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Preparation of Calcium Fluoride using Phosphogypsum by Orthogonal Experiment

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Abstract: The resource utilization of phosphogypsum is confronted with great challenge. Of all the different methods for phosphogypsum resource utilization, using phosphogypsum to fabricate calcium fluoride (CaF_2) is an effective resource utilization method. In this work, high-quality nano-calcium fluoride was successfully prepared in aqueous solution using calcined phosphogypsum by direct precipitation method. A series of orthogonal experiments were carried out in study. Here, the calcined phosphogypsum powder was mixed with NH_4F to react at 40°C for 70 min according to the optimum molar ratio (Ca/F=0.4). Meanwhile, the residue obtained by separating the mixture reacted was dried at 120°C for 90min. After preparation, the nano-calcium fluoride was analyzed by X-ray diffraction and scanning electron microscope, results found that the average particle diameter of calcium fluoride was around 70 nm. This work could increase the industrial chain of phosphogypsum application and apply a method to solve the fluorite resource shortage.

Keywords: Nano-calcium fluoride; Phosphogypsum; Orthogonal experiment; Characterization.

1 Introduction

Phosphogypsum (PG) is wasting slag of phosphate fertilizer industry, which is normally disposed of by dumping on land or by pumping into rivers or seas for a long time. It is well known that there are high concentrations of calcium sulfate, heavy metals, and rare-earth elements (REE) in PG. In the final stage of last century, many researchers studied how to exploit and recover them, and more important research achievements have been reported and put into practice. S. Al-Thyabat et al [1-3]. reported REE could be extracted indirectly from solutions of PG by ion exchange resin using both direct and counter current methods or adsorption technology. As soil amendments, PG was applied in cultivation of canola plants [4], sunflowers [5], tomatoes, green pepper plants [6] and so on. Results show that PG can immobilize heavy metals, thereby reducing the heavy metal content of fruit. Building material is another important application of PG treated to reduce activity concentrations of radioactive elements [7], such as binder [8], hardened tiles [9]. In addition to the aforementioned applications, PG was also used in the production of sulfuric acid [10], cement [11,12], salts [13], etc.

Calcium fluoride (CaF_2) is a colorless or white crystalline powder. Natural calcium fluoride is known as fluorite, and is an important initial material for the fluorine chemical industry. In the near future, the preparation of calcium fluoride will be a research focus due to the reducing of grades and reserves for fluorite [14]. Not only was calcium fluoride used in the chemical industry, but it is also widely used in metallurgy, building materials, light, optics, defense and other industries. Calcium fluoride was mainly used in different industries as a flux [15], an optical element [16], a novel fluorinating reagent and support of catalyst [17], an anticaries agent [18] and the like. In the reference [19], Calcium fluoride was fabricated in solution using PG, it is a great discovery, but the PG solubility is pretty small and there are many impurities in it, so it difficult to obtain pure and high concentration calcium sulfate solution for production of calcium fluoride.

Various methods containing precipitation, micro emulsion, hydrothermal, flame and so on can be used to prepare calcium fluoride. But in this work, the aim of this work is to investigate the preparation of calcium fluoride from PG and ammonium fluoride (NH_4F) by direct precipitation method.

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2 Material and methods

2.1 Materials

PG obtained by a Chinese fertilizer company in Sichuan, and the components are presented in Table 1. The other chemicals were purchased from Kelong Chemical Co., Ltd. (China), which are analytically pure (A.R.). All chemicals would be formulated into different concentration solutions by specific requirements to experiment.

Table 1: The main components of phosphogypsum (*w*/%).

CaO	SO_3	SiO_2	Al_2O_3	TP	TN	crystal water	Others
30.26	41.68	3.02	0.48	1.52	0.31	20.61	2.12

Where: *w* is weight percentage; TP is total phosphorus; TN is total nitrogen; Others contain mainly fluoride, ferric, copper, magnesium.

