

Adsorption Behavior of Fluoride at Normal Brick (NB) - Water Interface

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Abstract

Composition of normal brick (NB) particles, obtained from brick making kilns after the normal firing process, is determined through X-ray fluorescence, X-ray diffraction, and atomic absorption spectroscopic methods. Surface characterization of NB is achieved through surface titrations of NB suspensions prepared in aqueous NaNO₃ solutions of different ionic strengths. Experiments conducted by changing the medium pH and ionic strength, and introducing different interferents show that attraction of fluoride ions (F⁻) to the NB surface leads to the formation of inner-sphere complexes. It is proposed that surface adsorption is interpreted using Langmuir and Freundlich isotherms. Further, interaction of F⁻ by NB follows first order kinetics with a relatively large rate constant.

Keywords: Adsorption, fluoride, ion-exchange, normal brick (NB), surface titrations.

JEPS (2009), Vol. 3, pp. 140 – 146.

1. Introduction

Precipitation followed by complexation, adsorption, and electrochemical methods is commonly used for removal of fluoride (F⁻) from aqueous mediums [1-3]. Many of these methods are based on the addition of suitable chemicals during treatment of water contaminated with fluoride. Materials such as lime [4], silica gel [5], fluorspar [6], and moieties apatite [6] are used as adsorbents, while ionic resins are used for ion exchange [7]. In certain instances, adsorption equilibrium is followed by absorption and ion exchange, and hence it is difficult to isolate these processes. The relative extent of these processes depends mainly on the affinity of adsorbate molecules toward selective sites of the adsorbent. For instance, F⁻ removal by quartz follows only adsorption, while that by hydroxyapatite follows both adsorption and ion exchange [6].

Adsorption of F⁻ by natural or synthetic surfaces through incorporation into the crystal lattice with concomitant release of OH⁻ and Al³⁺ depends on the availability of such moieties in the substrate [8, 9]. Thus, waters rich in alkaline species such as bicarbonates favor leaching of F⁻ from rocks containing fluorides [10]. On the other hand, acidic conditions favor defluoridation of water when in contact with suitable adsorbents. Therefore, it can be argued that the medium pH is an important parameter in

fluoride adsorption systems [2]. It has also been reported that formation of aluminum-fluoride complexes, such as AlF_n³⁻ⁿ and Al(OH)_{3-m}F_m, occurs when F⁻ containing solutions are treated with aluminum salts [6, 11], thereby lowering the free F⁻ concentration in the solution. As many types of natural clay bear -OH groups on the surface and contain Al in the bulk [12, 13], such clay types have the ability to remove F⁻ from aqueous medium.

Transfer of a charged species from solution to a solid phase occurs via three essential steps: diffusion of the species to the surface of the adsorbent, adsorption of the species onto the adsorbent surface, and exchange of adsorbed species with some structural elements in the bulk of the adsorbent [14]. Therefore, adsorption is initially controlled by the surface chemistry of the adsorbent. If adsorption is followed by ion exchange, the adsorbate species occupy both surface and bulk sites, and it is not merely a surface chemical process. These processes may be easily characterized on synthetic, homogeneous surfaces [15, 16]. However, due to heterogeneity of natural clay, complications arise in understanding the microscopic features of such sorption processes on clay surfaces.

Modification of adsorbents would lead to stronger interactions with charged species if proper conditions are followed. Heat treatment of natural clay is a simple bulk modification method which would change the adsorptive properties of clay. Brick particles obtained by burning brick clay have been effective in removing F⁻ and many

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other ionic species [14, 16, 17]. Nevertheless, bulk and surface characterization of brick and the mechanism of the ion removal process have not been addressed in detail.

This work deals with the chemical investigation of normal brick (NB) particles, an effective solid medium for sorption of F^- from aqueous solution. NB is a poorly characterized material despite its strong ion-exchange properties. Its surfaces would exhibit properties different from raw clay, and further, some phase changes would have occurred during firing. In this work, special attention was focused on NB surfaces and their adsorption characteristics toward F^- , surface properties, and a possible mechanism of F^- sorption by NB.

