CHAPTER 1

An Introduction to Fluoride Removal from Water by Bone Char

Fluoride is one of the recognized essential elements for humans. It plays an important role in biological mineralization. Optimum fluoride intake will provide the protection against dental caries and also enhance the formation of healthy bones. Excessive intake leads to mottled enamel ranging from barely discernible to stained, pitted enamel and in the worst case, crippling skeletal fluorosis, depending on the intake amounts and the exposure time.

Fluoride is exposed to human beings through food, water, industrial and pharmaceutical products. The major contribution to daily fluoride intake is drinking water containing fluoride. The level of 1.0 mg/L is established as the most appropriate concentration at which effective caries reduction could be achieved while limiting dental fluorosis to an acceptable level. This value is further modified into a range of 0.7 – 1.2 mg/L depending on climatic conditions [1]. The higher the average temperature in a community, the lower the recommended level of fluoride in drinking water. For Thai populations the appropriate concentration of fluoride in drinking water is, however, set as 0.5 mg/L [2].

Chronic fluoride toxicity through excessive intake mainly through water supplies has been reported in many parts of Thailand. Fluoride content of more than 0.5 mg/L has been recorded from natural drinking water [3] and even bottled drinking water [4] because sources for water supplies, i.e. ground water, are contaminated by fluoride which was leached from fluoride bearing minerals. This creates problems of endemic dental fluorosis in Thailand especially in Lamphun [5] and Chiang Mai [6]. Fluoride removal from drinking water is therefore considerably important.

Many methods have been proposed for removing fluoride from water. The technology of defluoridation, for instance, reverse osmosis and electrodialysis, has been well developed. Experimental works and applications of these techniques require high initial cost as well as high costs in terms of operation and maintenance. In addition, they also require skill operators to make such techniques operationable. Developing countries are consequently trying to develop methods that could suit natural and human resources by utilizing local or available removal technology, i.e. lime and alum in co-precipitation technique and clay and bone char in sorption/ion exchange technique. In Thailand fluoride removal of domestic water by bone char has been favorable owing to its local availability, relative simplicity, cost effectiveness, and high removal efficiency, and successfully tested in the laboratory and household level [7, 8]. However, investigations of processes that take place during defluoridation by bone char are still lacking. For the present work, processes related to defluoridation by bone char will be studied using a flow injection technique for simultaneous monitoring of the ions involved in removal processes.

Research aims

To investigate the extent of fluoride ion in correlation with the hydroxide ion during defluoridation processes by bone char using a flow injection technique.

Research scope

In order to fulfill the objectives of the research, the experiments are concentrated on three main sections as followed :

1. Determination of fluoride by spectrophotometric flow injection method.
   Flow manifolds for fluoride determination will be designed and tested. Both chemical and flow injection variables such as concentration of fluoride reagents, flow rate, injection volume and reaction coil length will be investigated. Analytical characteristics, e.g. accuracy, precision and detection limit, will also be studied.
2. Hydroxide determination by flow injection analysis.
   Flow injection manifolds, optimum conditions and method validation for determination of hydroxide by flow injection analysis will be examined.
3. Ion exchange study of defluoridation in a flow system.
   Fluoride removal by bone char in a flow system will be carried out. During defluoridation processes both fluoride and hydroxide level in the effluent will be monitored simultaneously using the developed flow injection techniques.

1.1 Fluoride in the environment

Fluorine is one of the most naturally abundant elements. It comprises a number of rock-forming minerals. The chief deposit of fluorine is fluorite or fluorspar which is significant for industrial purpose. The other important fluorine-containing minerals are cryolite and fluorapatite, the latter commonly called rock phosphate. The major natural sources for the release of fluoride into the environment are weathering and dissolution of minerals, emission from volcanoes and liberation in marine aerosols. The utilization and production of phosphate ore as well as aluminium manufacture also contribute primarily to the release of fluoride from anthropogenic sources [9, 10].

Fluoride species are widely distributed and both naturally and anthropogenically exist in the atmosphere, water and sediment, soil, and biota. The cycling of fluoride through the biogeosphere is summarized in Figure 1.1. In the atmosphere, fluoride is in gaseous and particulate forms of which its mean concentration in ambient air is generally less than 0.1 $\mu g/m^3$. Fluoride concentration in surface water commonly ranges from 0.01 to 0.3 mg/L while that in sea water is between 1.2 and 1.5 mg/L. Fluoride in soil is mainly correlated with soil colloid or clay fraction with the total level ranging from 20 to 1000 μg/g [9]. Anthropogenic activities also raise up fluoride amount in the environment. Environment properties of fluorine are represented in Table 1.1.