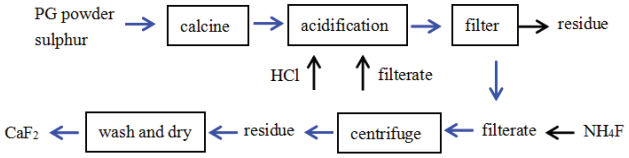

Figure 1: The process of calcium fluoride preparation.

2.2 Methods

2.2.1 Pretreatment of PG

Firstly, the block PG was broken down in tubular furnace (KTL1600) and grinded into powder. Then the 10 g PG powder was washed respectively with 200 mL distilled water, 50 mL 0.1 mol/L dilute alkali solution, 50 mL 0.1 mol/L dilute acid solution and 200 mL distilled water, respectively, to remove soluble impurities. Finally, the wet powder was dried in a drying oven (M331518) at 120°C for 120 min, and loaded into a clean reagent bottle to reserve.

2.2.2 Experiment method

According to the report by Yang [20], the decomposition temperature of PG was significantly lowered, when calcining with sulphur. So in this work, five grams of PG powder treated was mixed with activated carbon using an SO_4^{2-}/S molar ratio of 0.1, calcined at 800°C for 120 min in the nitrogen atmosphere, and the overflow gas was absorbed by sodium hydroxide solution. The residues were dissolved with 100 mL HCl (1+9), and stirred for 30 min at 300 r/min. Then the mixture was separated by percolation, and NH_4F was added in filtrate with the different Ca/F molar ratio to react at room temperature at 300 r/min. After reaction, the suspension was separated by centrifuge at 8000 r/min for 5 min, and the residue was washed with HCl (1+9) and distilled water for 3~5 times, respectively. Finally, the wet product was dried at 120°C. Meanwhile, the calcium fluoride preparation process was expressed in Figure 1.

2.2.3 Analysis method

According to the references reported by Zhang [21] and Nian [22], and the chemical analysis for CaF_2 describe as follows: 0.5000 g CaF_2 was weighted and moistened with ethanol in 250 mL beaker, with that 50 mL mixed acid (hydrochloric acid (38%) /boric acid (2 mol L^{-1}) / sulfuric acid (98%) = 250/100/25(v/v/v)) was used to treat this sample. The mixed solution was heated in beaker covered with a watch glass to boil slightly for 30 min, and cooled at room temperature. After that, the watch glass and beaker were rinsed by distilled water, and the mixture solution was diluted to 100 mL and heat to boil again. After heating, the solution was filtered with a rapid filter paper in a 250 mL volumetric flask, and the hot distilled water containing a few drops of hydrochloric acid was used to rinse beaker and residue for 5 times and 10 times, respectively. When the solution cooled, the test solution was diluted with distilled water to 250 mL. After dilution, 25 mL sample solution was pipetted in a 250 mL beaker, and diluted to 100mL with distilled water, and then 5mL triethanolamine, 20 mL 200 g/L potassium hydroxide solution and the appropriate amount of mixing indicator were added respectively. The EDTA standard solution was used to titrate sample solution until the green fluorescence of the test solution disappeared (observed on the black background liner). Calculation formula as follows:

$$\omega_{CaF_2} = \frac{T \times (V_2 - V_1) \times V}{m \times V_1} \times 100 - A$$

T is the titer of EDTA standard solution for calcium fluoride (g/mL); V, V_1, V_2 are the total volume of sample solution, sample solution volume for titration and the consumed EDTA standard solution volume, respectively (mL); m is the weight of the sample (g); A is the mass fraction of calcium carbonate in the sample which converted into the equivalent of calcium fluoride (%), $A = m_{CaCO3} \times 0.7808$.

The phase of the obtained nano powders was determined by powder X-ray diffraction (D8 Advance, BRUKER AXS). Scans were performed between 10 ° < 2θ < 90 °. The estimated standard uncertainty of the 2θ measurement is 0.01 °. Phase and element content were determined by SEM (MERLIN Compact, Carl Zeiss AG).

