]^{-1} + [4 + C_1 x^{C_2} \exp(-C_3 x^{C_4})]^{-2} [C_1 x \exp(-C_3 x^{C_4}) (C_2 x^{-C_2-1} + C_3 C_4 x^{C_4-1} x^{-C_2})] \quad \text{S(20)}$$

$C_1=4.581$ ;  $C_2=0.7237$ ;  $C_3=0.0120$ ;  $C_4=0.528$ .

First,  $x_{ij}$  can be calculated using Eq. S(18), and then  $J(x)$  and  $J'(x)$  can be accurately calculated using Eqs. S(19) and S(20). Secondly,  ${}^E\theta_{ij}$  and  ${}^E\theta'_{ij}$  can be obtained from Eqs. S(16) and (17), and then  $\phi_{ij}^{\phi}$ ,  $\phi_{ij}$ , and  $\phi'_{ij}$  can be obtained using Eqs. S(13)-(15).

**Table S1.** Pitzer parameters of ions in the system at 25 °C [1].

species	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\psi$	species	$\theta_{CCr}$	species	$\psi_{CCr(x)}$
Na-Cl	0.0765	0.2644	—	0.00127	Cl-OH	-0.05	Na-Ca (Cl)	-0.007
Na-OH	0.0864	0.253	—	0.0044	Cl-HCO <sub>3</sub>	0.03	Na-H (Cl)	-0.004
Na-HCO <sub>3</sub>	0.0277	0.0411	—	—	Cl-CO <sub>3</sub>	-0.02	Ca-H (Cl)	-0.015
Na-CO <sub>3</sub>	0.0399	1.389	—	0.0044	OH-CO <sub>3</sub>	0.1	Na-NH <sub>4</sub> (Cl) <sup>a</sup>	-0.0028
Ca-Cl	0.3159	1.614	—	-0.00034	HCO <sub>3</sub> -CO <sub>3</sub>	-0.04	OH-Cl (Na)	-0.006

Ca-OH	-0.01747	-0.2303	-5.72	——	Na-Ca	0.07	OH-Cl (Ca)	-0.025
Ca-HCO <sub>3</sub>	0.4	2.977	——	——	Na-H	0.036	CO <sub>3</sub> -OH (Na)	-0.017
H-Cl	0.1775	0.2945	——	——	Ca-H	0.092	CO <sub>3</sub> -HCO <sub>3</sub> (Na)	0.002
NH <sub>4</sub> -Cl <sup>a)</sup>	0.0521	0.1916	——	-0.003	NH <sub>4</sub> -Na <sup>a</sup>	-0.0046		

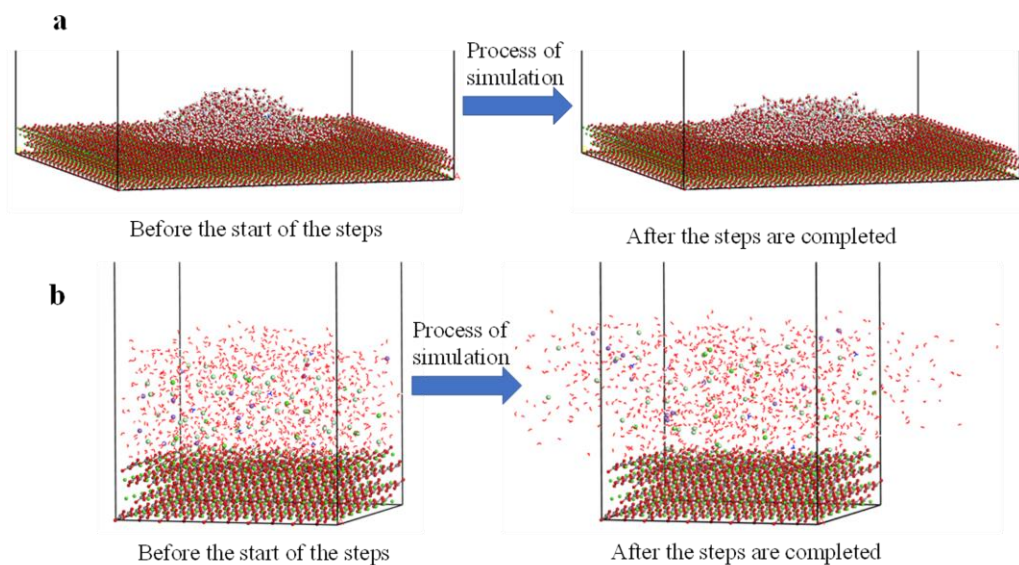
a) from reference [2]

Refer to the detailed solution method [1], the results can be substituted into HW Eqs. S(1)-(4) to calculate the permeability coefficient and activity coefficient of electrolyte solution. The parameters are shown in Table S1.

## 2. MD simulation

To understand the interaction between calcite and solution system, the optimized model was constructed after direct contact between the two phases. The movement information about the molecules and ions in the calcite and liquid phase was obtained by MD simulations. The canonical ensemble (NVT) and COMPASS force field were used in MD simulation calculation. The Ewald method was used to calculate the electrostatic interaction. When calculating the contact angle, Steepest Descent was selected to find the lowest energy conformation. The duration is 200,000 fs (timestep is 1fs), while the calculation time is 8-9 h, and 3D schematic diagram and process of MD simulation of contact angle are shown in Fig. S1a. When calculating interface interaction, the Conjugate Gradient method was used to minimize the structure, and the time used for 200000 steps is 200000 fs, and calculation time is 44-50 h, and 3D schematic diagram and process of MD simulation of interfacial interaction is shown in Fig. S1b. The remaining setting is as follows: temperature: 298 K.

