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Colloids and Surfaces A: Physicochemical and Engineering Aspects

Effects of fluoride and polymeric additives on the dissolution of calcite and the subsequent formation of fluorite

Taewook Yang [a], Wansoo Huh [b], Jae Young Jho [a],[**], Il Won Kim [b],[*]
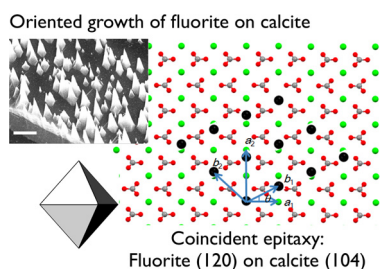
[a] School of Chemical and Biological Engineering, Seoul National University, Seoul 151-742 Republic of Korea
[b] Department of Chemical Engineering, Soongsil University, Seoul 156-743 Republic of Korea

HIGHLIGHTS

- Kinetics of fluoride removal by calcite.
- Polymeric additives as the inhibitors of the fluoride removal.
- Phase transformation of calcite into fluorite.
- Epitaxy for the oriented growth of fluorite on calcite.

GRAPHICAL ABSTRACT

Oriented growth of fluorite on calcite

Coincident epitaxy: Fluorite (1 2 0) on calcite (1 0 4)

ARTICLE INFO

ABSTRACT

Fluoride is a problematic contaminant of the ground water arising from both natural and man-made origins. In this report, the fluoride uptake by calcite (calcium carbonate) was examined with emphasis on the effects of model organic compounds (polymers) and the possible adhesion of fluorite (calcium fluoride) on calcite. The primary route of the fluoride removal was fluorite formation through dissolution-and-recrystallization. While all model polymers affected the kinetics of fluorite formation, the positively charged poly(ethylene imine) had the most inhibiting influence. The observation of the calcite single crystals using atomic force microscopy revealed that the inhibitory effect was attributed to the retarded diffusion of fluoride to the calcite surface, which was also in accordance with the analysis of bulk experiments with calcite powders. It was also found that the oriented growth of fluorite was induced on the calcite (1 0 4) surface probably by the epitaxy with the (1 2 0) plane of fluorite. The current results could be of critical implications in the process design of fluoride removal by considering organic interferences and minimizing the need of flocculation step.

1. Introduction

Fluoride is one of the more problematic ion contaminants when present in ground water because it could cause fluorosis by reconfiguring apatite minerals of human hard tissues [1–3]. It could be an especially challenging issue in regions where fluoride-containing minerals are abundantly present, such as China, India, and North Africa [4]. Additionally, wastewater that contains fluoride is produced from various industries where glass, semiconductor, and aluminum are manufactured and processed [5–7].

Methods to remove fluoride from aqueous solutions include precipitation, adsorption, electrodialysis among other techniques [5,8,9]. Precipitation is one of the more common methods, and calcium salts, such as calcium chloride, calcium hydroxide, and calcium carbonate, have been especially useful for the initial treatment of high fluoride-concentration water [5,10–14]. When the calcium salts are added, fluoride forms relatively insoluble calcium

* Corresponding author. Tel.: +82 2 820 0614; fax: +82 2 812 5378.
** Corresponding author. Tel.: +82 2 880 8346; fax: +82 2 884 7355.
E-mail addresses: jyjho@snu.ac.kr (J.Y. Jho), iwkim@ssu.ac.kr (I.W. Kim).

fluoride (fluorite), of which particles are subsequently flocculated for better separation [5,12,13]. Among the conventional calcium sources, calcium carbonate is advantageous in its natural abundance, most notably in limestone (calcite) [11,14,15]. In addition, calcium carbonate seems effective in removing fluoride below the equilibrium concentration of ca. 8 mg/L, K_{sp} of calcium fluoride being 3.45×10^{-11} at 25 °C, when excess amounts are used under acidic conditions [11,14–16]. The mechanism of the fluoride removal by calcium carbonate appears through surface adsorption as well as fluorite precipitation [17], although the interaction and possible adhesion of fluorite on the surfaces of calcium carbonate are not well understood.

In the present study, fluoride uptake by calcium carbonate was studied. Specifically, calcite was utilized among the several anhydrous polymorphs (calcite, aragonite, and vaterite) of calcium carbonate because of its large availability. Upon the exposure of calcite to the aqueous solutions of fluoride, the kinetics of fluoride removal was monitored. Also, the effects of model polymers were investigated to identify possible organic interferences during fluoride uptake, which had implications in the practical applications because of the addition of polymers during the flocculation procedure and the expected presence of natural organic matters in ground water [5,12,13,18,19]. In addition to the monitoring of the bulk solutions, phenomena on the calcite surfaces were closely observed to promote the mechanistic understanding of the fluoride uptake.

2. Experimental

2.1. Materials

Calcite (geological CaCO$_3$) was purchased from Hansol Education Co. (Seoul, South Korea). Sodium fluoride (NaF, ACS reagent, purity ≥99.0%) was obtained from Sigma–Aldrich (St. Louis, USA). Poly(ethylene glycol) (PEG: [CH$_2$CH$_2$O]$_n$, M_w 8,000 and 100,000), poly(acrylic acid) (PAA: [CH$_2$CH(COOH)]$_n$, sodium salt, 35 wt% solution in water, M_w 15,000), and poly(ethylenimine) (PEI: [CH$_2$CH$_2$NH]$_n$, M_w 25,000) were from Aldrich (St. Louis, USA). Deionized water (DIW, resistivity >18.0 MΩ cm) was from Direct Q3 of Millipore (Billerica, USA).

