

Research Article

Synthesis of Fluorite (CaF_2) Crystal from Gypsum Waste of Phosphoric Acid Factory in Silica Gel

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Abstract

This paper report the synthesis and characterization of fluorite single crystal prepared from gypsum waste of phosphoric acid production in silica gel. Instead of its high calcium, gypsum was used to recycle the waste which was massively produces in the phosphoric acid production. The gypsum waste, the raw material of CaCl_2 supernatant, was dissolved in concentrated HCl and then precipitated as calcium oxalate (CaC_2O_4) by addition of ammonium oxalate. The CaCl_2 was obtained by dissolving the CaC_2O_4 with HCl 3M. The crystals were grown at room temperature in silica gel and characterized by AAS, FTIR and powder XRD. The optimum crystal growth condition, which is pH of gel, CaCl_2 concentration and growth time, were investigated. The result shows that at optimum condition of pH 5.80, CaCl_2 concentrations of 1.2 M, and growth time of 144 hours, colorless crystals with the longest size of 3 mm, were obtained (72.57%). Characterization of the synthesized crystal by AAS indicates that the obtained crystal has high purity. Meanwhile, analysis by FTIR spectra shows a Ca-F peak at 775 cm^{-1} , and powder-XRD analysis confirms that the obtained crystal was fluorite (CaF_2). © 2012 BCREC UNDIP. All rights reserved

Keywords: minerals; calcium; by-product; gel method; supernatant

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1. Introduction

In Gresik Petro Chemical Factory, gypsum wastes were produced as by product of phosphoric acid in a large volume, for about 400 – 500 thousand tons annually. As reported by the Environmental Bureau of P.T. Gresik Petro Chemical, the gypsum and other solid by-products were mostly used for coast reclamation, mixed or

dumped for landfill in acidic soils [1,2].

Gypsum or CaSO_4 contains high calcium and can be recycled and converted into industrial grade of calcium compounds, such as calcium oxalate. Based on our previous research, calcium-based waste can be use as raw material of supernatant for synthesis of piezoelectric material of calcium tartrate tetrahydrate [3,4]. Moreover, many

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literatures suggest that gel method is feasible and promising for the crystal growing of low solubility salts [5-7]. In this paper, the targeted calcium crystals were CaF_2 . This crystal is also known as fluorite, a naturally occurred mineral, which posses many industrial applications.

Acid grade fluorite, which is the highest grade (97% or more of CaF_2), accounts for about 95 % of fluorite consumption in the US where it is used to make hydrogen fluoride and hydrofluoric acid by decomposing the fluorite with sulfuric acid. This highest grade is also used in the production of AlF_3 and cryolite (Na_3AlF_6), which are the main fluorine compounds used in alumunium smelting. The middle grade is ceramic grade fluorite (85–95 % of CaF_2), which is used in opalescent glass manufacture, enamels and cooking utensils. Mean while, the lowest grade of natural fluorite (metallurgical grade) is commonly used as a flux to lower the melting point of raw materials in steel production to aid the removal of impurities [8].

Instead of glass, synthesized fluorite is also used in some high-performance telescopes and camera lens elements. Lenses made from fluorite exhibit less chromatic aberration than those made of ordinary glass due to fluorite's very low dispersion. Even at high magnifications, fluorite elements allow crisp images of astronomical objects in telescopes [9].

Fluorite has a uniquely high transparency at 157 nm, hence exposure tools for the semiconductor industry using fluorite as optical elements for ultraviolet light at this wavelength. Fluorite objective lenses are manufactured and their transparence to ultraviolet light enables them to be used for fluorescence microscopy [10]. The fluorite also serves to correct optical aberrations in these lenses. Nikon has previously manufactured at least one all-fluorite element camera lens (105 mm $f/4.5$ UV) for the production of ultraviolet images [11].

Due to high potential application of fluorite and high calcium that contains in gypsum waste of phosphoric acid production, we decided to investigate the possibility of converting the waste into valuable fluorite crystal. In this paper, the synthesis and characterization of fluorite (CaF_2) from gypsum waste at room temperature using silica gel as growth medium is detailed. The optimum crystal growth condition, which is pH of gel, CaCl_2 concentration and growth time, were investigated and discussed.

