# Supplementary Information

## Efficient conversion mechanism of calcium fluoride in fluoride-containing sludge by calcination

Hang Zhao[1,3], Mengjun Chen[2], Feihua Yang[3],

Haile Yan[4], Xiaoguang Zhang[1*], De'an Pan[5 *]

[1] *College of Materials Science and Engineering, Beijing University of Technology, No. 100, Pingleyuan Street, Chaoyang District, Beijing, 100124, China.*

[2] *Key Laboratory of Solid Waste Treatment and Resource Recycle (SWUST), Ministry of Education, Southwest University of Science and Technology, 59 Qinglong Road, Mianyang, 621010, China.*

[3] *State Key Laboratory of Solid Waste Reuse for Building Materials, Beijing Building Materials Academy of Sciences Research, Beijing, 100041, China.*

[4] *Key Laboratory for Anisotropy and Texture of Materials (Ministry of Education), School of Material Science and Engineering, Northeastern University, Shenyang, Liaoning Province, 110819, China.*

[5] *College of Resources and Safety Engineering, Chongqing University, Chongqing 400044, China.*

** Corresponding Author: Fax: +86-10-67396234; Tel: +86-10-67396234; Emails: zhangxg@bjut.edu.cn and 15801662924@139.com.*

**Determination of total fluorine content in fluoride-containing sludge:**

1). Weigh 0.10g ~0.25 dried and sifted fluoride-containing sludge (FCS) and place it in a nickel crucible with an appropriate amount of sodium hydroxide base added in advance. The surface of the sample was evenly covered with 3g NaOH, which was then put into the Muffle, followed by alkali melting digestion according to the heating procedure in following table.

2). After digestion, when the temperature dropped to room temperature, the nickel crucible was removed, and the nickel crucible was leached several times with about 80ml hot water (about 80℃~90℃), and the solution was transferred to the polyethylene beaker.

3). The solution was diluted at constant volume and measured by ion chromatograph.

**Table S1. Solid waste alkali melt digestion temperature program**

| Heating procedure | Alkali fusion temperature (℃) | hold time (min) |
|---|---|---|
| **1** | **360** | **10** |
| **2** | **500** | **10** |
| **3** | **600** | **10** |

**Water leaching procedure:** The leaching test of roasting slag was carried out in 500 mL beaker with deionized water as leaching agent. In each experiment, 15 g of roasting slag was used to examine the effects of the L/S (4 to 20 mL/g), time (10 to 30 minutes), and speed (200 to 400 rpm) on the conversion efficiency. The $Ca^{2+}$ content was measured using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) to calculate the conversion efficiency using the following Eq. (1):

$$\eta = \frac{C \times V}{m} \times 100\% \qquad (1)$$

Where η is the conversion efficiency (%), C is the concentration of $Ca^{2+}$ in the leachate (g/L), V is the volume of the leachate (L), and m means the Ca content in the roasting slag.

**Table S2. Leaching experimental arrangement.**

| Factors | Levels |
|---|---|
| L/S | 4, 8, 12, 16, 20 mL/g |
| Time | 10, 15, 20, 25, 30 min |
| Stirring speed | 200, 250, 300, 350, 400 r/min |

Roasted slags obtained under optimal conditions (3.0 times the theoretical $Mg(NO_3)_2{\cdot}6H_2O$ dosage, 200°C, 4.0 h) were used in water leaching experiments to examine the effects of leaching time, L/S , and stirring speed on conversion efficiency. From **Fig. S2a**, it can be observed that with the increase in the L/S, the $CaF_2$ conversion efficiency gradually increases and then tends to stabilize. When the L/S ratio increased from 4 to 8, the conversion efficiency increased from 89.72% to 99.08%; further, increasing the L/S would lead to unnecessary water consumption., The $CaF_2$ conversion efficiency reaches 98.97% when the leaching time is 15 minutes (**Fig. S2b)**. However, with further increases in time, there is no significant change in the conversion efficiency. **Fig. S2c** shows that when the stirring speed is 300 rpm, the conversion efficiency is 98.85%. When the stirring speed exceeds 300 rpm, the conversion efficiency remains unchanged.

