

Reaction between calcium phosphate and fluoride in phosphogypsum

Masamoto Tafu*, Tetsuji Chohji

Department of Ecomaterials Engineering, Toyama National College of Technology, 13 Hongo-machi, Toyama 939-8630, Japan

Available online 11 August 2005

Abstract

Phosphogypsum is the principal by-product produced by the wet processes involved in the manufacture of phosphoric acid, and generally contains an amount of fluoride that needs to be fixed or removed. Calcium hydrogen phosphate dihydrate (DCPD) reacts with fluoride ions in solution to form fluorapatite (FAp) in a reaction that is both selective and sufficiently efficient. We investigated the reaction between DCPD and the fluoride in phosphogypsum. The results demonstrated that the fluoride in phosphogypsum is able to be fixed by the reaction with DCPD, forming stable fluoride compounds such as fluorapatite.

© 2005 Elsevier Ltd. All rights reserved.

Keywords: Gypsum; Impurities; Surfaces; Chemical properties

1. Introduction

A calcium hydrogen phosphate dehydrate (DCPD, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) reacts with fluoride ions in a solution and forms fluorapatite (FAp, $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$).^{1,2} This reaction is utilized in the development of dental phosphate cements.³ We have previously applied the reaction to pre-concentration of fluoride in water⁴ and for monitoring trace amounts of fluoride in air.⁵

Phosphogypsum is the principal by-product produced by the wet processes involved in the manufacture of phosphoric acid. The main component of phosphate rock is FAp, and so fluorides, such as sodium fluoride (NaF), calcium fluoride (CaF_2), and sodium hexafluorosilicate (Na_2SiF_6),⁶ are contained as impurities in phosphogypsum. In Japan, regulation concerning fluoride in water and soil are currently being strengthened. If the fluorides in gypsum can be fixed to a stable compound, FAp, by reaction with DCPD, it is expected that environmental impacts from gypsum can be alleviated in the future. However, it is not clear whether DCPD is able to fix, as FAp, the fluoride in hexafluorosilicate, which is a fluoride complex contained in phosphogypsum.

In this paper, we proposed from our experimental results that DCPD could fix the fluoride in hexafluorosilicate as FAp, and we develop a novel method to fix the fluoride in gypsum using DCPD.

2. Experimental

2.1. Reagents

The DCPD and sodium hexafluorosilicate used were guaranteed reagent grade (Wako Pure Chemical Co. Ltd., Japan). Phosphogypsum (containing 0.13 wt.% of fluoride) was provided from the phosphoric acid manufacture process.

To dissolve in FAp, a dissolving solution containing 0.10 mol dm^{-3} of *trans*-1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetic acid monohydrate (CyDTA) and sodium chloride was used. The pH value was adjusted to 7.0 by 0.50 mol dm^{-3} of 2-[4-(2-hydroxyethyl)-1-piperazinyl]ethanesulfonic acid (HEPES) and hydrochloric acid.

Total ion strength of the adjusting buffer solution containing CyDTA (TISAB) was prepared by the JIS⁷ regulation for fluoride determination with ion selective electrode (ISE). CyDTA and HEPES were purchased from Dojindo Co. (Kumamoto, Japan). Water was purified by a multi-step commercial filtration and deionization process (Mill-Q water).

* Corresponding author. Tel.: +81 76 493 5479; fax: +81 76 492 3859.
E-mail address: tafu@toyama-nct.ac.jp (M. Tafu).

2.2. Fixation of fluoride in hexafluorosilicate by DCPD

Various amounts of DCPD were added in a mixture of water to 10 cm³ of sample solution containing sodium hexafluorosilicate in a polypropylene bottle. The mixture was shaken in a reciprocal shaker (Type NR-1, TAITEC, Japan) at room temperature for various periods. The solid phase was filtered by suction using a 0.45 μm membrane filter and then dissolved with 10 cm³ of the dissolving solution. The concentration of fluoride ions in the solution was measured by a standard addition method using an ISE (Orion ionplus 9609BN, Thermo Electron Corp., USA) and an ion meter (PCM 700, Thermo Electron Corp.). Fig. 1 shows a diagram of the method.

