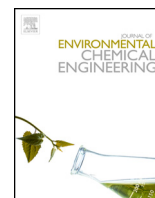




Contents lists available at ScienceDirect

## Journal of Environmental Chemical Engineering

journal homepage: [www.elsevier.com/locate/jece](http://www.elsevier.com/locate/jece)

## 1 Surface complexation modeling of fluoride sorption onto calcite

2 Q Sakambari Padhi\*, Tomochika Tokunaga\*\*

3 Geosphere Environment Systems Laboratory, Department of Environment Systems, Graduate School of Frontier Sciences, The University of Tokyo, Kashiwa,  
4 Chiba 277-8563, Japan

## ARTICLE INFO

## Article history:

Received 23 January 2015

Accepted 27 June 2015

## Keywords:

Fluoride

Calcite

Adsorption

Precipitation

Surface complexation modeling

## ABSTRACT

Calcite and various calcium salts have been used to remove fluoride from drinking water and waste water in many countries, and calcareous soils retard the mobility of fluoride in soil. Adsorption of fluoride onto calcite could be important at low fluoride concentration. In this study, a series of batch experiments with calcite equilibrated solutions was conducted to investigate the mechanisms of fluoride uptake by calcite. The range of initial fluoride concentration was from 2.5 to 10 mg/l. Effects of pH, ionic strength, and solid concentration were evaluated. Fluoride uptake was found to be strongly pH dependent whereas ionic strength also affected fluoride removal. A constant capacitance model was used to model fluoride sorption onto calcite, where fluoride adsorption was described by the formation of two surface complexes,  $>CaF^0$  and  $>CO_3FCa^0$ . The formation of  $>CaF^0$  complex was evidenced from thermodynamic approach, whereas inclusion of  $>CO_3FCa^0$  was necessary to explain fluoride sorption to calcite surface. Fluoride sorption was modeled with and without precipitation. The results showed that, at lower fluoride concentration, adsorption was the governing mechanism for fluoride removal by calcite whereas a combined mechanism of adsorption and fluorite precipitation was necessary to describe fluoride interaction with calcite at low pH and higher fluoride concentration. Thus, adsorption of fluoride to calcite can influence the mobility of fluoride in soil under suitable conditions where calcite is abundant. Also, surface adsorption should also be considered in addition to precipitation in defluoridation methods, which use calcite or limestone as one of the defluoridating agents.

© 2015 Published by Elsevier Ltd.

## 5 1. Introduction

6 Fluoride contamination of groundwater has been reported from  
7 many parts of the world, particularly in arid and semi-arid areas of  
8 southeast Asia including India, China, and many countries in Africa,  
9 and USA [1]. The detrimental effects of long-term intake of fluoride  
10 (exceeding WHO guideline value of 1.5 mg/l) in drinking water  
11 include dental and skeletal fluorosis [2] among other health  
12 effects. High fluoride concentration in groundwater can be due to  
13 natural dissolution of fluorine bearing minerals in rock and soil. It  
14 can also be due to agricultural activities or mineral processing. The  
15 fluoride concentration in a soil solution is mainly controlled by the  
16 pH and content of clay fraction in soil [3] and high levels of soluble  
17 fluoride in soil may leach to the shallow groundwater under  
18 suitable conditions [4–10]. On the contrary, laboratory studies on  
19 fluoride sorption on soil [11,12] and field studies [13] concluded  
20 that little fluoride from soil would be leached to groundwater.

Thus, the contribution of adsorbed fluoride in soil to groundwater  
contamination is still controversial.

Calcite has been treated not to be a major contributor to  
sorption [14,15], although studies with natural materials contain-  
ing calcite have implicated calcite as an important sorbent for  
cations and anions [16–18]. Furthermore, the interaction of  
fluoride with calcite can be important due to the fact that many  
water bodies with high fluoride contamination are found to be in  
equilibrium or saturated with respect to calcite [19]. In addition,  
calcite and limestone have been used for fluoride removal from  
drinking water and waste water [20,21]. Therefore, it is necessary  
to better understand the mechanism of fluoride sorption on calcite.

A considerable amount of research has investigated the mecha-  
nism of fluoride removal by calcite using a variety of macroscopic and  
spectroscopic techniques. For example, fluorite ( $CaF_2$ ) precipitation  
was considered to be the main mechanism for fluoride removal by  
calcite [6,21–23], whereas Fan et al. [24] found that fluoride uptake  
by calcite occurred by surface adsorption. Turner et al. [20] extended  
the work by Fan et al. [24] using crushed limestone and by  
considering high fluoride concentration where fluorite precipitation  
is known to occur and concluded that fluoride was removed by a  
combination of surface adsorption and precipitation. Similarly, Nasr  
et al. [25], in the presence of acetic acid, found that at low initial

\* Correspondence author. Tel.: +81 4 7136 4713; fax: +81 4 7136 4713.