Based on the above studies, the water leaching conditions were determined as follows: L/S of 8 mL/g, leaching time of 15 minutes, and stirring speed of 300 rpm. Under these conditions, the $CaF_2$ conversion efficiency can reach 98.85%.

**Characterizations**: The $Ca^{2+}$ concentration in the solution was determined using inductively coupled plasma-optical emission spectroscopy (ICP-OES, Optima 8300, Perkinlemer, Waltham, MA, USA). The phase composition of the reaction slag was characterized by X-ray diffraction using Cu-K-α radiation (XRD, Axios MAX, PANalytical B.V., Almelo, Netherlands). Scanning electron microscopy was employed to examine the morphology and elemental composition of the reaction residues (SEM; SU-8020, 175 HITACHI; Japan).

**Chemical analysis of magnesium fluoride (GB/T 21994.3-2008):**

**Determination of fluoride content-distillation-thorium nitrate titration volumetric method:**

1). Weigh 0.1g sample and 2g $Na_2CO_3$ in a platinum crucible and melt at 800℃ for 20min. The melt is transferred to a distillation flask, and the frit adhering to the crucible is washed with hot water and added to the distillation flask.

2). Collect the distillation liquid with a capacity of 500mL, add 20ml $H_2SO_4$ distillation flask through the drip bucket, and when the distillation and burning temperature reaches 150℃, pass steam to maintain the temperature at 145℃ ± 5℃, collect 400mL distillation liquid to stop distillation, wash the condensate tube lotion and collect the lotion, dilute the 500mL volume flask to the scale and shake well for use.

3). 50.00ml solution was removed from a 500ml volumetric bottle into a conical bottle, adding 5 drops of alizarine red S indicator, adjusting to red with hydrogen NaOH, then adding HCl to yellow, adding 3ml $CH_3COOH$, adding 2 drops of methylene blue indicator, and titrating with thorium nitrate standard solution until the solution was lavender red as the end point.

The mass fraction of fluorine is calculated according to the formula：

$$W(F)=\frac{C*(V3-V4)*10^{-3}}{M}*100$$

M-Mass of the sample, expressed in grams (g).

C- Actual mass concentration of thorium nitrate standard titration solution in milligrams per milliliter (mg/mL)

V3- Standard volume of thorium nitrate consumed when titrating a sample solution, in milliliters (mL):

V4- The volume of nitrate needle standard solution consumed when titrating a blank test solution, in milliliters (mL)

**Determination of magnesium-EDTA volumetric method:**

1). Weigh 0.5g sample in platinum dish, add 5ml HF and 10mL $H_2SO_4$, mix

thoroughly on electric furnace until white smoke disappears, cool to room temperature, then add 5ml HF and 10mL $H_2SO_4$ until white smoke disappears. Continue to add 10 ml HCL and 30mL $H_2O$ into the platinum dish, heat the solution until it is clear, then transfer it to 250ml beaker, add water until the volume is about 125mL, cover the table dish, heat the solution to a slightly boiling boil, evaporate the solution to about 70mL, remove and add 2 drops of methyl orange, slowly add ammonia water to make the solution yellow. Heat, boil and keep warm for 5 to 10 minutes, transfer the filtrate into a 250mL volumetric bottle, wash the beaker with hot ammonium chloride ammonia liquid and wash the sediment 10 times, cool the solution to room temperature, dilute it with water to the scale, shake well and set aside (V1).

2). Transfer 50.00 mL of the $V_1$ solution into an Erlenmeyer flask, add 1.0 mL of $HNO_3$, and heat to boiling until the red color fades. After cooling to room temperature, add 5 mL of triethanolamine, 12 mL of ammoniacal buffer solution, and 4 drops of magnesium indicator. Titrate with EDTA standard solution until the endpoint is indicated by a blue color. Record the volume consumed as V2.