2.2. Reaction of calcite with fluoride

The reaction started by placing ground calcite (131.5 mg) in the aqueous solution of 50-ppm fluoride (2.63 mM NaF (aq), 20 mL), which set Ca/F = 1:2. It proceeded in a reaction vessel (diameter 27 mm, height 61 mm) made with isotactic polypropylene. The solution was at room temperature (ca. 20–25 °C) and under vigorous stirring (ca. 120 rpm) with a Teflon-coated magnetic stir bar (rod-shaped: length 14 mm, diameter 5 mm). The initial pH of the NaF solution before reaction was 3 or 7, which was adjusted with a small amount of 1 N HNO$_3$ (aq). The drift of pH, as the reaction proceeded, was left unaltered to observe spontaneous reaction pathways.

Variation of the fluoride concentration was monitored *in situ* with a fluoride-selective electrode. An Orion 4-Star pH/ISE Benchtop meter of Thermo Electron Corporation (Waltham, USA) was used with an Orion 9609BNWP Combination fluoride electrode and an Orion 8102BNUWP ROSS Ultra glass combination pH electrode. Each reaction was monitored at every hour, and the reported value of fluoride concentration was the average of the five independently performed experiments. After 24 h, the solid phases were filtered, washed with DIW, and dried in a 60 °C convection oven for further examination.

In addition to the bulk experiments with ground calcite, single crystals of calcite were utilized to examine the effects of fluoride on the calcite surfaces. A typical experiment with a single crystal of calcite (ca. 2–3 mm in each dimension) was performed as follows. A single crystal was attached to a circular cover glass by UV curable adhesive, and it was placed in the aqueous solution of 50-ppm fluoride (2.63 mM NaF (aq), 20 mL) with a top surface freshly cleaved. After a set amount of reaction time (1, 2, 6, 12, and 24 h), it was lightly washed in DIW for 2–3 s and dried without touching the top surface using nitrogen gas and tissue paper. The surfaces of the single crystals were microscopically examined as described in the characterization section. The initial pH of the NaF solution was 7 to enable stepwise investigation of the surface phenomena by reducing the dissolution rate of calcite and subsequently slowing the interaction of fluoride with calcium.

The effects of polymeric additives during the reaction of calcite with fluoride were also studied. The reaction conditions were the same as those without additive as described above except that the desired types and amounts of polymers were pre-dissolved in the NaF solutions.

2.3. Characterization

Surface area of ground calcite was measured using methylene blue (MB) as a molecular probe for adsorption area, which has been known as a more suitable method for the applications in the liquid environment [20,21]. Ground calcite powder (100 mg) was placed in a MB aqueous solution (0.10 mM, 20 mL, pH 7). After equilibrating for 24 h, the calcite powder was filtered, and the UV absorbance of the filtrate was measured at 665 nm (Jasco V-560 UV/Vis Spectrophotometer, Tokyo, Japan). The remaining MB concentration in the filtrate was calculated against a pre-obtained calibration curve. From the average of five measurements, the surface area of the ground calcite was obtained using 1.3 nm^2 of occupying area per MB molecule [22].

Zeta-potential measurement was performed using a Zetasizer 2000 of Malvern Instrument (Malvern, UK). Ground calcite powder (20 mg) was dispersed in DIW (20 mL) at pH 7. After 1–2 min of shaking, 2–3 mL of the solution was used for the measurement at 25 °C. The reported zeta-potential value was the average of five measurements. Measurement at acidic pH was impractical because of the large solubility of calcite and its dynamic surfaces at this condition.

The crystal phases before and after the fluoride reactions were identified by wide-angle X-ray diffraction. A Bruker (Billerica, USA) D8 Advance General Area Detector Diffraction System (GADDS) was used with Cu K$_\alpha$ (λ = 0.154 nm) radiation generated at 40 kV and 45 mA. A frame of diffraction data (20–60°) was collected with a Hi-Star multi-wire 2D area detector for 300 s by placing the detector at the center of the 2θ range. Data was integrated to display a typical 2θ plot versus intensity. Spectral data were analyzed by using EVA 9.0.0.2 software containing references from the Joint Committee on Powder Diffraction Standards (JCPDS).

Morphologies of the ground calcite and its reaction products were observed via scanning electron microscopy (SEM: JEOL JSM-6401F, Tokyo, Japan). Thin Au coating (Cressington Sputter Coater 108, Watford, UK) was applied to minimize surface charging. When the surfaces of the calcite single crystals were observed, the same procedure was applied.

The surfaces of the single crystals were also observed by atomic force microscopy (AFM) before SEM preparation and observation. AFM was operated in the contact mode using a MFP3D-SA (Asylum research, Santa Barbara, USA) equipped with an Olympus Micro Cantilever OMCL-AC240TS-C2. Scan speed was 1 Hz, and the pixel size of the image was 256.