2. Materials and Methods

2.1 Materials

Standard solutions of F^- (1.0 to 50 ppm) and $NaNO_3$ were prepared using analytical grade NaF and $NaNO_3$ (BDH). Solutions of different pHs were prepared using NaOH and HCl (BDH). Standard solutions for atomic absorption spectroscopic (AAS) measurements were prepared using analytical grade chemicals. Buffers containing phosphates and carbonates were not used due to possible precipitating reactions with NB particles. NB particles (adsorbent) were obtained from a kiln located in the Central Province of Sri Lanka. Particles of diameter (d) less than 1 mm were used for all wet experiments, while finely ground samples ($d < 75 \mu m$) were used for surface titrations, X-ray diffraction (XRD), and X-ray fluorescence (XRF) measurements.

2.2 Instrumentation

Orion Model 520A ion selective electrode was used to measure fluoride ion concentration. Turbidity of each solution was measured using a turbidity meter (HF Scientific, Model DRT15CE), while absorbance was measured using a UV-160 spectrophotometer (Shimadzu). Solution pHs were measured with a pH meter (WPA Model 018). An atomic absorption spectrophotometer (Buck Instruments Model 200-A) was used for quantitative analysis of metal ions in an aqueous medium at recommended wavelengths. Centrifugation was done to remove suspended particles when turbidity problems were encountered. XRD patterns of NB samples were recorded on a Siemens X-ray diffractometer (Model- D50000) using $Cu-K\alpha$ X-ray beam (1.54056 nm). For XRF analysis, X-ray fluorescence spectrophotometer (Model-DF500FG-456) was used.

2.3 Research design

NB, being based on a natural substance having a variable composition, reflects many difficulties in quantitative analysis. Consequently, the method of sampling and the number of trials selected should be given sufficient attention. Representative samples were thus

prepared by grinding many pieces of kiln-burnt NB samples prepared using the clay from the same area. XRD patterns were obtained using at least three laboratory samples from one representative sample, and the results were averaged to minimize errors associated with the heterogeneous nature of NB. Further, all solution measurements were taken in triplicate to report average values.

2.4 Evaluation of surface properties

An NB clay suspension of fine powder having an amount of 20 g/L in a $NaNO_3$ solution of known concentration was stirred for 2 hours under a dry N_2 atmosphere to remove dissolved carbon dioxide. Then the mixture was stirred overnight in a carbon dioxide-free environment to form a homogeneous suspension. The initial pH of the suspension was measured and raised to a known higher pH value (~ 9.5) using NaOH. The resulting solution was then titrated on the Auto Titrator (Orion Model 940) with HNO_3 of known concentration until the pH reached between 3.5 and 4.0. Purging with dry N_2 was continued during the titration. A back titration was also carried out using the same NaOH solution to ensure the same changes in pH during the titration. Results were analyzed and all graphs were drawn using Excel and Origin Computer software. The entire procedure was repeated for three ionic strengths.

2.5 Effect of solution pH

A 10.00 g sample of NB was mixed with 100.0 ml of 20 ppm standard F^- solution. The solution pH was brought to pH = 1 using NaOH/HCl, then the mixture was stirred for 10 minutes, and allowed to settle for 2 hours. The supernatant was filtered using suction. The F^- concentration in the filtrate was measured using an ion selective electrode. The same procedure was repeated by changing the pH to 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12.

2.6 Interference studies

The extent of F^- removal in the presence of interfering species was determined by mixing equal volumes of 20 ppm F^- with each of Cl^- , Br^- , and I^- of the same concentration. A 10-minute stirring time and a 2-hour equilibration time were allowed for these measurements.

2.7 Effect of ionic strength

Solutions of F^- of concentration 20 ppm were prepared in $NaNO_3$ solutions of different ionic strengths varying from 0.0010 mol L⁻¹ $NaNO_3$ to 1.0 mol L⁻¹ $NaNO_3$. A 100.0 ml aliquot of each solution was mixed with 10.0 g of NB sample, shaken for 10 minutes and allowed to stand for 2 hours to reach equilibrium. The supernatant was filtered using suction. The F^- concentration in the filtrate was measured using an ion selective electrode.