3). Transfer 50.00 mL of the $V_1$ solution into an Erlenmeyer flask, add 1.0 mL of $HNO_3$, and heat to boiling until the red color fades. After cooling to room temperature, add 5 mL of triethanolamine, 10 mL of potassium hydroxide solution, and a small amount of calcium indicator. Titrate with EDTA standard solution until the endpoint is indicated by a blue color. Record the volume consumed as V3.

Calculate the mass fraction of magnesium (%) according to the formula:

$$W(Mg)=\frac{C*(V2-V3)*0.02431}{M}* 100\%$$

M-Mass of the sample, expressed in grams (g).

C-Actual concentration of the EDTA standard titration solution, expressed in moles per liter (mol/L).

V2- Volume of the EDTA standard solution consumed in the titration of the aliquot using the magnesium indicator, expressed in milliliters (mL).

V3-Volume of the EDTA standard solution consumed in the titration of the aliquot

using the calcium indicator, expressed in milliliters (mL).

0.02431-The amount of magnesium equivalent to 1 mL of 1 mol/L EDTA standard solution.

## Supplementary Figures:

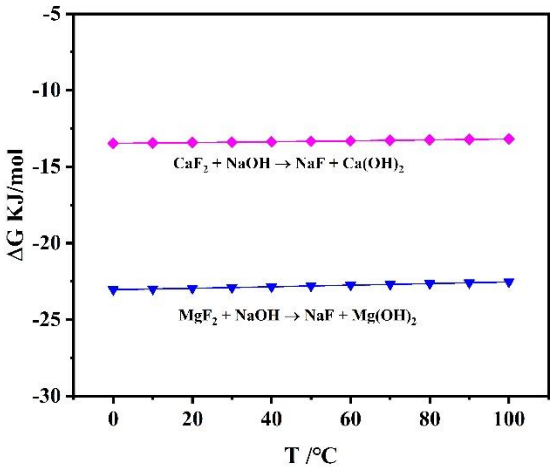


**Fig. S1. Thermodynamic calculation of $CaF_2$+NaOH, $MgF_2$+NaOH.**

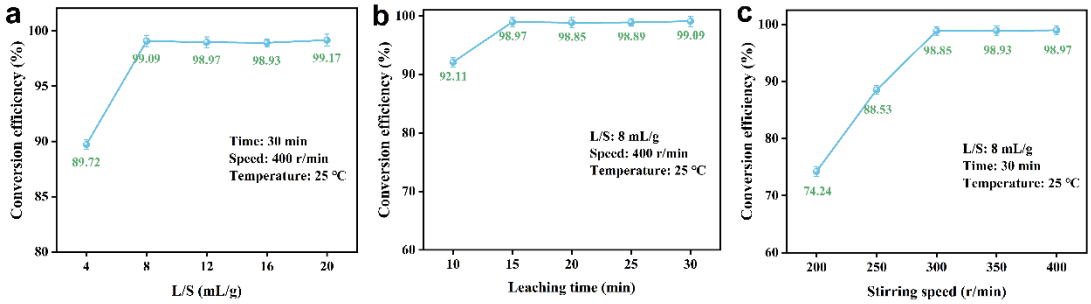


**Fig. S2. Effect of (a) L/S, (b) time, and (c) speed on conversion efficiency.**

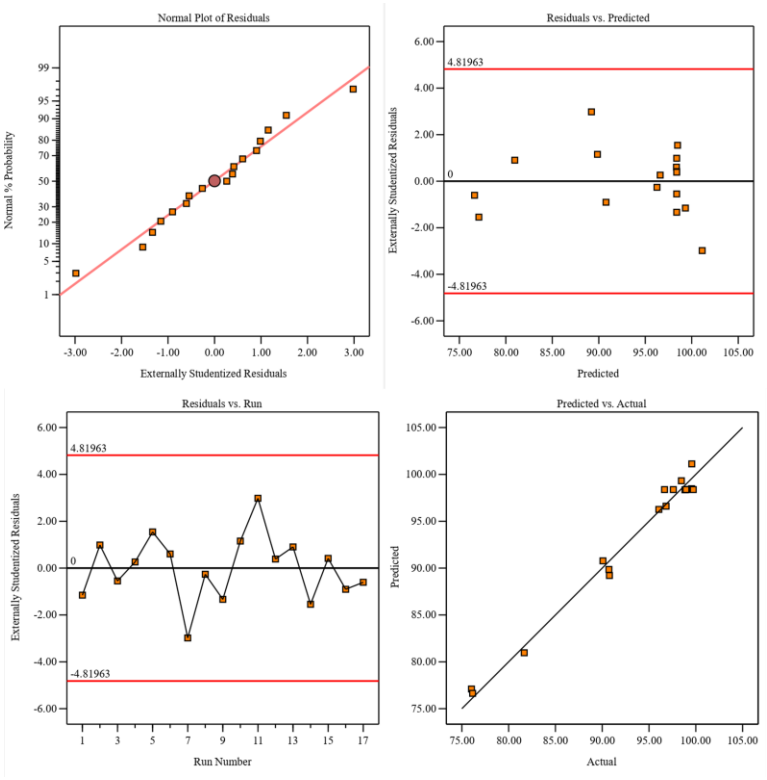


**Fig. S3. Diagnostic plots of the RSM model: (a) normal probability plot of internally studentized residuals; (b) comparison between residuals and prediction; (c) comparison between residuals and actual values; (d) comparison between predicted and actual values.**

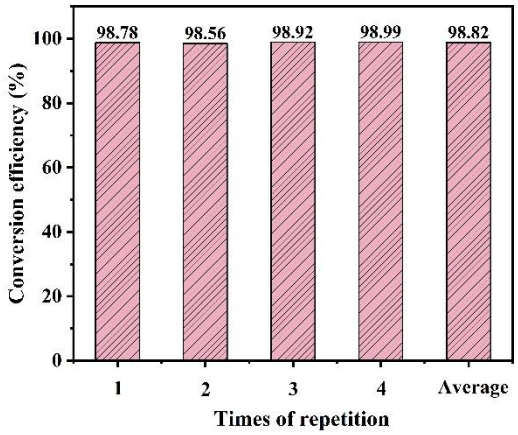


**Fig. S4. The repeated experimental data results under the optimized conditions from response surface experiments.**

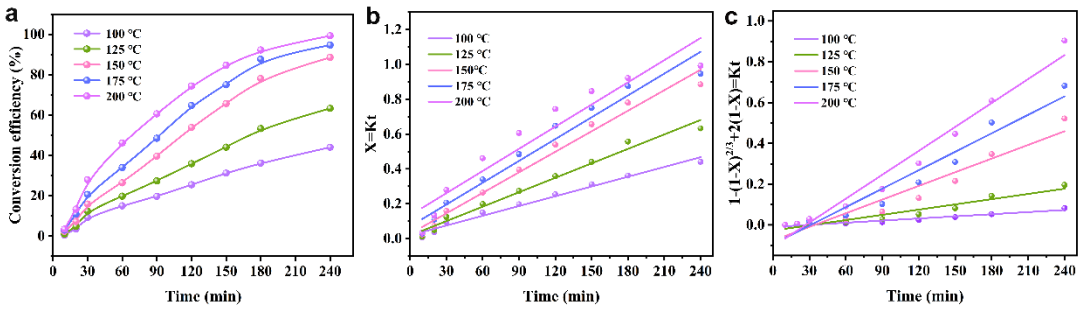


**Fig. S5. (a) Effects of temperature on the $CaF_2$ leaching efficiency, relation plot of (b) x=kt (c), and (c)1-3(1-x)2/3+2(1-x)=kt at different temperatures.**