\*\* Correspondence author. Tel.: +81 4 7136 4708; fax: +81 4 7136 4709.

E-mail addresses: [padhi@geoenv.k.u-tokyo.ac.jp](mailto:padhi@geoenv.k.u-tokyo.ac.jp) (S. Padhi),  
[tokunaga@k.u-tokyo.ac.jp](mailto:tokunaga@k.u-tokyo.ac.jp) (T. Tokunaga).

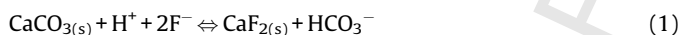
fluoride concentration (5 mg/l), fluoride was mainly removed by adsorption at calcite surface whereas at high fluoride concentration (50 mg/l), fluorite precipitation occurred. Calcite is found to adsorb divalent metals [26], arsenate and arsenite [27] and phosphate [28], and the extent of adsorption depends on the solution chemistry in the corresponding studies.

The objective of this study is to further investigate and elucidate the mechanism of fluoride sorption on calcite through a series of batch experiments. The initial fluoride concentration used in our study is equal to or below 7.5 mg/l, which is the equilibrium fluoride concentration considering fluorite dissolution to pure water and within the range of fluoride concentration observed naturally in groundwater except for a few areas where the fluoride concentrations are quite high [29]. For comparison, we also tested high fluoride concentration (10 mg/l). In this study, the surface complexation model (SCM) developed by Pokrovsky and Schott [30] for calcite is extended to model the adsorption of fluoride.

## 2. Theoretical background of fluoride removal by calcite from aqueous phase

### 2.1. Fluorite precipitation

Fluorite precipitation in a solution can occur when the solubility limit of fluorite is reached. The equilibrium fluoride concentration in pure water is 7.5 mg/l considering an equilibrium constant of fluorite ( $\log K_{\text{fluorite}}$ ) of  $-10.5$ , which is based on the thermodynamic database of Visual Minteq 3.0 [31]. A broad range of fluoride solubility, i.e.,  $\log K_{\text{fluorite}}$  values ranging from  $-8.27$  to  $-11.23$ , was reported from experimental measurements at  $25^\circ\text{C}$  and 1 atm pressure condition [32]. Mineral saturation in aqueous solution in the Visual Minteq 3.0 is determined by saturation index ( $SI = \log(IAP/K_{\text{sp}})$ ; where IAP is the ion activity product and  $K_{\text{sp}}$  is the solubility constant) of the mineral. SIs are approximate indicators of equilibrium because of the uncertainty in the analytical measurements and in the thermodynamic constants used to calculate the equilibrium constants. The equilibrium formation constants for reactions relevant to the calcite–fluorite– $\text{Ca}^{2+}$ – $\text{H}^+$  system used in this study were taken from the default database of Visual Minteq 3.0 (See Supporting information, Table S1). The equilibrium fluoride concentration in a calcite–fluorite system depends on the  $\text{Ca}^{2+}$  concentration and pH of the solution which is explained by the following equations:



$$K_{\text{cal.flour}} = \frac{a_{\text{HCO}_3^-}}{a_{\text{H}^+}} \times (a_{\text{F}^-})^2 \quad (2)$$

where  $K_{\text{cal.flour}}$  is the equilibrium constant for the calcite–fluorite system,  $a_{\text{HCO}_3^-}$ ,  $a_{\text{H}^+}$ , and  $a_{\text{F}^-}$  are the activities of  $\text{HCO}_3^-$ ,  $\text{H}^+$ , and  $\text{F}^-$  in solution, respectively.

### 2.2. Adsorption of fluoride at calcite surface

Previous studies on fluoride removal by calcite in a system under the condition that fluorite precipitation should not occur showed that a considerable amount of fluoride was removed by calcite [20,24]. Thus, adsorption of fluoride should be considered in addition to fluorite precipitation when the mechanism of fluoride removal by calcite is inferred.

SCMs were widely used to investigate cation and anion adsorption at the metal oxides and calcite surfaces [27,28,33] and were described by many models, e.g., non-electrostatic, diffuse layer, constant capacitance, triple layer, and so on [34]. An SCM

**Table 1**

Surface complexation reactions for surface speciation of calcite and fluoride sorption along with intrinsic surface complexation reactions ( $\log K_{\text{int}}$ ).