In addition, calcite belongs to the  $R\bar{3}c$  space group, with unit cell parameters  $a = b = 0.4988$  nm,  $c = 1.7061$  nm,  $\alpha = \beta = 90^\circ$ ,  $\gamma = 120^\circ$ , and each primary unit cell contains two chemical molecules. In the simulation, the most stable growth plane (104) of calcite was used to construct a supercell of  $4.0479 \times 3.9920 \times 10.000$  nm<sup>3</sup> with a total surface of 1600 atoms. The composition of aqueous solution system changed with the reaction time (0 min: 1000 H<sub>2</sub>O, 15 Ca<sup>2+</sup>, 45 Cl<sup>-</sup> and 15 Na<sup>+</sup>; 10 min: 1000 H<sub>2</sub>O, 13 Ca<sup>2+</sup>, 45 Cl<sup>-</sup>, 15 Na<sup>+</sup>, and 4 NH<sub>4</sub><sup>+</sup>; 20 min: 1000 H<sub>2</sub>O, 13 Ca<sup>2+</sup>, 46 Cl<sup>-</sup>, 15 Na<sup>+</sup>, and 5 NH<sub>4</sub><sup>+</sup>).

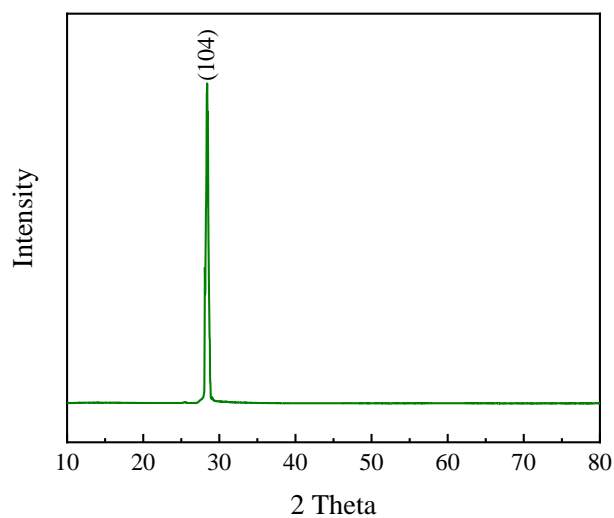


**Fig. S1** 3D schematic diagram and process of MD simulation of (a) contact angle between crystal plane (104) of calcite and solution reacted for 20 min; (b) the cell to calculate the interaction energy of system after reacting for 20 min.

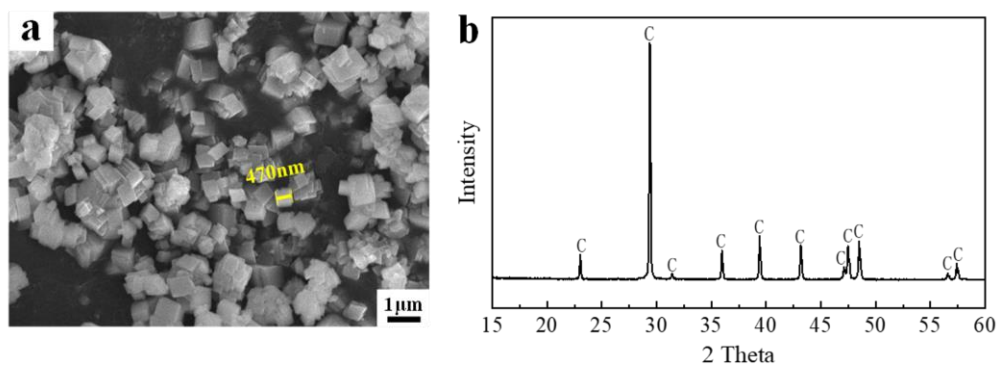
**Table S2.** Energy calculations of molecular simulation.

Time /min	Energy of calcite /( $\text{kcal}\cdot\text{mol}^{-1}$ )	Energy of solution /( $\text{kcal}\cdot\text{mol}^{-1}$ )	Energy of system /( $\text{kcal}\cdot\text{mol}^{-1}$ )	Energy of interaction /( $\text{kcal}\cdot\text{mol}^{-1}$ )
0	186668.06	-39667.63	-242097.45	15761.76
10	186668.06	-38877.81	-241242.35	15696.48
20	186668.06	-39239.46	-241589.29	15681.77

### 3. Supplementary figures



**Fig. S2** XRD pattern of (104) crystal plane of calcite single crystal specimen.



**Fig. S3** (a) SEM image and (b) XRD pattern of the carbonation product when the distiller waste reacted with the mixing gas (20 vol.% CO<sub>2</sub> and 80% air).

When the mixing gas (20 vol.% CO<sub>2</sub> and 80% air) was flowed into distiller waste, the product was cubic calcite with an edge length of about 500 nm, as shown in Fig. S3. Thus, when distiller waste reacted with 20 vol.% CO<sub>2</sub> from industrial exhaust gas, there would be no CaCO<sub>3</sub> hollow spheres in the product. As reported in Res. [3], the concentration of CO<sub>2</sub> will significantly affect the morphology of the product.

#### References

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