2. Materials and Methods

Laboratory reagents, which are acetic acid glacial, NaF, $\text{Na}_2\text{SiO}_4 \cdot 9\text{H}_2\text{O}$, HCl, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$,

MgSO_4 , $(\text{NH}_4)_2\text{C}_2\text{O}_4$, NH_4OH , and solvents, i.e. were used without further purification and obtained from standard commercial suppliers. Gypsum waste was obtained from phosphoric acid factory of Gresik Petro Chemical in East Java, Indonesia. This research, which conducted in 2006, was mostly done in Inorganic Chemistry Laboratory of Brawijaya University. Mean while, instrumentations used in this research were IKAMAG® RH hot plate, HERAEUS KR170E Oven, Orion 420A pH-meter, Jasco FTIR-5300, AA-6200 AAS, and Shimadzu 6000 powder XRD.

2.1 Preparation of Supernatant

Before the gypsum waste was used, the concentration of Ca and Mg were measured by AAS. The concentration of calcium is important in order to gain initial information which will be used to prepare the amount of chemicals needed and to calculate the yield, while magnesium is commonly found in nature along with calcium and its concentration in the waste need to be measured to confirm whether the waste have to be purified or not. Due to similarity of chemical properties between Ca and Mg, the presence of significant amount of Mg will probably influence and interfere the synthesis of targeted CaF_2 .

The supernatant was prepared in two stages which were precipitation of calcium oxalate and preparation of supernatant solution in several concentrations. Calcium oxalate was precipitated by dissolving 0.5 g of gypsum with 15 mL of HCl (1:1) and 200 mL of water. The solution was then added with 2 drops of methyl red solution and then heated. In that hot solution, 50 mL of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ 0.3 M was added slowly. In order to increase the precipitation yields and reduced the possibility of co- and post-precipitation by Mg, NH_4OH (1:1) was mixed in the solution until it turns yellow. The solution was stand at room temperature and then filtered off. The obtained powder was then rinse with dilute $(\text{NH}_4)_2\text{C}_2\text{O}_4$ several times and dried in an oven to give dry powder of calcium oxalate.

Mean while, the supernatant solution was made by dissolving calcium oxalate in 30 mL of HCl 3M, heated and then added with water until its volume reach 50 mL. The concentrations of supernatant were varied by dissolving different amount of calcium oxalate to obtain certain concentration of CaCl_2 , which were 3.84 g (0.6 M); 5.12 g (0.8 M); 6.41 g (1.0 M); 7.69 g (1.2 M); and 8.97 g (1.4 M).

2.2 Synthesis of Fluorite in Silica Gel

Synthesis of fluorite in silica gel was conducted

in three stages, which were determination of optimum pH of gel, determination of optimum supernatant concentration of CaCl_2 , and determination of optimum growth time, respectively.

The gel was prepared by mixing 8 mL sodium metasilicate 1.72 M and 6 mL NaF 1 M in which the pH was varied from 5.4 until 6.2 by adding acetic acid 2 M. The mixed solution was placed in a single tube for a day until the gel was formed. Next, 8 mL of CaCl_2 1.0 M was added slowly onto the gel via the inner wall to avoid the gel surface damage, then closed with aluminium foil and placed in a tube rack. The reaction was stand at room temperature for 120 hours. The grown crystals were isolated by dissolving the gel with hot water and then filtered off. The crystals then dried in an oven (105 °C) and saved in desiccators. The optimum pH was determined based on the highest yield (%).

For other concentrations of supernatant (0.6; 0.8; 1.2 and 1.4 M), the synthesis was done at optimum pH, which was obtained from previous step. The procedures were similar and the optimum concentration was decided based on the highest yield (%). Mean while, for determination of growth time, the synthesis was conducted at optimum pH of gel and at optimum concentration of supernatant. The growth times were varied from 96 to 192 hours and all procedure were analogue to previous steps.