Table 1: Percentage of each element present in NB determined from XRF and AAS analysis

Element	Na	K	Ca	Mg	Al	Ti	Cr	Mn	Fe	Cu	Zn
% w/w	14.23*	0.16	0.42	8.57*	24.85	1.00	0.05	0.18	12.96	0.01	0.01

* Obtained from AAS measurements

2.8 Investigation of adsorption isotherms

A 10.00 g sample of NB was mixed with 100.0 cm of 1.0 ppm F⁻ solution. Then the mixture was stirred for 10 minutes and allowed to stand for 2 hours to achieve equilibrium. After the supernatant was filtered by suction, the fluoride ion concentration in the filtrate was measured using an ion selective electrode. The same experiment was repeated for different initial concentrations of F⁻ ranging from 1.0 ppm to 50 ppm.

2.9 Kinetics measurements

A 50.00 g NB sample was mixed with 500.0 ml of 20 ppm standard F⁻ solution. Then the mixture was stirred. A 20.00 ml aliquot of the supernatant was withdrawn at 2 minutes intervals. The F⁻ concentration in each sample was measured using an ion selective electrode.

3. Results and Discussion

3.1 Chemical components of NB

Comparison of the d-values of XRD patterns of NB samples (Figure 1) with the standard database suggests that NB used in this investigation consist of clay minerals such as sodium-magnesium-aluminum silicate hydroxide hydrate $\{Na_x[Al,Mg]_2Si_4O_{10}(OH)_2 \cdot zH_2O\}$, calcium-aluminum-iron-silicate hydroxide $\{Ca_3AlFe(SiO_4)(OH)_8\}$, calcium-magnesium-iron-aluminum-silicate-hydroxide $\{Ca[Mg_{2.6}Al_{0.7}Fe_{0.12}][Si_{1.32}Al_{2.68}]O_{10}(OH)_2\}$, and $Al_2(Si_3Al)O_{10}(OH)_2/KAl_2(Si_3AlO_{10})(OH)_2$ (elite), in addition to normal constituents such as quartz (SiO₂) and topaz $[Al(F,OH)_2SiO_4]$. This observation is further supported by XRF and AAS studies, which conclude the presence of significant amounts of Al, Fe, Mg, and Na, and small amounts of Ca, Cr, Cu, K, Mn, Ti, and Zn in NB samples (Table 1).

3.2 Evaluation of surface properties

Surface titration of powdered NB samples conducted with HCl and NaOH at different ionic strengths indicates that the surface charge is highly pH-dependent (Figure 2). The surface charge density vs. pH curves intersect at a common point of pH 8.2, which is the point of zero charge (PZC). The surface charge density for each pH was

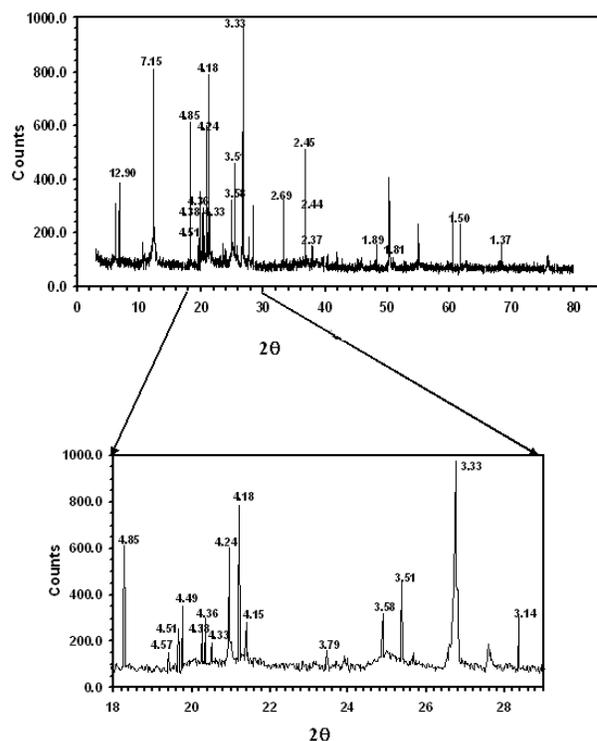


Figure 1: XRD patterns of NB recorded using Cu-K X-ray beam (1.54056 nm) (top), and enlarged view of the spectrum from 18° to 29° 2θ range (bottom). The d-values are indicated above each peak.