2.3. Fixation of fluoride in phosphogypsum by DCPD

Five grams of phosphogypsum containing various amount of DCPD was added to a 50 cm³ of sample of water in a polypropylene bottle. The mixture was shaken at room temperature for 1 day. The liquid and the solid phase were separated by suction using a 0.45 μm membrane filter. 1.0 cm³ of TISAB was added to 10 cm³ of the liquid phase, and the concentration of fluoride ions in the obtained solution was measured by a standard addition method using the ISE and the ion meter. The crystalline phase of the solid phase was analyzed by powder X-ray diffraction (Miniflex, Rigaku, Co. Ltd., Tokyo, Japan). Field emission scanning electron microscope (FE-SEM, JSM-6700F, JEOL,

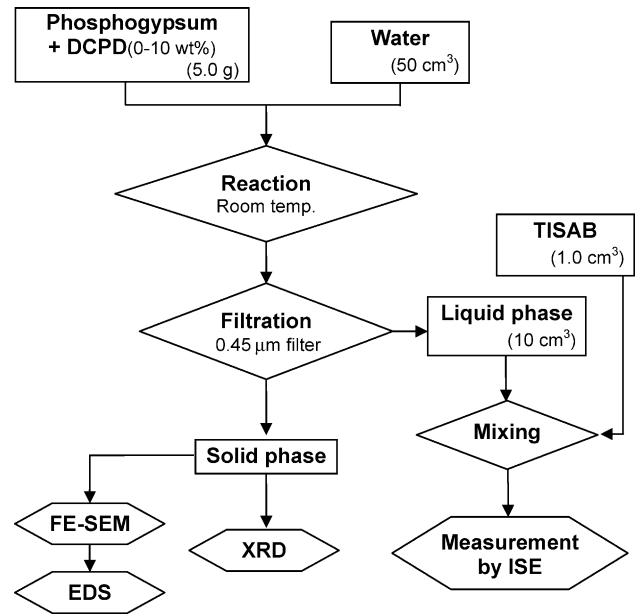


Fig. 2. Procedure for the determination of fluoride in an aqueous solution.

Tokyo, Japan) and energy dispersive X-ray spectroscopy (EDS, JED-2300, JEOL, Tokyo, Japan) were also carried out for microstructure observation and elemental analysis of the solid phase. A diagram of the method is shown in Fig. 2.

3. Results and discussion

3.1. Fixation of fluoride in hexafluorosilicate by DCPD

The fixation ability of fluoride in hexafluorosilicate, which is one of the impurities in phosphogypsum, was experimentally investigated. Various amounts of DCPD were added as a mixture in water to a 10 cm³ of sample solution contained in

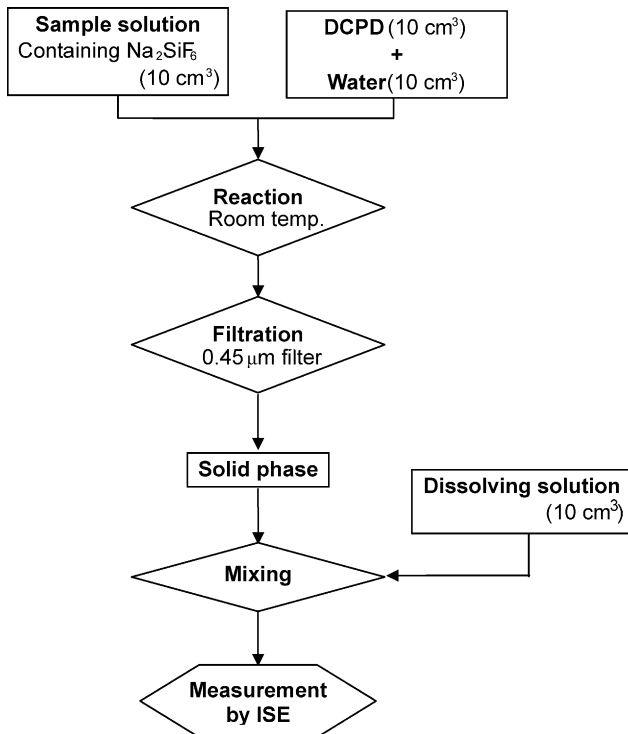


Fig. 1. Procedure for the determination of fluoride in FAp.

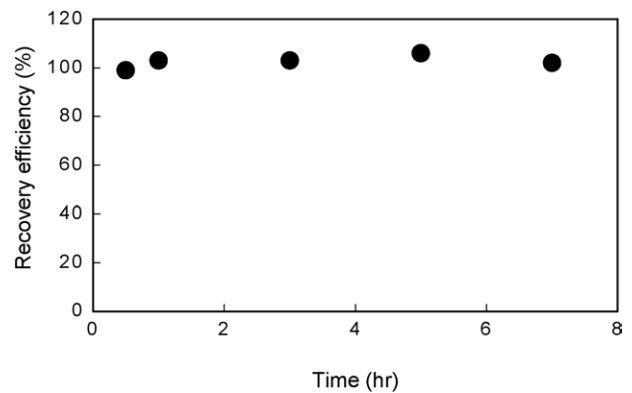


Fig. 3. Recovery efficiency of fluoride in hexafluorosilicate by reaction of DCPD. Concentration of hexafluorosilicate is 1.6 mg dm⁻³ (1.0 mg dm⁻³ as fluoride).