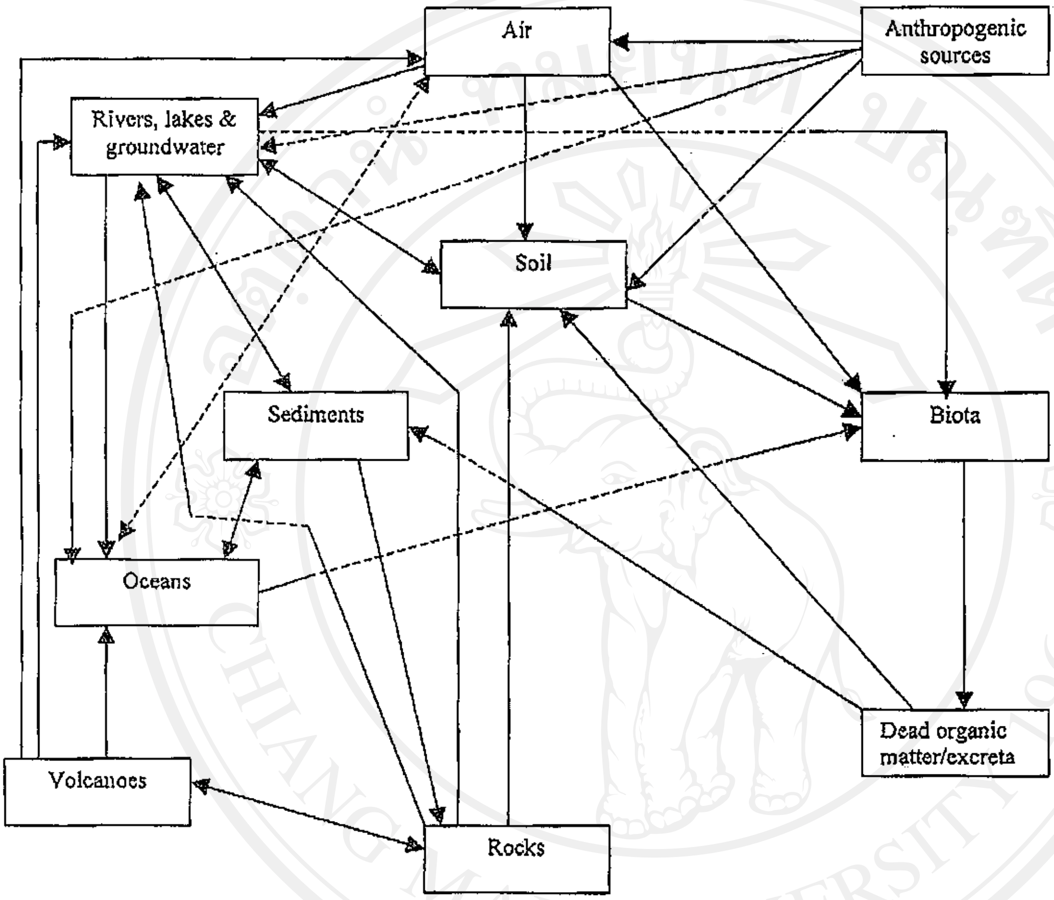


Figure 1.1 Cycling of fluoride through the biogeosphere [9].

Table 1.1 Environmental Properties of fluorine [11, 12].

Geological data	Abundance	Biological role
Chief deposit and sources	**Sun** (relative to H =	**Essential to mammals**
Fluorspar CaF_2	1×10^{12}) : 3.63×10^{-4}	including humans;
Fluorapatite $Ca_5(PO_4)_3F$	**Earth's crust**/ ppm : 950	some compounds very
Cryolite Na_3AlF_6	**Sea water**/ppm : 1.3	toxic, e.g. HF and F_2 gas
World production of	**Fresh water**/ppm : 0.1-1	**Levels in humans**
fluorspar/tonnes y^{-1} :	**Atmosphere**(CFCs)/ppm :	Muscle/ppm : 0.05
4.7×10^6	0.0006	Bone/ppm : 2000-12000
Reserves of fluorspar /	**Residence time**/years :	Blood/mg dm^{-3} : 0.5
tonnes : 123×10^6	400000	Daily dietary intake :
World production of	**Classification** :	0.3-0.5 mg
fluorine gas/tonnes y^{-1} :	accumulating	Toxic intake : 20 mg (F^-)
2400	**Oxidation state** : I	Lethal intake : 2 g (F^-)
		Total mass of element in
		average (70kg) person :
		2.6 g

1.2 Fluoride in natural waters

Fluoride in natural waters is classified as secondary constituents according to relative abundance of dissolved solids in potable water (Table 1.2). Its characteristics are tabulated in Table 1.3.