calculated using Equation (1) [18].

$$\sigma = \left(\frac{F}{a \times s} \right) \{ (C_a - C_b) - [H^+] + [OH^-] \} \quad (1)$$

where, F is the Faraday's constant (96490 C/mol), a is the solid content of the NB suspension (10 g/L), s is the specific surface area (estimated to be 4 m²/g according to geometric and mass considerations), Ca and Cb are the calculated concentrations of the acid and the base in the medium at a particular point of titration, respectively, and

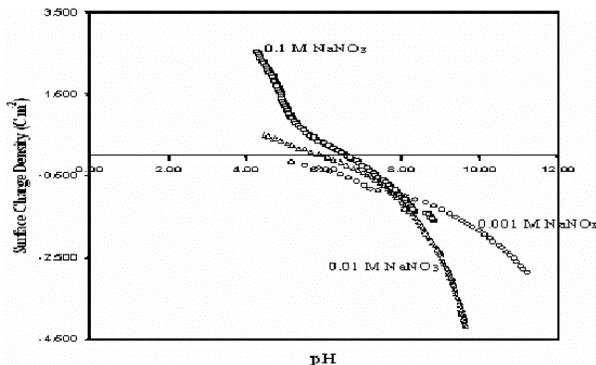


Figure 2: Surface charge density variation of NB with solution pH at different ionic strengths.

$[H^+]$ and $[OH^-]$ are the hydrogen and hydroxyl ion concentrations in the medium according to the measured pH value at a particular point of titration.

3.3 Interference studies and ionic strength effects

The F^- removal is not much influenced by the presence of other halides present in solution (Table 2). In parallel with this observation, the increase in concentration of noninteracting ions such as Na^+ and NO_3^- shows only a marginal effect on the percent removal of F^- by NB (Figure 3). Further, thorough mixing of F^- -adsorbed NB with deionized water does not leach F^- into the solution. All these observations suggest the irreversible adsorption of F^- on the NB surface. The slight variation of the extent of interference on F^- removal is probably due to the size factor of the halides.

Table 2: Effect of halides on F^- - NB interaction*

Interferent	Cl^-	Br^-	I^-
Percent removal	57.9	58.1	60.0

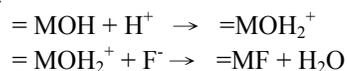
*20 ppm solution of F^- with each of Cl^- , Br^- and I^- of the same concentration, 10 minutes stirring, 2 hours equilibration

3.4 Proposed mechanism for F^- - NB interactions

As NB consists of many clay minerals, as stated above, F^- would show different affinity toward each mineral. Hence, the net effect of F^- removal by NB would be a complex composite effect of all types of interactions. The percent removal of F^- decreases with increase in pH (Figure 4) which indicates the involvement of H^+ during F^- - NB interaction. The removal of more than 60% F^- at neutral pH, which is equivalent to 12 mg/L reduction, is a significant finding.

Surfaces of many clay minerals contain exposed -OH groups in aqueous medium, either due to -OH groups already attached to metals such as Ca, Al, and Fe, or due to the interaction of siloxane groups (-SiOSi-) present in many clay minerals with water forming -SiOH terminals [19]. At low pHs, these surface hydroxide groups undergo

protonation forming $-OH_2^+$ terminals. Direct replacement of $-OH_2^+$ by F^- occurs on the surfaces of minerals that do not contain Al, such as quartz, as shown in the following scheme.



where $=MOH$ indicates -OH groups attached to surface metal atoms. Additionally, pH-independent removal of F^- may also occur as shown below.



The latter mechanism is feasible for -Si-OH surfaces due to the possibility of forming Si-Si bonds.