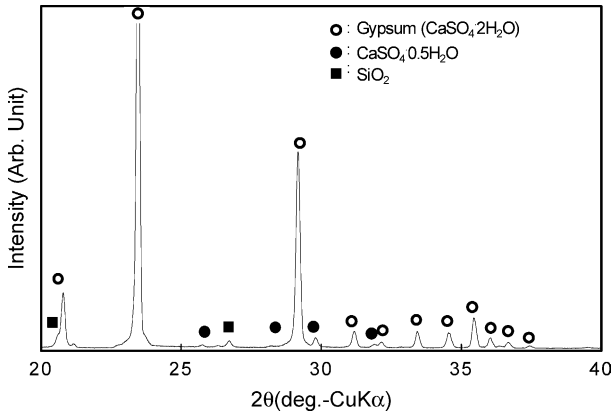


Fig. 4. Powder X-ray diffraction pattern of phosphogypsum.

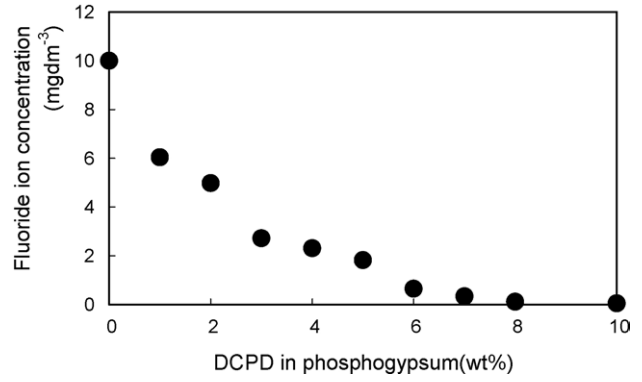
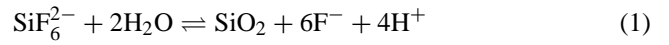


Fig. 5. Fluoride ion concentration leached from phosphogypsum containing various amounts of DCPD. Phosphogypsum/water ratio is 5.0 g/cm³, leaching time is 1 day.

a polypropylene bottle. The concentration of sodium hexafluorosilicate in the sample solution was adjusted to 1 mg dm⁻³ as fluoride ions. The mixture was then shaken at room temperature for various periods. The recovery coefficient of the fluoride collected from the separated solid phase is shown in Fig. 3; all the fluoride ions in hexafluorosilicate were fixed by the reaction of DCPD within 1 h. Although hexafluorosilicate is the fluoride complex of silicate, fluoride ions are released in aqueous solution as shown by following

equation.⁸



DCPD and fluoride ions in a solution, resulting in the formation of FAp.

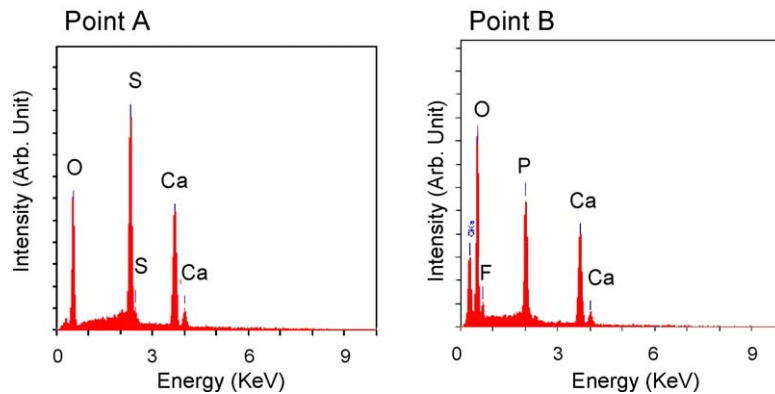
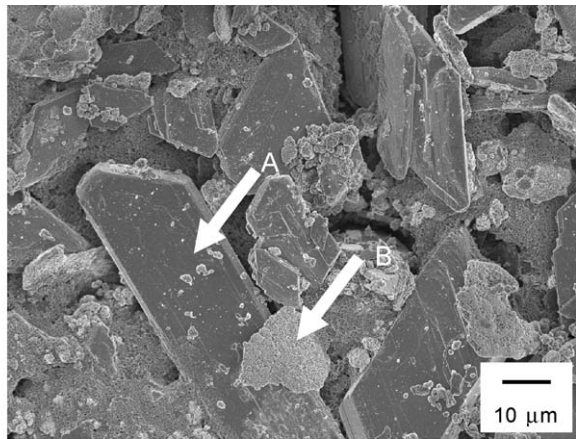
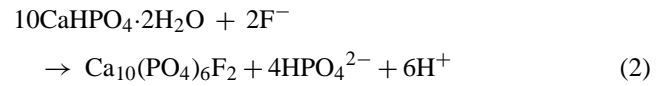


Fig. 6. FE-SEM image and the EDS analysis results of the phosphogypsum containing 10% of DCPD after reacted 1 day in water. Experimental conditions are same as Fig. 5.