2.3 Characterization of Obtained Crystals

Crystals obtained at optimum concentration were analyzed by FTIR, AAS, and powder-XRD. The FTIR and AAS analysis were conducted in Laboratorium Dasar Bersama of Airlangga University – Surabaya using Jasco FTIR-5300 and AA-6200 AAS, respectively, while powder-XRD analysis was performed in Chemistry Laboratory of Gadjah Mada University – Yogyakarta using Shimadzu 6000 powder XRD.

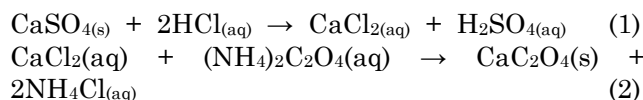
3. Result and Discussion

3.1 Preparation of Supernatant

Based on AAS data, the concentration of calcium and magnesium in the gypsum waste were 993.46 ppm and 83.05 ppm, respectively. The ratio of Ca:Mg concentrations in the waste was found around 12:1. This data was not only confirming the high amount of calcium contained in the waste, but also showing that the concentration of magnesium in waste was low. The influence of magnesium during precipitation of calcium could be reduced by adding excess amount of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ and NH_4OH

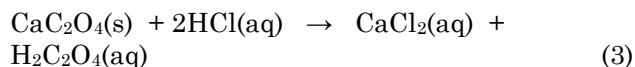
(1:1). Hence, separation of Mg from the waste was not performed in this research.

Theoretically, calcium oxalate can be precipitated from the mixture solution of gypsum and HCl by adding ammonium oxalate due to low K_{sp} value of CaC_2O_4 which is 2.6×10^{-9} [12]. The preparation of supernatant is shown in chemical equation (1) and (2):



The concentration of Mg in gypsum waste was insignificant and the K_{sp} value of MgC_2O_4 is higher than that of CaC_2O_4 , which is 8.5×10^{-5} . Hence, the possibility of MgC_2O_4 to be precipitated by ammonium oxalate is also low. Instead of avoiding MgC_2O_4 precipitation, the influence of Mg toward co- and post-precipitation of calcium oxalate, were also reduced by adding excess amount of ammonium oxalate and ammonium hydroxide.

The obtained calcium oxalate was then reacted with concentrated HCl until all dissolved and forms calcium chloride, as shown in equation (3):



To prepare several concentration of CaCl_2 , the mass of calcium oxalate were varied, as detailed in procedure section. Finally, all supernatants were added with water until 50 mL in order to get targeted concentration.

3.2 Synthesis of Fluorite in Silica Gel

The synthesis was done firstly by determining the optimum pH of gel because it is the important parameter which influences the whole reaction that might occurred in the gel. In some cases, the pH of gel determines the chemical species that presence in the gel. In this research, pH of gel was varied from 5.4 to 6.2. The proposed pH value was chosen because it is expected that the reaction between calcium ions and fluoride ions in gel occurred in acid condition. Mean while, at pH 7 and above (basic), the calcium could easily precipitate as calcium hydroxide.

Experimental data shows that pH of gel influence the crystal yields (%) significantly (based on F-test and BNT-test with α 0.01). Moreover, the optimum pH was achieved at 5.8 with yield of 54.98 %. The effect of pH of gel toward crystal yield is given in Figure 1.

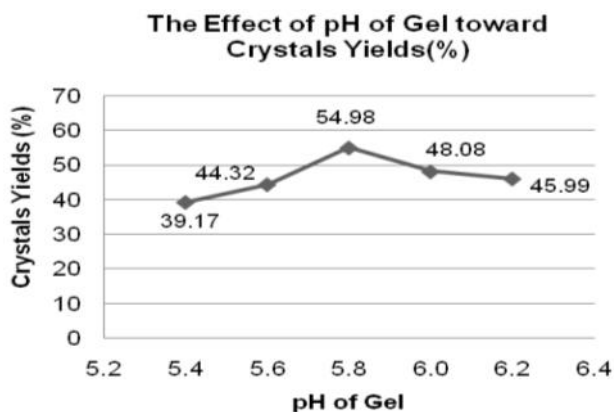
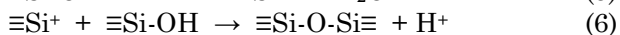
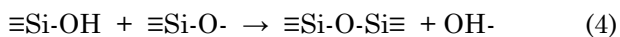