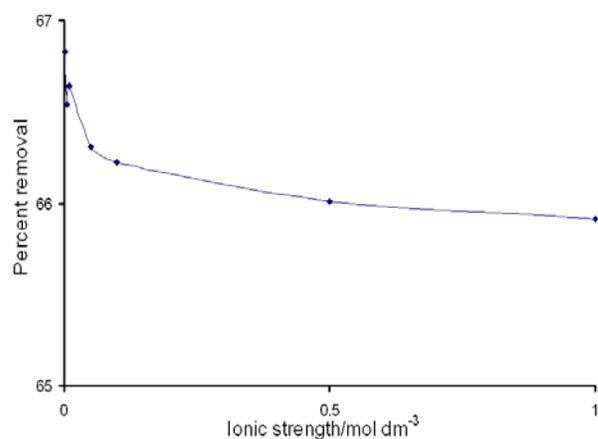


Figure 3: Effect of ionic strength on percent removal of F^- by NB [100.0 ml of 20 ppm F^- , $NaNO_3$ solutions of different concentrations, 10 minutes stirring, 2 hours equilibration].

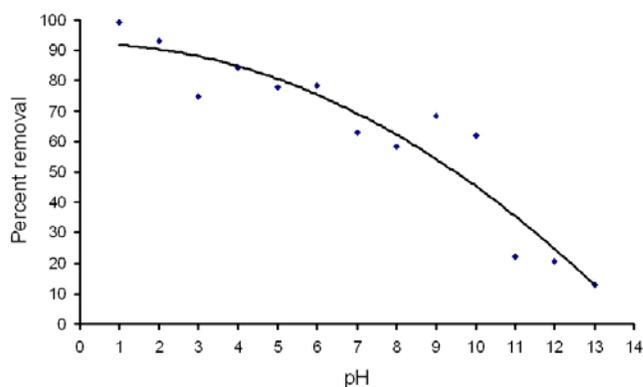


Figure 4: Effect of solution pH on percent removal of F^- [10.00 g NB, 100.0 ml of 20 ppm F^- , 10 minutes stirring, 2 hours equilibration].

The fluoride removal process is complicated when Al is present in the lattice, as F^- interacts with the lattice in one or more of the following ways.

1. Al is released into the solution from clay minerals with the concomitant entry of fluoride into the mineral structure [20].

2. Cryolite, Na_3AlF_6 , is formed after treatment of NB particles with F^- [21].

Thus, the removal of F^- by brick particles is not a simple replacement of $-OH_2^+$ by F^- . Structural changes would occur in the lattice during incorporation of F^- .

The marginal effect of ionic strength on the extent of F^- removal and independence of F^- removal by other halides provides supportive evidence to predict that an inner sphere complex is formed during F^- -NB interaction. Therefore, the overall process can be represented as surface adsorption followed by incorporation of F^- into the lattice. The latter step is more complicated than a normal ion-exchange process.

In a basic medium, as there would be no protonation, surface-OH groups would predominantly exist as $-O^-$ terminals attached to metal atoms present in the NB surface, and hence F^- would not show strong affinity toward the brick surface, showing very low removal values. Further, when no pH control is done, aqueous F^- -NB particle suspensions show a pH of 4.5 to 5.5, and consequently, F^- removal is less than that is observed at pH = 1. Higher F^- removal at acidic pHs is also supported by the fact that the NB surface bears a positive charge at low pHs (Figure 2). At neutral or basic pHs, NB surface would more strongly attract cations.

3.5 Adsorption isotherm studies

The variation of the amount of F^- adsorbed (Q), expressed in mg of F^- per g of NB, was investigated with the equilibrium concentration of F^- , C_e in solution. The plot of $1/Q$ vs. $1/C_e$ (Langmuir isotherm [22]) results in a straight line with a high regression coefficient of 0.9979, indicating monolayer coverage [Figure 5 (top)]. However, adsorbed species would incorporate into the lattice, as described earlier, and hence surface adsorption would continue even after the monolayer coverage was complete. For this reason, the Freundlich isotherm, the plot of $\ln Q$ and $\ln C_e$, would also be valid. This is clearly evident in Figure 5 (bottom) which also has a high regression coefficient of 0.9886.