Table 1.2 Relative abundance of dissolved solids in potable water [13].

Major Constituents (1.0 to 1000 mg/L)	Secondary Constituents (0.01 to 10.0 mg/L)	Minor Constituents (0.0001 to 0.1 mg/L)	Trace Constituents (generally less than 0.001 mg/L)
Sodium	Iron	Antimony*	Beryllium
Calcium	Strontium	Aluminum	Bismuth
Magnesium	Potassium	Arsenic	Cerium*
Bicarbonate	Carbonate	Barium	Cesium
Sulfate	Nitrate	Bromide	Gallium
Chloride	Fluoride	Cadmium*	Gold
Silica	Boron	Chromium*	Indium
		Cobalt	Lanthanum
		Copper	Niobium*
		Germanium*	Platinum
		Iodide	Radium
		Lead	Ruthenium*
		Lithium	Scandium*
		Manganese	Silver
		Molybdenum	Thallium*
		Nickel	Thorium*
		Phosphate	Tin
		Rubidium*	Tungsten*
		Selenium	Ytterbium
		Titanium*	Yttrium*
		Uranium	Zirconium*
		Vanadium	
		Zinc	

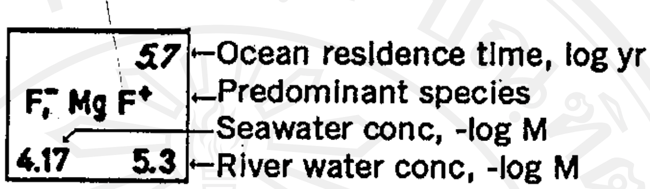
* These elements occupy an uncertain position in the list.

The dominant species of dissolved fluoride in natural water at neutral pH is the fluoride ion. As the pH decreases below 5.5, the proportion of protonated- fluoride species, i.e. HF and HF_2^-, increases. However, if there is adequate aluminium in water, aluminium-fluoride complexes, i.e. AlF^{2+}, AlF_2^+ and AlF_3, are normally predominant below pH 5.5. Fluoride also exists in ion pair species with magnesium and calcium in sea water in which MgF^+ is a principal ion pair form [9].

Variation of fluoride concentration in surface waters depends on geographical location and vicinity to discharge sources. Typical concentrations are displayed in Table 1.3. In the regions where minerals containing high fluoride content and geothermal or volcanic activities appear, higher fluoride levels have been observed. The inborn major source contributed to the amount of fluoride in water derives from the solvent action of water on fluoride-bearing minerals, namely fluorite, apatite, hornblende and micas [14]. Fluoride occurrence in ground water is concisely summarized elsewhere [15].

Usage of water supply containing fluoride has beneficial as well as prejudicial effects on human health. An appropriate fluoride concentration in drinking water has potential to reduce the prevalence of dental caries. Exposure to higher level, however, causes adverse effects on teeth and bone, for instance, dental fluorosis, skeletal fluorosis and bone fracture. Supply for drinking water must be regulated for fluoride by an authoritative organization.

Table 1.3 Characteristics of fluoride in natural water [13, 16, 17].

Major source	Amphiboles(hornblende), apatite, fluorite, mica
Major species in water	
Concentration in natural water	Concentrations generally do not exceed 10 mg/L in ground water or 1.0 mg/L in surface water. Concentrations may be as much as 1600 mg/L in brines.
Certain concentrations (mg/L)	River <0.6 mg/L Lake <0.3 Impoundment <1.0 mg/L Ground water <7.0 mg/L Sea water 1.3 mg/L
Effect upon usability of water	Fluoride concentration between 0.6 and 1.7 mg/L in drinking water has a beneficial effect on the structure and resistance to decay of children's teeth. Fluoride in excess of 1.5 mg/L in some areas causes mottled enamel in children's teeth. Fluoride in excess of 6.0 mg/L causes pronounced mottling and disfiguration of teeth.