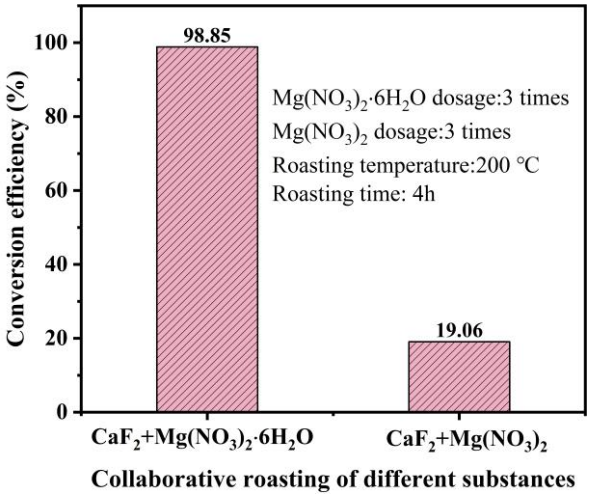


**Fig. S6. Conversion efficiency of $CaF_2$ and $Mg(NO_3)_2{\cdot}6H_2O$, $Mg(NO_3)_2$ reaction under optimal roasting conditions.**

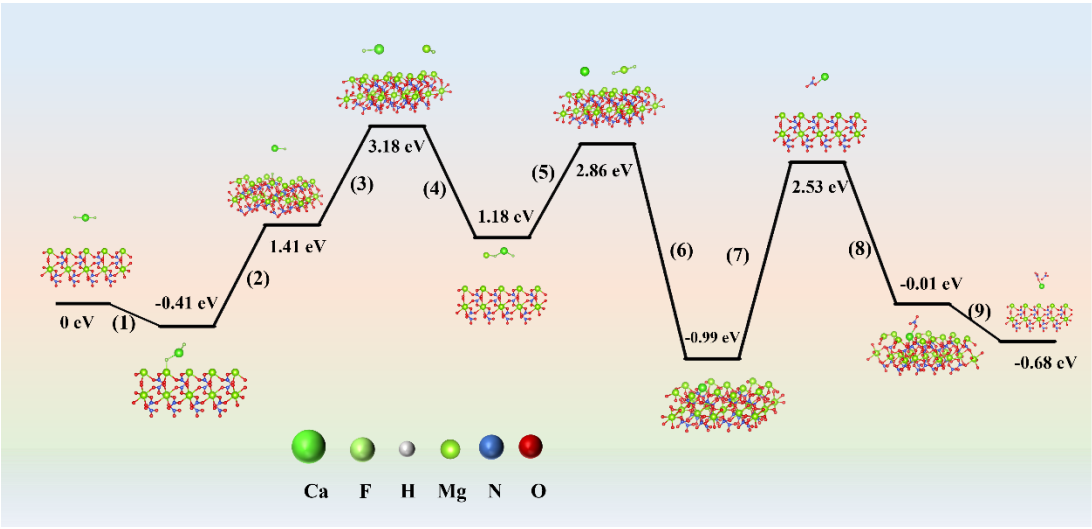


**Fig. S7. Potential energy profiles for the transformation of $CaF_2$ + $Mg(NO_3)_2$.**

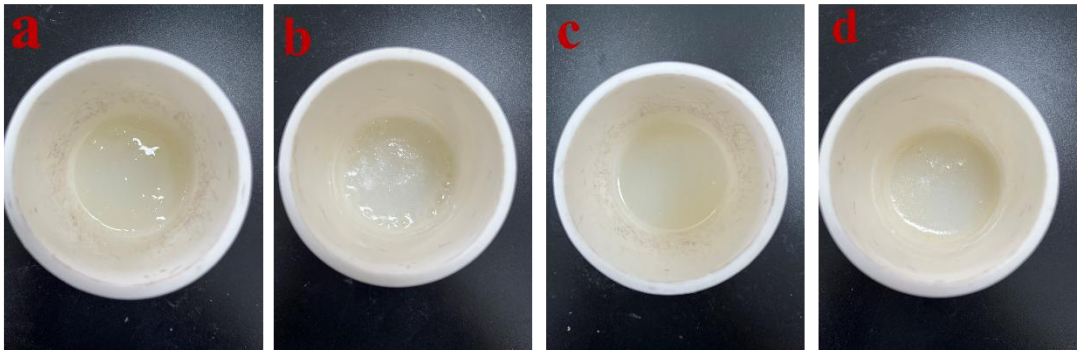


**Fig. S8. $CaF_2$ with $Mg(NO_3)_2*6H_2O$ were calcined for different times (a) 1.0 h, (b) 2.0 h, (c) 3.0 h, (d) 4.0 h.**