3.6 Kinetics analysis

Kinetics of the F^- removal process is also an important aspect in addition to equilibrium aspects. Reaction kinetics control transfer of F^- towards the NB surface—an important fact if NB is used for the removal of F^- from water. Detailed kinetics analysis performed by curve fitting to integrated rate equation for different reaction orders clearly indicates that the 1st order fit is the best with a high regression coefficient of 0.9911 (Figure 6). The rate

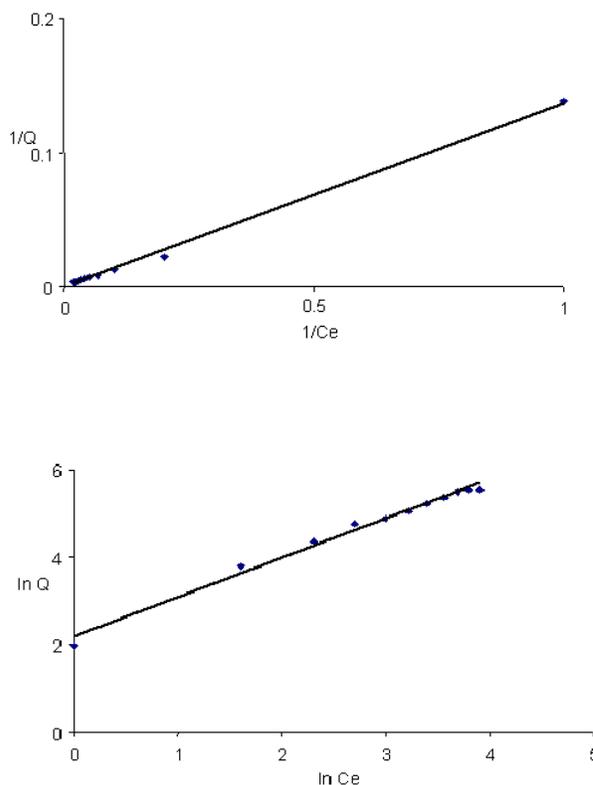


Figure 5: Adsorption isotherm models: Langmuir model (top) and Freundlich model (bottom).

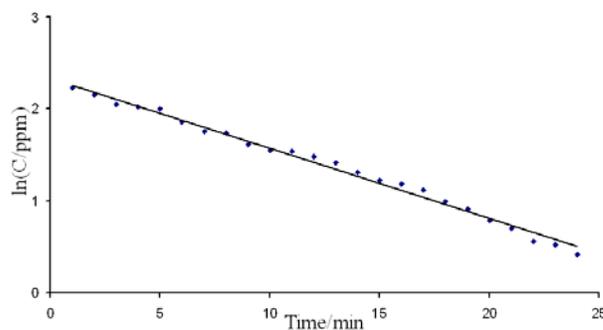


Figure 6: First order fit of the F^- removal process by NB, where C is the concentration of F^- in solution at different reaction times.

constant for F^- removal by NB is determined to be $7.66 \times 10^{-2}/s$. Such a relatively high rate constant compared to that of normal chemical reactions supports that NB can be used for efficient removal of F^- from aqueous medium.

4. Conclusions

NB consists of many clay minerals containing silicate and hydroxide groups in addition to normal constituents such as quartz and topaz. Surface titrations indicate that the point of zero charge of NB surfaces occurs at pH = 8.2. It is suggested that $-OH_2^+$ terminals formed in acidic medium, in minerals that do not contain Al, is replaced by F^- . Further, F^- is also incorporated to Si-OH surfaces promoting the formation of Si-Si bonds. Al containing constituents of NB tend to form AlF_6^{3-} in the matrix after incorporation of F^- . The extent of F^- removal, as measured by percent removal, does not significantly change upon the changes in ionic strength and interferences, supporting the formation of an inner-sphere complex during interaction of F^- with minerals present in NB. The pH – percent removal relationship investigated within a wide pH range from 1 to 13 gives further support in this regard. The validity of the Langmuir and Freundlich isotherm models with high regression coefficients indicates initial surface adsorption followed by lattice incorporation when F^- solutions are treated with NB. The F^- removal process by NB follows the first order kinetics with a rate constant of 7.66×10^{-2} /s.

5. Acknowledgement

The authors wish to acknowledge the National Science Foundation of Sri Lanka for partial financial support provided through Research Grant Number (RG/2004/E/04).

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