DCPD reacted with the fluoride ions generated from hexafluorosilicate by the reaction (1), and formed FAp, quantitatively.

3.2. Fixation of fluoride in phosphogypsum by DCPD

Fig. 4 shows powder X-ray diffraction patterns of phosphogypsum. In addition to the diffraction peak of gypsum, there are diffraction peaks of various impurities, such as silicon oxide and calcium sulfate hemihydrate. However, there are no diffraction peaks of fluorides such as calcium fluoride, because the fluoride content is too small to detect by X-ray diffraction.

The fixation ability of fluoride in a phosphogypsum sample by reaction with DCPD was investigated in batch experiments; 5 g of phosphogypsum containing various amounts of DCPD added to 50 cm³ of water in a polypropylene bottle. The mixture was shaken at room temperature for 24 h. The fluoride ion concentration of the solution separated from the mixture is shown in Fig. 5. When phosphogypsum was added into water, the fluoride ion concentration in the solution was 10 mg dm⁻³. On the other hand, the concentration of fluoride ion in the solution with added phosphogypsum of more than 6 wt.% was decreased to less than 1 mg dm⁻³. From this result, it is surmised that the fluoride in phosphogypsum was fixed in the sample as an insoluble substance, such as FAp. In the result of powder X-ray diffraction analysis of phosphogypsum after the reaction with DCPD, diffraction peaks of FAp are not detected because of amount of FAp is very small. The microstructure of the solid phase was observed by FE-SEM, as shown in Fig. 6. In this figure summarizes the EDS analysis results for the particular sites within the SEM photograph too. In FE-SEM photograph, rectangle particles (A in Fig. 6) and particles with another shape (B in Fig. 6) can be clearly observed. The EDS analysis result of the point A indicated that Ca, S, and O were detected from the rectangle particle. This result shows that the particle is gypsum particle. On the other hands, the EDS result of the point B indicated that Ca, P, O, and F were detected from the particle. This result shows that the particle is FAp particle. From these results, fluoride in phosphogypsum was fixed by the reaction with DCPD, and formed fluorapatite.

4. Summary

In this study, we investigated the reaction between DCPD and fluoride in phosphogypsum. The results demonstrated that the fluoride in phosphogypsum was able to be fixed by the reaction with DCPD, forming stable fluoride compounds such as fluorapatite. Fluoride is contained not only in phosphogypsum, but also in waste gypsum board. It is suggested that the reaction with DCPD to FAp is applicable to fixing fluoride in various types of gypsum. Further studies for optimization of the conditions for fixation, and the application of them to various gypsum samples are now in progress.

Acknowledgements

The authors deeply appreciate the helpful support with the experiments given by Mr. Hideyo Inami and Ms. Momoko Hayashi (Toyama National College of Technology). This study was supported by the Industrial Technology Research Grant Program in '04 from the New Industrial Technology Development Organization (NEDO), Japan (#04A19013).

References

- Duff, E. J., Orthophosphate-I formation of apatites from calcium phosphates in potassium fluoride solutions. *J. Inorg. Nucl. Chem.*, 1970, **32**, 3103–3106.
- Chow, L. C. and Brown, W. E., Reaction of dicalcium phosphate dihydrate with fluoride. *J. Dent. Res.*, 1973, **52**(6), 1220–1227.
- Chow, L. C., Development of self-setting calcium phosphate cements: biomaterials. *J. Ceram. Soc. Jpn.*, 1991, **99**(10), 954–964.
- Tafu, M., Kagaya, S. and Chohji, T., A separation method for simplified determination of fluoride by using calcium phosphate. *Anal. Sci.*, 2001, **17**, i753–i756.
- Tafu, M. and Chohji, T., A simplified method for determination of trace amounts of fluoride in the air by using transform reaction of calcium hydrogenphosphate dihydrate (DCPD). *J. Ecotech. Res.*, 2004, **10**(2), 83–89 (in Japanese).
- Kaji, K. and Tsuda, T., Fluoride and phosphate in the by-produced gypsum of phosphoric acid process. *Gypsum Lime*, 1960, **48**, 162–167 (in Japanese).
- Japan Industrial Standard of Analytical method for Industrial Water, JIS K0101–1998.
- Iler, R. K., *The Chemistry of Silica*. John Wiley and Sons, New York, 1979, p. 213.