1.3 Fluoride in drinking water

Fluoride is omnipresent in the environment; accordingly, sources for drinking water possibly contain some small quantity of fluoride. Standards for fluoride in drinking water have consequently been established and are shown in Table 1.4. World Health Organization (WHO) guideline for fluoride regulation concerning public health significance is established as 1.5 mg/L which can be necessarily adapted to locally climatic conditions. A recommended fluoride level of 0.5 – 1.0 mg/L is an appropriate range for all areas [1]. In Thailand 0.5 mg/L has been evaluated and accepted as an compromised concentration for protection against dental caries and limiting dental fluorosis [2].

Countries facing endemic dental fluorosis due to excess fluoride in drinking water have been reported throughout the world [18]. In Thailand the chronic problem is widely observed in Lumphun [5] and Chiang Mai [6] where natural drinking water [3] and even bottled drinking water [4] contain more than 0.5 mg/L of fluoride. Superfluous fluoride in water sources, i.e. ground water, is thus defluoridated to an acceptable level prior to utilization.

Table 1.4 Fluoride regulations in drinking water [19, 20].

Standards	Guideline*	Limit
U.S. Environmental Protection Agency	MCL, mg L^{-1}	4.0
	SMCL, mg L^{-1}	2.0
World Health Organization	Guideline, mg L^{-1}	1.5
Canadian Drinking Water	MAC, mg L^{-1}	1.5
European Economic Community	MAC, µg L^{-1}	1500@ 8-12 °C
		700@ 25-30 °C
UK Water Regulations	Max, mg L^{-1}	1.5

* MCL = Maximum contaminant levels

SMCL = Secondary maximum contaminant levels

MAC = Maximum acceptable concentration (Canadian)

MAC = Maximum admissible concentration (European)

Max = Maximum level

1.4 Water treatment processes for fluoride removal

Various water treatment processes, e.g. conventional coagulation, sorption/ion exchange and membrane methods, have been applied for the removal of fluoride from water and wastewater. Precipitation/coagulation including lime softening are usually unfavorable owing to their relative low efficiency and large amount of chemicals required. Not only offer anion exchange resins relative low capacity and high cost, they also have low selectivity of preference for fluoride; generally not preferable for fluoride removal. Among treatment processes which are tabulated in Table 1.5 depending on removal efficiency, adsorption on activated alumina and reverse osmosis, special methods for the removal of inorganic contaminants, are recognized as Best Available Technology (BAT) for fluoride. Electrodialysis, bone char and distillation are additionally listed as BAT treatments which are concluded in the literature [21].

Defluoridation methods for drinking water are comprehensively summarized [15, 22-25] and divided into three categories with unique properties : precipitation, adsorption/ion exchange and membrane technique (Table 1.6). The crucial bases of the potential methods especially in a household or community level are relative simplicity, high removal efficiency, cost effectiveness and based principally on available resources and skills. Alternative removal technologies suited locally natural and human resource have consequently been established for particular areas [26]. For instance, Nalgonda technique of the National Environmental Engineering Research Institute carried out in Nalgonda district in Andhra Pradesh, India, removes fluoride by floc of lime and alum. Prasanti technology using activated alumina for adsorption of excessive fluoride has been conducted by Satya Sai University for Higher Learning in Prasanti Nilayam in Anantpur district, Andhra Pradesh. Defluoridation of domestic water by bone char primarily available in Thailand due to above advantages has been developed by the Intercountry Centre for Oral Health (ICOH), Chulalongkorn University and WHO, and successfully tested in a laboratory and household level [7, 8].

Table 1.5 Removal efficiency of water treatment processes for fluoride [20].

Treatment		Effectiveness[a]
Conventional coagulation	Alum	P
	Iron	P
Lime softening		P
Ion exchange	Cation	P
	Anion	L
Adsorption	PAC[b]	P
	GAC[b] (bone char)	E
	Activated alumina	E
Membrane process	Reverse osmosis	E
	Electrodialysis	E

[a] E - excellent, 90-100% G - good, 70-90% F – fair, 40-70%

L – low, 20-40% P – poor, 0-20%

[b] PAC = powdered activated carbon, GAC = granular activated carbon

Table 1.6 Defluoridation methods for drinking water [15].