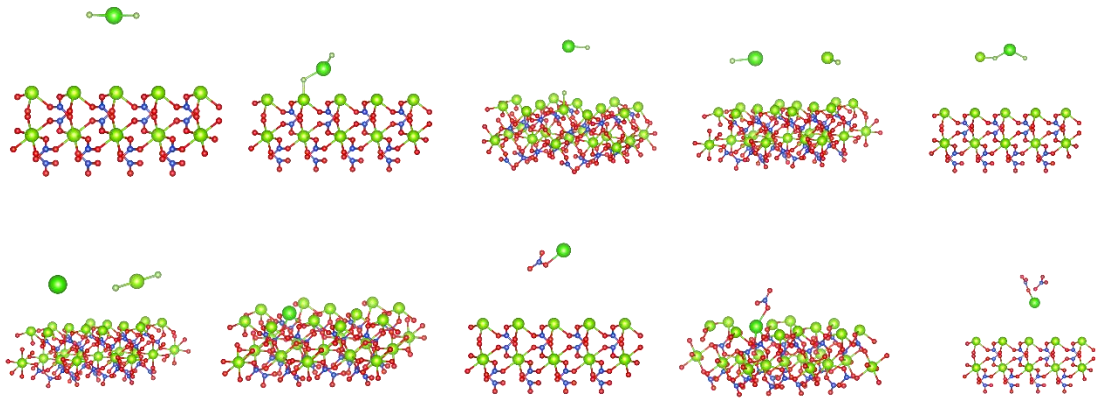

**Fig. S9. The elementary structure of each step in reaction $CaF_2 + Mg(NO_3)_2$.**

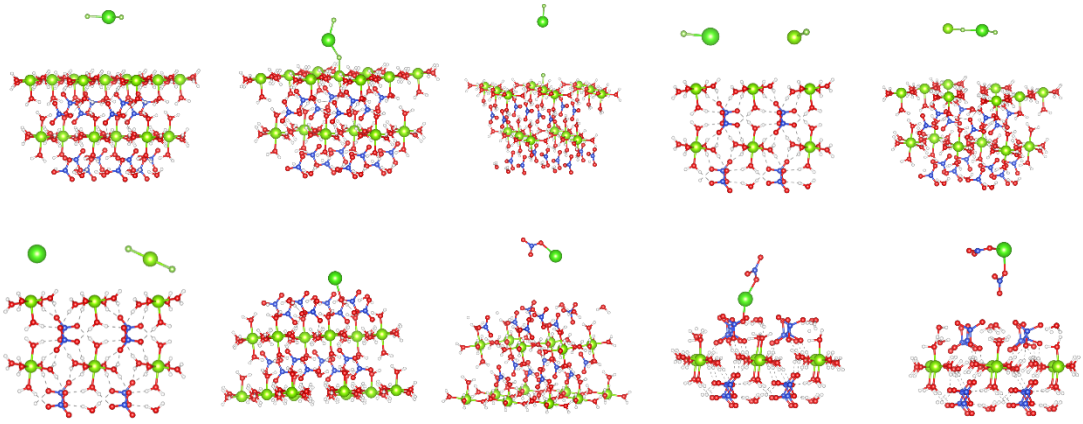

**Fig. S10. The elementary structure of each step in reaction $CaF_2 + Mg(NO_3)_2{\cdot}6H_2O$.**

## Supplementary Tables:

**Table S3. Roasting experimental arrangement.**

| Factors | Levels |
|---|---|
| Roasting time | 2, 4, 6, 8, 10 h |
| $Mg(NO_3)_2 \cdot 6H_2O$ dosage | 1.5, 2.0, 2.5, 3.0, 3.5 times |
| Roasting temperature | 100, 150, 200, 250, 300 ℃ |