Surface complexation reactions	$\log K_{\text{int}}$
$>\text{CO}_3\text{H}^0 = >\text{CO}_3^- + \text{H}^+$	$-5.1^{\text{a}}$
$>\text{CO}_3\text{H}^0 + \text{Ca}^{2+} = >\text{CO}_3\text{Ca}^+ + \text{H}^+$	$-1.7^{\text{a}}$
$>\text{CaCO}_3^- + \text{H}_2\text{O} = >\text{CaOH}_2^+ + \text{CO}_3^{2-}$	$-5.25^{\text{a}}$
$>\text{CaCO}_3^- + \text{HCO}_3^- = >\text{CaHCO}_3^0 + \text{CO}_3^{2-}$	$-3.929^{\text{a}}$
$>\text{CaCO}_3^- + \text{F}^- = >\text{CaF}^0 + \text{CO}_3^{2-}$	$-3.2^{\text{b}}$
$>\text{CO}_3\text{H}^0 + \text{Ca}^{2+} + \text{F}^- = >\text{CO}_3\text{FCa}^0 + \text{H}^+$	$2.2^{\text{b}}$
Model parameters	
BET surface area ( $\text{m}^2/\text{g}$ )	0.199
Solid loading ( $\text{g}/\text{l}$ )	20
Capacitance ( $\text{F}/\text{m}^2$ )	$44^{\text{c}}$
Aqueous reaction for fluorite precipitation	$\log K$
$\text{Ca}^{2+} + 2\text{F}^- = \text{CaF}_2$	10.5

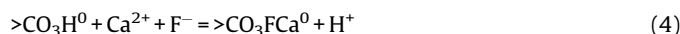
<sup>a</sup> Pokrovsky and Schott (2002).

<sup>b</sup> Optimized in this study.

<sup>c</sup> Calculated as  $\kappa = I^{1/2}/\alpha$ , where  $\kappa$  is the capacitance,  $\alpha$  is an empirical parameter equal to 0.006 for calcite and  $I$  is the ionic strength (moles/l) [36].

explaining surface charge and dissolution kinetics of calcite was proposed by van Cappellen et al. [35], which was further evaluated and refined [33,36]. Successful applications of the modified model were found in literatures [27,28,33]. Based on surface sensitive spectroscopic techniques, surface titration and electrokinetic study, SCMs for calcite dissolution were postulated which assumed two surface sites at calcite surface [35], i.e.,  $>\text{Ca}$  and  $>\text{CO}_3$  with a 1:1 stoichiometry and each with a site density of  $8.22 \mu\text{mol}/\text{m}^2$  [37]. When exposed to aqueous solution, the species to be formed at the  $>\text{Ca}$  and  $>\text{CO}_3$  sites are as follows:  $>\text{CaOH}_2^+$ ,  $>\text{CaOH}^0$ ,  $\text{CaO}^-$ ,  $>\text{CaHCO}_3^0$ ,  $>\text{CaCO}_3^-$ ,  $>\text{CO}_3\text{Ca}^+$ ,  $>\text{CO}_3\text{H}^0$ , and  $>\text{CO}_3^-$  [33]. The reactions for the formation of these species along with the equilibrium formation constants are listed in Table 1.

Fluoride adsorption to both  $>\text{Ca}$  and  $>\text{CO}_3$  sites was considered in this study. This was supported by the fact that fluoride sorption was found to occur on the entire calcite surface as observed by atomic force microscopy [20]. Here, fluoride sorption at the  $>\text{Ca}$  and  $>\text{CO}_3$  sites of calcite surface was set to be represented by the following reactions:



Here, the choice of fluoride surface complexation formation reactions was based on the analogy between aqueous and surface complex formation (Reaction (3)) and to explain pH dependency of our observed data (Reaction (4)). The details are discussed in the subsequent section (Section 4.3.2.2).

## 3. Materials and experimental procedures

### 3.1. Materials

All chemicals used in the experiments were reagent grade and used without further purification. Milli-Q water was used to prepare the solutions. Fluoride solutions were prepared by dissolving appropriate amount of analytical grade NaF (Wako Pure Chemicals Industries Ltd.). The solution was diluted to get the desired fluoride concentration. Reagent-grade calcite ( $\text{CaCO}_3$ ) was used throughout the study. The XRD patterns collected by an X-ray diffractometer using  $\text{Cu K}\alpha$  radiation operated at 40 kV and 20 mA confirmed it to be pure calcite. The specific surface area was determined using a five-point N<sub>2</sub>-BET method (NOVA station B) for the two lots of calcite used in this study, and was  $0.199 \text{ m}^2/\text{g}$  for the smaller fraction ( $180 \mu\text{m}$ ) and  $0.138 \text{ m}^2/\text{g}$  for the larger fraction ( $700 \mu\text{m}$ ), respectively.

Download English Version:

<https://daneshyari.com/en/article/10277192>

Download Persian Version:

<https://daneshyari.com/article/10277192>

[Daneshyari.com](https://daneshyari.com)