Ethical approval: The conducted research is not related to either human or animals use.

3 Results and discussion

3.1 Preparation of nano-calcium fluoride

Orthogonal experimentation was exploited in this work, and the experiment factors of Ca/F molar ratio, reaction and drying time were presented in Table 2. The results of calcium fluoride preparation according to $L_9(3^4)$ orthogonal table were also listed in Table 3, and the variance analysis results were shown in Table 4. From table 3 and 4, it can be found that the order of calcium fluoride preparation effect follows the order of A > C > D (the reaction time > the reaction temperature > Ca/F molar ratio), which further confirmed that reaction time as a very significant effect factor for calcium fluoride preparation, the Ca/F molar ratio and reaction temperature had also significant effect on preparation.In conclusion, the optimal processes were A3C2D3, which the Ca/F molar ratio was 0.4, the reaction time and temperature were 70 min and 40°C, respectively.

3.2 Verification experiment

As reaction initial materials, PG powder and NH_4F were used for nano-calcium fluoride synthesis by the method previously described in section 2.2.2, according to the optimized preparation condition at reaction time 70 min, reaction temperature 40°C, and Ca/F molar ratio 0.4. An amount of upper product were taken to detect the content of CaF_2, the results were shown in Table 5. Under this condition, the average content of CaF_2 in samples and RSD was 98.15% and 0.02%, respectively. This result showed good consistent with the orthogonal experiment. Therefore, the results of orthogonal test were stable and credible.

3.3 XRD analysis

The XRD analysis of nano-calcium fluoride was shown in Figure 2. From present figure, it can be found that the

Table 2: Factors and levels of orthogonal text.

Levels	Factors		
	A Reaction time/ min	C Reaction temperature/ min	D Ca/F molar ratio
1	15	20	0.6
2	45	40	0.5
3	70	60	0.4

Table 3: Orthogonal text results.

No.	Factors				CaF_2 content/ %
	A	Black	C	D	
1	1	1	1	1	86.58
2	1	2	2	2	88.46
3	1	3	3	3	88.09
4	2	1	2	3	95.36
5	2	2	3	1	91.33
6	2	3	1	2	92.38
7	3	1	3	2	95.89
8	3	2	1	3	97.68
9	3	3	2	1	98.09
k1	87.71	92.61	92.21	92.00	
k2	93.02	92.49	93.97	92.24	
k3	97.22	92.85	91.77	93.71	
R	9.51	0.36	2.20	1.71	

Table 4: Variance analysis results.

Source of variance	sum of square (SS)	degrees of freedom (df)	F	Significant
A	136.28	2	648.95	**
C	8.12	2	39.10	*
D	5.134	2	24.45	*
Error	0.21	2	1	

$F_{0.05(2,2)}$=19.0, $F_{0.01(2,2)}$=99.0.

Table 5: Verification experiment results.

No.	CaF_2 content/ %	Average content of CaF_2/ %	RSD/ %
1	98.12		
2	98.27	98.15	0.02
3	98.06		

RSD is relative standard deviation.

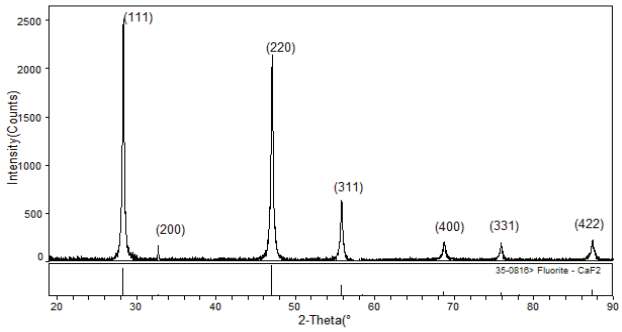

Figure 2: XRD patterns show that the nanoparticles CaF_2. Where the sample was produced on the basis of the reaction time 70 min, the temperature 40°C, the Ca/F molar ratio 0.4.