Figure 1: The effect of pH of gel toward crystal yield (%)

Below and above 5.8, the crystal yields were slightly lower, with lowest yield of 39.17 % obtained at pH of 5.4. The result indicates that at 5.4 to 6.2, the yield were reasonably high. If pH of gel changed below 5, it is predicted that the lower yield would be obtained. This is likely due to high H⁺ ions in the initial solution add another step of reaction mechanism. Generally at moderate concentration of acid, the polymerization can be achieved directly from the reaction of ≡Si-OH groups and ≡Si-O⁻ groups, as shown in equation (4), but at high concentration of acid, the ≡Si-OH will form ≡Si⁺ first and produce H₂O. This water will also contribute to the homogeneity of the gel. The stability of Si-O-Si networks, which provide a place of crystal nuclei to grow, could also decrease due to too many water inside gel. Next, as given in equation (5) and (6), the ≡Si⁺ then reacts with ≡Si-OH groups to form [≡Si-O-Si≡]. Therefore, it takes more time for the gel to be polymerized homogenously and ready to use.



The optimum pH of gel was then used in the determination of optimum supernatant concentration. The effect of CaCl₂ concentrations toward crystals yield is shown in Figure 2. Experimental data reveals that supernatant concentrations influence the crystal yields (%) significantly (based on F-test and BNT-test with α 0.01). Moreover, the optimum CaCl₂ concentration was gained at 1.2 M with yield of 65.29 %.

The crystal yields were gradually increased from concentration of 0.6 to 1.2 M, and then decrease steeply at concentration of 1.4 M. This is

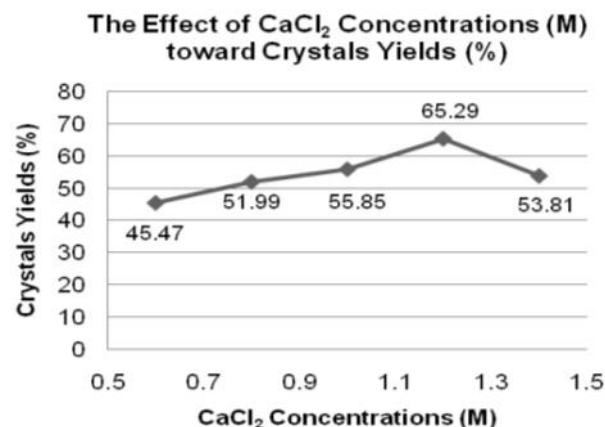
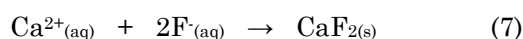


Figure 2: The effect of CaCl₂ concentrations toward crystals yield (%)

reasonable due to at 1.4 M, the concentration gradients between calcium ions of supernatant and fluoride ions in the gel surface was much higher. This condition leads to the formation of too many crystal nuclei which eventually grew into many small crystals around the gel surface and only few crystals could grow deeper into the gel. In addition, at the optimum CaCl₂ concentration, the crystal yield was higher (54.98 %) than that of at optimum pH of gel (65.29 %). This result indicates that both parameters were equally taking important role, and if both parameters were applied, then the crystal yield could be significantly increased. Fluorite crystal in the gel was yielded after the reaction of calcium ions and fluoride ions (equation (7)) and was predicted to be easily formed because CaF₂ has very low K_{sp} value which is 3.9 x 10⁻¹¹ [13].



The optimum pH of gel as well as the optimum CaCl₂ concentrations was then used in the determination of optimum growth time. The effect of growth time toward crystals yield is shown in Figure 3. Experimental data confirms that growth time also influence the crystal yields (%) significantly (based on F-test and BNT-test with α 0.01), and the optimum growth time was achieved at 144 hours (6 days) with yield of 72.57%. The growth time was used in hours scale since the growth of fluorite is relatively fast and can be observed during the first week of aging time. Moreover, less growth time is also considered more efficient in terms of economic issue in the production plan.