**Table S4. Three variables at the different levels.**

| Independent variable | code | Level of factors | | |
|---|---|---|---|---|
| | | -1 | 0 | 1 |
| Time /h | A | 2 | 4 | 6 |
| $Mg(NO_3)_2.6H_2O$ dosage /times | B | 2.5 | 3.0 | 3.5 |
| Temperature /℃ | C | 150 | 200 | 250 |

**Table S5. The chemical compositions of the untreated FCS (XRF, wt%).**

| **Element** | **Ca** | **O** | **F** | **Si** | **Al** | **Others** |
|---|---|---|---|---|---|---|
| **Contents** | **40.78** | **28.29** | **19.08** | **4.68** | **2.91** | **3.74** |

**Table S6. The chemical compositions of the treated FCS (XRF, wt%).**

| **Element** | **Ca** | **Mg** | **F** | **Si** | **Al** | **Others** |
|---|---|---|---|---|---|---|
| **Contents** | **38.33** | **36.25** | **21.52** | **1.62** | **0.73** | **2.15** |

**Table S7. Details of the $MgF_2$ in the standard YS/T 691-2009 and the recovered product (wt.%).**

| Class | Content | | | | | | |
|---|---|---|---|---|---|---|---|
| | F | Mg | Ca | $SiO_2$ | $Fe_2O_3$ | $SO_4^{2-}$ | $H_2O$ |
| | > | > | < | < | < | < | < |
| Grade 1 | 60 | 38 | 0.3 | 0.20 | 0.3 | 0.6 | 0.2 |
| Grade 2 | 45 | 28 | - | 0.9 | 1.1 | 1.3 | 1.0 |
| **This work** | **60.1** | **38.2** | **0.25** | **0.19** | **0.18** | **0.53** | **0.16** |

(Nd indicates not detected)

**Table S8. Experimental designs and the actual experimental results.**

| Run | A: Time | B: $Mg(NO_3)_2.6H_2O$ dosage | C: Temperature | $CaF_2$ conversion efficiency: (%) |
|---|---|---|---|---|
| 1 | 4 | 2.5 | 250 | 98.46 |
| 2 | 4 | 3 | 200 | 99.73 |
| 3 | 4 | 3 | 200 | 97.60 |
| 4 | 2 | 3.5 | 200 | 96.82 |
| 5 | 6 | 3 | 250 | 99.55 |
| 6 | 4 | 3.5 | 250 | 98.84 |
| 7 | 6 | 3.5 | 200 | 99.57 |
| 8 | 6 | 2.5 | 200 | 96.05 |
| 9 | 4 | 3 | 200 | 96.66 |
| 10 | 4 | 3.5 | 150 | 90.72 |
| 11 | 2 | 2.5 | 200 | 90.77 |
| 12 | 4 | 3 | 200 | 98.94 |
| 13 | 6 | 3 | 150 | 81.66 |
| 14 | 2 | 3 | 150 | 76.02 |
| 15 | 4 | 3 | 200 | 98.98 |
| 16 | 2 | 3 | 250 | 90.08 |
| 17 | 4 | 2.5 | 150 | 76.15 |

**Table S9. Analysis of ANOVA.**

| Source | Sum of Squares | df | Mean Square | F Value | p-value | |
|---|---|---|---|---|---|---|
| Model | 1025.97 | 9 | 114.00 | 49.13 | < 0.0001 | significant |
| A-A | 66.90 | 1 | 66.90 | 28.83 | 0.0010 | |
| B-B | 75.14 | 1 | 75.14 | 32.39 | 0.0007 | |
| C-C | 486.33 | 1 | 486.33 | 209.61 | < 0.0001 | |
| AB | 1.60 | 1 | 1.60 | 0.6899 | 0.4336 | |
| AC | 3.67 | 1 | 3.67 | 1.58 | 0.2489 | |
| BC | 50.31 | 1 | 50.31 | 21.68 | 0.0023 | |
| $A^2$ | 48.57 | 1 | 48.57 | 20.93 | 0.0026 | |
| $B^2$ | 2.81 | 1 | 2.81 | 1.21 | 0.3077 | |
| $C^2$ | 280.10 | 1 | 280.10 | 120.73 | < 0.0001 | |
| Residual | 16.24 | 7 | 2.32 | | | |
| Lack of Fit | 10.16 | 3 | 3.39 | 2.23 | 0.2270 | not significant |
| Pure Error | 6.08 | 4 | 1.52 | | | |
| Cor Total | 1042.21 | 16 | | | | |