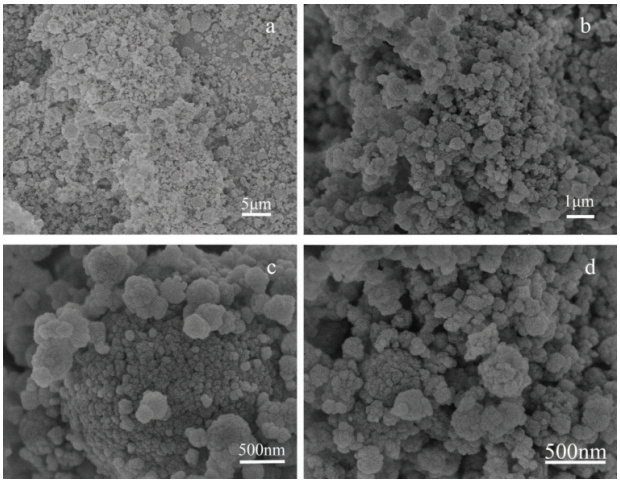

Figure 3: SEM images of CaF_2 nano-powder. Where the sample was produced on the basis of the reaction time 70 min, the temperature 40°C, the Ca/F molar ratio 0.4.

powder was indeed pure CaF_2. The diffraction peaks of nano samples were highly consistent with CaF_2 standard card (PDF: 35-0816), and there are no impurity peaks. This indicates the feasibility of synthesizing CaF_2 nanoparticles using direct precipitation method from PG and NH_4F. Calcium fluoride average particle diameter was around 70nm, which could be obtained by calculating using Scherrer formula $L=k\lambda/\beta\cos\theta$ (where L is grain size, k is Scherrer constant, λ is incident X-ray wavelength, β is full width at half maximum value and θ is diffraction angle), according to the XRD data for crystal planes (111), (220), (311), respectively. The CaF_2 nano-powder had a good crystalline that was 69.36% on the basis of calculating using MDI jade 5.0.

3.4 SEM analysis

The SEM images of CaF_2 nano-powder was shown in Figure 3 at a higher magnification. These images indicated that particles ranging from < 20 nm to about 150 nm in size and more uniformly dispersed. The larger particles exhibited numerous spherical protuberances on the surfaces, suggesting that the smaller CaF_2 granules could adhere to them, and lead to a more serious agglomeration.

4 Conclusions

Direct precipitation method and orthogonal experiment were used to prepare nano- calcium fluoride from the PG decomposition residue with activated carbon. The CaF_2 content of sample reached about 98.15%. The purified product was synthesized by the reaction time 70 min, the reaction temperature 40°C, and the Ca/F molar ratio 0.4. The analysis of XRD and SEM showed that the average particle diameter was around 70nm and the crystalline of product was 69.36%. And moreover, this simple method could increase the industrial chain of PG application and apply a method to solve the fluorite resource shortage.

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Conflict of interest: Authors state no conflict of interest.

References

[1] Al-Thyaba S., Zhang P., REE extraction from phosphoric acid, phosphoric acid sludge, and phosphogypsum, Mineral Processing and Extractive Metallurgy, 2015, 124, 143-150.
[2] Lokshin E.P., Tareeva O.A., Elizarova I.R., Ruling out accumulation of thorium in sulfuric acid solutions for leaching of phosphogypsum, Russian Journal of Applied Chemistry, 2015, 8, 719-723.
[3] Lokshin E.P., Tareeva O.A., Elizarova I.R., Sorption of rare-earth elements from phosphogypsum sulfuric acid leaching solutions, Theoretical Foundations of Chemical Engineering, 2015, 49, 773-778.