Removal method	Capacity/ dose	Working pH	Interferences	Advantages	Disadvantages	Relative Cost
Precipitation						
Alum (aluminium sulphate)	150 mg/ mg F	Non-specific	-	Established process	Sludge produced, treated water is acidic, residual Al present	Med-high
Lime	30mg/mg F	Non-specific	-	Established process	Sludge produced, treated water is alkaline	Med-high
Alum+lime ('Nalgonda')	150 mg alum+ 7mg lime/mg F	Non-specific, optimum 6.5	-	Low-tech, established process	Sludge produced, high chemical dose, residual Al present	Med-high
Gypsum + fluorite	5 mg gypsum + <2 mg fluorite/mg F	Non-specific	-	Simple	Requires trained operators Low efficiency, high residual Ca, so_4	Low-med
Adsorption/ion exchange						
Activated carbon	Variable	<3	Many	-	Large pH changes before and after treatment	High
Plant carbon	300 mg F/kg	7	-	Locally available	Requires soaking in potassium hydroxide	Low-med
Zeolites	100 mg F/kg	Non-specific	-		Poor capacity	High
Defluoron 2	360 g F/m^3	Non-specific	Alkalinity		Disposal of chemicals used in resin regeneration	Medium
Clay pots	80 mg F/kg	Non-specific	-	Locally available	Low capacity, slow	Low
Activated alumina	1200 g F/m^3	5.5	Alkalinity	Effective, well-established	Needs trained operators, chemicals not always available	Medium
Bone	900 g F/m^3	>7	Arsenic	Locally available	May give taste; degenerates Not universally accepted	Low
Bone char	1000 g F/m^3	>7	Arsenic	Locally available High capacity	Not universally accepted	Low
Other						
Electrodialysis	High	Non-specific	Turbidity	Can remove other ions. Used for high salinity	Skilled operators High cost. Not much used	Very high
Reverse osmosis	High	Non-specific	Turbidity	Can remove other ions. Used for high salinity	Skilled operators High cost	Very high

1.5 Defluoridation by bone char

Bone charcoal is ground animal bone charred to remove all organic substances and mainly consists of apatite or calcium phosphate compound, i.e. $Ca_{10}(PO_4)_6(OH)_2$. It contains calcium phosphate (57-80%), calcium carbonate (6-10%) and activated carbon (7-10%) [27]. It has a porous structure with a large surface area and a special affinity for fluoride. Typical properties of bone char are shown in Table 1.7.

Table 1.7 Chemical and physical properties of bone char [28].

Chemical composition		Physical properties	
Items	Limits	Items	Limits
Acid-Insoluble ash	3 wt% max	Bulk density (dry)	640 kg/m^3
Calcium carbonate	7–9 wt%	Carbon surface area	50 m^2/g
Calcium sulfate	0.1–0.2 wt%	Moisture	5 wt% max
Carbon content	9–11 wt%	Pore size distribution	7.5–60,000 nm
Hydroxyapatite	70–76 wt%	Pore volume	0.225 cm^3/g
Iron as Fe_2O_3	<0.3 wt%	Total surface area	100 m^2/g

Hydroxyapatite, the main constituent of bone char, is one of biological apatites which are rarely stoichiometric and usually calcium-deficient. It can incorporate a wide variety of impurities, for instance, hydroxide replacement by fluoride or chloride or a vacancy caused by the reversal of OH^- direction in apatite structure which are substantially discussed in the literatures [29-31]. The effects of ionic substitutions as well as chemical and physical characteristics of hydroxyapatite crystal are also mentioned [30, 31].

Defluoridation capacity of charred bone depends largely on the charring procedure. Investigations of the significance of duration and temperature of bone char processing and the admission of air oxygen during charring by Dahi [32] showed that when access of oxygen was restricted, i.e. pyrolysis process, fluoride removal capacity was at optimum, independent of charring time and temperature. While bones were exposed to atmospheric oxygen, i.e. calcination process, the defluoridation capacity was drastically reduced, for temperature above 500 °C, making a good agreement with the results of other investigators [33, 34]. The specific surface area was the highest for pyrolysed bone, and much lower for calcined bone. Pyrolysis provided the best bone char quality where the product was black all over and had the highest possible defluoridation capacity [32, 35]. Additional study by Larsen [36] on the efficiency of defluoridation by char produced from various parts of bones and charred for various lengths of time at various temperatures demonstrated that bone samples charred for shorter periods at lower temperature (400 °C for 4 hours) resulted in a better quality fluoride adsorbent, not depending on whether the char originated from compact or spongy bone.