$R^2$: 0.9844 Adjusted $R^2$: 0.9644 Predicted $R^2$: 0.8349 Adeq Precision: 20.9646 C.V.%: 1.63

**Table S10. The rate constant (k) and the coefficient of determination ($R^2$) for F leaching from the $CaF_2$ at different temperatures.**

| Model | Equation | Temperature (°C) | $k$ ($min^{-1}$) | $R^2$ |
|---|---|---|---|---|
| External diffusion control | $x = kt$ | 100 | 0.0018 | 0.9813 |
| | | 125 | 0.0027 | 0.9824 |
| | | 150 | 0.0039 | 0.9798 |
| | | 175 | 0.0041 | 0.9580 |
| | | 200 | 0.0042 | 0.9154 |
| Chemical reaction control | $1-(1-x)^{1/3} = kt$ | 100 | 0.0007 | 0.992 |
| | | 125 | 0.0012 | 0.9910 |
| | | 150 | 0.0022 | 0.9932 |
| | | 175 | 0.0027 | 0.9931 |
| | | 200 | 0.0033 | 0.9963 |
| Interior diffusion control | $1-3(1-x)^{2/3} + 2(1-x) = kt$ | 100 | 0.0003 | 0.9585 |
| | | 125 | 0.0009 | 0.9341 |
| | | 150 | 0.0022 | 0.9300 |
| | | 175 | 0.0030 | 0.9484 |
| | | 200 | 0.0039 | 0.9716 |

**Table S11. The reaction ($CaF_2$+$Mg(NO_3)_2$) and energy corresponding to the step.**

| | Reaction | Bond energy (eV) |
|---|---|---|
| 1 | $Mg(NO_3)_2$+*$CaF_2$ | -0.41 |
| 2 | $Mg(NO_3)_2$+*F+ • CaF | 1.82 |
| 3 | $Mg(NO_3)_2$+ • MgF + • CaF | 1.77 |
| 4 | $Mg(NO_3)_2$+ • FMgFCa | -2.00 |
| 5 | $Mg(NO_3)_2$+ • Ca+$MgF_2$ | 1.68 |
| 6 | $Mg(NO_3)_2$+*Ca | -3.85 |
| 7 | $Mg(NO_3)_2$+ • $CaNO_3$ | 3.52 |
| 8 | $Mg(NO_3)_2$+*$CaNO_3$ | -2.54 |
| 9 | $Mg(NO_3)_2$+$Ca(NO_3)_2$ | -0.67 |

( • representative adsorption, * representative instability)

**Table S12. The reaction ($CaF_2$+$Mg(NO_3)_2$·$6H_2O$) and energy corresponding to the step.**

| | Reaction | Bond energy (eV) |
|---|---|---|
| 1 | $Mg(NO_3)_2$·$6H_2O$ +*$CaF_2$ | -1.33 |
| 2 | $Mg(NO_3)_2$·$6H_2O$+*F+ • CaF | 1.11 |
| 3 | $Mg(NO_3)_2$·$6H_2O$ + • MgF + • CaF | 1.07 |
| 4 | $Mg(NO_3)_2$·$6H_2O$+ • FMgFCa | -2.00 |
| 5 | $Mg(NO_3)_2$·$6H_2O$ + • Ca+$MgF_2$ | 1.68 |
| 6 | $Mg(NO_3)_2$·$6H_2O$ + *Ca | -3.64 |
| 7 | $Mg(NO_3)_2$·$6H_2O$ + • $CaNO_3$ | 2.32 |
| 8 | $Mg(NO_3)_2$·$6H_2O$ +*$CaNO_3$ | -3.77 |
| 9 | $Mg(NO_3)_2$·$6H_2O$ + $Ca(NO_3)_2$ | -0.26 |

( • representative adsorption, * representative instability)