At period of 96 to 144 hours, the crystal yields were significantly increased by 30 %, which was

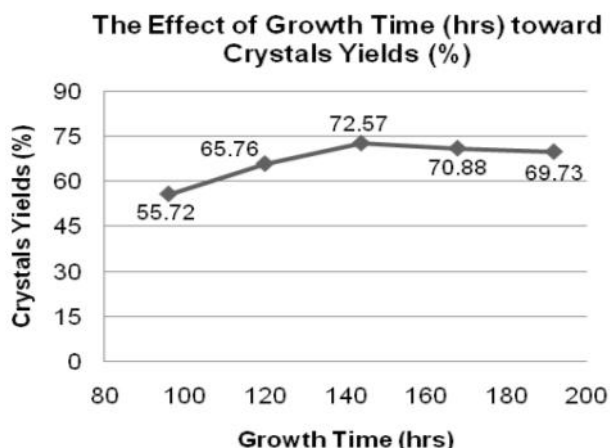


Figure 3: The effect of growth time toward crystals yield (%)

55.72 % to 72.57 %. Then, the graph decreased relatively steadily to 69.73 % at growth time of 192 hours. If more growth time was used i.e. 216 hours, the crystal yield could be predicted to be relatively constant. This is due to the crystal formation rate of fluorite was likely high only during the first week of growth time. Hence, adding more growth time will be considered as ineffective, especially in term of economical issue. Moreover, when all optimum parameters were combined, the crystal yield was getting higher and reaches 72.57 %. Based on the result of three optimum parameters, this research was considered successful, since the raw material that used was prepared from low grade (waste). Although this research only focus on three parameters, further development of the process could be conducted by investigating other factors such as glass tube type, temperature, etc.

In addition, further investigation of the synthesis of fluorite (CaF_2) crystals from gypsum waste in silica gel, in terms of economic aspect, is also needed. This is due to production cost of synthesized CaF_2 is higher than if the waste were directly dumped for landfill or sale in industrial market. However, the potential market of synthesized CaF_2 should also be considered since the abundance of natural CaF_2 (fluorite) is limited and the exploration of such minerals at some point might lead to the environmental degradation.

3.3 Characterization of Obtained Crystals

In order to confirm whether the product is fluorite as expected, the obtained crystal was then analyzed and characterized by AAS, FTIR, and powder XRD. The picture of obtained crystal is given in Figure 4. The biggest white block crystal

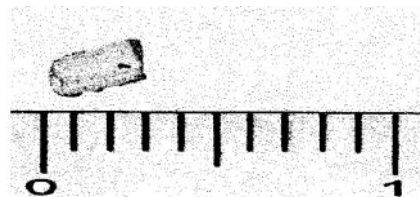


Figure 4: White block crystal of synthesized CaF_2 (in cm)

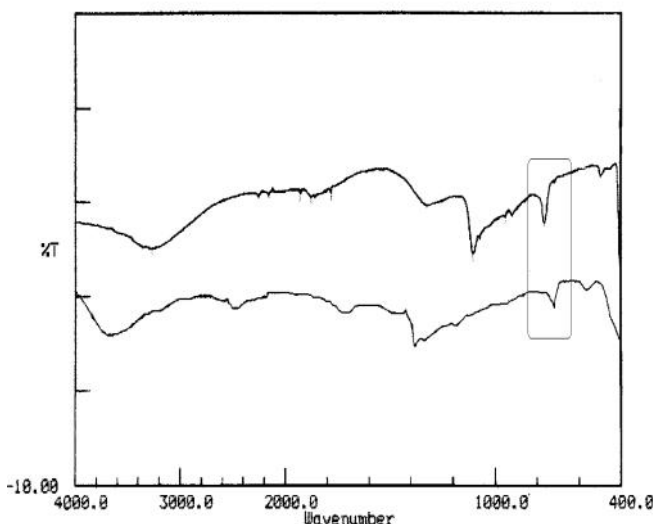


Figure 5: FTIR spectrum of standard (lower) and synthesized (upper) CaF_2

was grown until 3 mm long.