Many researchers have studied on fluoride uptake behavior as well as removal efficiency by animal charred bone. Fluoride removal is found to be pH dependent, the decrease in the pH of raw water increases the removal efficiency. Because charred bone is soluble in acid, a pH of 7.0 or higher is selected to achieve a good removal efficiency while limiting losses of the media [37]. Bhargava [38] studied the effect of variables such as the contact time, size of the adsorbent, initial fluoride concentration, pH and dose of adsorbent on the fluoride adsorption by fish bone charcoal in a batch system. It was found that the amount of fluoride adsorbed per gram of adsorbent increased with the increase in initial fluoride concentration for a given particle size. Fluoride removal was also found to be a function of pH and time. The equilibrium fluoride concentration decreased with increasing adsorbent doses at any given initial solute concentration. Relevant relationships between variables have also been formulated. Furthermore, Fangsrekam [39] studied the adsorption behavior of fluoride on bone char and had fluoride removed from natural fluoridated water .It was reported in her study that fluoride adsorption was endothermic and followed Freundlich isotherm representing a multilayer type. The same type of adsorption isotherm was confirmed by Seepila [40].

Fluoride removal from aqueous solution by bone char and related materials, extensively reviewed by Bregnhøj [41], is a complicated process and not completely understood. Early investigators [25] proposed that a removal process was an ion exchange in which the carbonate radical of the apatite comprising bone, $Ca(PO_4)_6{\cdot}CaCO_3$, was replaced by fluoride to form insoluble fluorapatite.

$$Ca(PO_4)_6{\cdot}CaCO_3 + 2F^- \rightarrow Ca(PO_4)_6{\cdot}CaF_2 + CO_3^{2-} \qquad (1\text{-}1)$$

In the regeneration of exhausted media with sodium hydroxide, fluoride was removed in the form of sodium fluoride, and fluorapatite became hydroxyapatite whose hydroxyl radical was the exchange object in the removal reaction. Nevertheless, William [42] suggested that fluoride concentration was the most important factor in controlling the course of the reaction with hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, which is a major component of charred bone. Fluorapatite was formed in the reaction with fluoride in low concentration (up to 200 – 500 mg/L), but with higher concentration there was the possibility of the precipitation of calcium fluoride provided its solubility product was exceeded. These reactions can be written as

$$Ca_{10}(PO_4)_6(OH)_2 + 2F^- \rightarrow Ca_{10}(PO_4)_6F_2 + 2OH^- \qquad (1\text{-}2)$$

and

$$Ca_{10}(PO_4)_6(OH)_2 + 20F^- \rightarrow 10CaF_2 + 6PO_4^{3-} + 2OH^- \qquad (1\text{-}3)$$

Reaction (1-2) underwent at least two distinct pathways : direct ion exchange between F^- and OH^- of hydroxyapatite as shown in equation (1-2), and precipitation of fluorapatite using Ca^{2+} and PO_4^{3-} already exist in solution in equilibrium with the hydroxyapatite which would be dissolved to replace these ions. The latter can be regarded as dissolution/recrystallisation process whose products might also contain some OH^-.

Furthermore, White [43] demonstrated that the reaction products of fluoride with apatite, i.e. hydroxyapatite and powdered enamel, were the mixture of fluorapatite (FAP), fluorohydroxyapatite (FHAP) and calcium fluoride with increased amounts of CaF_2 promoted by increased fluoride concentration or decreased pH. Under all conditions FAP or FHAP was a reaction product of fluoride immobilization regardless of whether CaF_2 was formed. pH measurements indicated the release of hydroxide during fluoride uptake by apatites corresponding to ion exchange formation of FAP/FHAP or dissolution/reprecipitation formation of CaF_2. He also concluded that the reaction of fluoride at the apatite interface were significantly more complex than simple reactions of ion exchange, crystal growth of fluorapatite, and recrystallisation of calcium fluoride.

Other processes involving fluoride immobilization by bone char were proposed by Bregnhøj [41]. An adsorption of fluoride accompanying with calcium adsorption or phosphate desorption was the initial step followed by recrystallization. Hydroxide release was not directly proportional to fluoride uptake as expected in stoichiometric ion exchange (equation 1-2).

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