[4] Mahmoud E., El-Kader N.A., Heavy Metal Immobilization in Contaminated Soils using Phosphogypsum and Rice Straw Compost, Land Degradation & Development, 2015, 26, 819-824.
[5] Elloumi N., Zouari M., Chaari L., et al., Effect of phosphogypsum on growth, physiology, and the antioxidative defense system in sunflower seedlings, Environ Sci Pollut Res Int., 2015, 22, 14829-14840.
[6] Al-Hwaiti M., Al-Khashman O., Health risk assessment of heavy metals contamination in tomato and green pepper plants grown in soils amended with phosphogypsum waste materials, Environmental Geochemistry and Health, 2015, 37, 287-304.
[7] Al-Hwaiti M.S., Assessment of the radiological impacts of treated phosphogypsum used as the main constituent of building materials in Jordan, Environmental Earth Sciences, 2015, 74, 3159-3169.
[8] Liu L., Zhang Y., Tan K., Cementitious binder of phosphogypsum and other materials, Advances in Cement Research, 2015, 27, 567-570.
[9] Zhou J., Sheng Z., Li T., et al., Preparation of hardened tiles from waste phosphogypsum by a new intermittent pressing hydration, Ceramics International, 2016, 42, 7237-7245.
[10] Wang Y., Liu M., Sun H., et al., Preparation of sulfuric acid from phosphogypsum by ammonium-transferred method: Technical principle and process evaluation, Chemical Industry And Engineering Progress, 2015, 34, 196-201.
[11] Yoon S., Mun K., Hyung W., Physical Properties of Activated Slag Concrete Using Phosphogypsum and Waste Lime as an Activator, Journal of Asian Architecture and Building Engineering, 2015, 14, 189-195.
[12] Shen Y., Qian J., Huang Y., et al., Synthesis of belite sulfoaluminateternesite cements with phosphogypsum, Cement & Concrete Composites, 2015, 63, 67-75.
[13] Zhao H., Lia H., Bao W., et al., Experimental study of enhanced phosphogypsum carbonation with ammonia under increased CO_2 pressure, Journal of CO_2 Utilization, 2015, 11, 10-19.
[14] Zhou L., Tang T., Qian Y., et al., Research Progress in Preparation of Calcium Fluoride, Contemporary Chemical Industry, 2015, 44, 2254-2256.
[15] Li Y., Xv X., Wang B., et al., Research on the fluxed effect of LiF and $B_2O_{3,}$ Journal of University of Science and Technology Beijing, 2002, 24, 429-431.
[16] Su L., Xun J., Yang W., et al., Growth and application of CaF_2 single crystal, Journal of the Chinese Ceramic Society, 2003, 11, 1203-1206.
[17] Quan H., Tamura M., Gao R., et al., Preparation and application of porous calcium fluoride-a novel fluorinating reagent and support of catalyst, Journal of Fluorine Chemistry, 2002, 116, 65-69.
[18] Koeser J., Carvalho T.S., Pieles U., et al., Preparation and optimization of calcium fluoride particles for dental applications, Journal of Materials Science: Materials in Medicine, 2014, 25, 1671-1677.
[19] Douahem H., Hammi H., HamzaouiA. H., et al., Modeling and optimization of phosphogypsum transformation into calcium fluoride using experimental design methodology, Journal of the Tunisian Chemical Society, 2016, 18, 106-113.
[20] Yang J., Liu J., Wang X., et al., Study on preparation of calcium sulfide by using sulphur to reduce phosphogypsum, Inorganic Chemicals Industry, 2015, 3, 45-48.
[21] Zhang X., Zhang Q., Liu H., The determination of calcium fluoride in fluorit, Geology of Chemical Minerals, 2017, 1, 58-60.
[22] Nian J., Zhang L., Zhu C., et al., Determination of calcium oxide and calcium fluoride in steel slag powder deoxidizer by EDTA complexometric titration, Metallurgical Analysis, 2014, 6, 20-27.