Analysis by AAS shows that the calcium contains in the crystal was 47.96 %, which is slightly lower than that of calculated CaF_2 (51.33 %). This is likely due to small amount of water molecules that might adsorb in the crystal during the analysis. This percentage of calcium also indicates that the crystal has high purity.

Moreover, analysis by FTIR and comparison by FTIR spectrum of standard CaF_2 suggests that a peak at 775 cm^{-1} that was observed was correspond to the Ca-F stretching (mark with square shape). The FTIR spectrum of obtained crystal is presented in Figure 5.

Furthermore, analysis by powder-XRD confirms that the obtained crystal was fluorite. This can be seen from the peaks observed on the XRD diffraction graph between synthesized crystal and the standard crystal taken from the crystal database (JCPDS). There were 6 highest peaks in the graph that was shown by the synthesized CaF_2 (Figure 6), which having identical pattern with those observed in standard CaF_2 . The differences

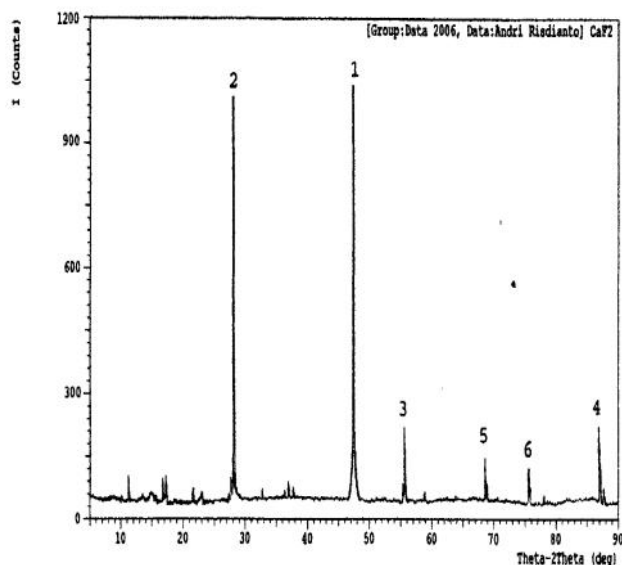


Figure 6: XRD analysis of synthesized CaF₂

between d-spacing values of both crystals (Table 1) were also relatively small. In addition, in terms of relative intensity (I/I₀) order, those 6 peaks were also identical with that of observed in the database

4. Conclusion

Based on result and discussion, it is concluded that gypsum waste of phosphoric acid factory can be used as raw material of CaCl₂ supernatant in the synthesis of potential and high purity of fluorite (CaF₂) single crystal in silica gel. The result shows that at optimum condition of pH 5.80, CaCl₂ concentrations of 1.2 M, and growth time of 144 hours, colorless crystals with the longest size of 3 mm, were obtained (72.57 %). All parameters used in this research were also statistically gives significant influences toward crystal yields. Characterization of the obtained crystal shows that it contains 47.96 % of calcium, and FTIR spectra show a Ca–F peak at 775 cm⁻¹, and powder-XRD analysis confirms that the obtained crystal was fluorite (CaF₂).

Acknowledgments

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Table 1: Selected crystallography data of standard (JCPDS) and synthesized CaF₂

Peak No	JCPDS*			Synthesized CaF ₂		
	2θ	d	I/I ₀	2θ	d	I/I ₀
1	87.3854	1.1151	16	87.3814	1.1151	16
2	75.8483	1.2533	9	75.8329	1.2535	8
3	68.6703	1.3657	10	68.7689	1.3640	10
4	55.7664	1.6471	30	55.8667	1.6444	18
5	47.0101	1.9314	100	47.0843	1.9285	100
6	28.2726	3.1540	99	28.2184	3.1520	97

* = JCPDS-International Centre for Diffraction Data (No. 88-2301), PCPDFWIN v. 2.2. (2001)

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