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The usage of calcium phosphate systems for onsite defluoridation treatment

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ABSTRACT

Over 200 million people in over 35 countries are affected by excessive fluoride in their waters. For people that do not have access to a centralized water treatment plant, there is a need for an on-site defluoridation system that requires no special operational expertise, does not use hazardous chemicals, and is sustainable by the local population. 8 different calcium phosphate precipitation systems were analyzed and tested for fluoride removal effectiveness. An effective system would have final fluoride concentrations less than 1.5 mg/L and final solutions with pH within drinkable limits. Phosphoric acid with the addition of a calcium carbonate source was found to have a 99.8% fluoride removal rate. Monosodium phosphate with addition of slaked lime was also found to be effective with a 99.98% fluoride removal rate. An optimal slaked lime to monosodium phosphate ratio that achieved effective fluoride removal and neutral pH was found. With 0.45 g of $Ca(OH)_2$ and 1 g of NaH_2PO_4, initial fluoride concentrations up to 100 mg/L or more could be reduced to near zero concentrations, and a volume of approximately 337 mL of water with a concentration of 5 mg/L F^- could to be reduced to less than 1.5 mg/L F^-.

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Introduction

Approximately thirty nine percent of the world's population (5.3 billion people) do not have access to a safe drinking water source.[1] Approximately one fifth of the population in developing countries live under acute water shortage and the water that is available can be contaminated with fecal matter and other physical, biological, radiological, and chemical contaminants.[2–4] One specific contaminant of concern is excessive fluoride. Water with concentrations of 1.5 mg/L F^- or lower is beneficial by strengthening bones and teeth. According to WHO, water with a concentration of 1.5 mg/L F^- or less is considered safe for consumption.[5] Above this concentration, there are many detrimental effects, ranging from "mottled teeth" and tooth decay in the 1.5 mg/L F^- – 4 mg/L F^- to stooped backs and crooked hands and feet in the 4 mg/L F^- – 10 mg/L F^- range.[6] These effects occur because the electronegative fluoride ions are attracted to the positively charged calcium ions in bone and teeth and also displaces the hydroxide anions "within the apatite network" that makeup our bones and teeth.[7–8] Fluoride can also lead to non-skeletal fluorosis, such as harmful effects to erythrocytes, ligaments, spermatozoa, thyroid glands and destruction of filaments in the muscle tissues leading to muscle weakness.[9] The gastrointestinal system is also adversely affected by high fluoride ingestion causing gastric irritation such as nausea, vomiting and gastric pain.[10] Excessive fluoride in water negatively affects a person's basic ability to function and has negative neurological affects, causing serious economic and social consequences to the government and the people.[11] People are forced to retire early from working and depend on others, and children are unable to do basic daily tasks.[12]

Fluorosis has become a global concern by affecting over 200 million people in more than 35 countries, such as China, India, Sri Lanka, Pakistan, and the Rift Valley countries in Africa. 80 million of the people are from East Africa.[13–18] Large geographical belts are affected with excessive fluoride in water when there is volcanic activity or there are mountains with sediments of marine origins. Another large source of fluoride contamination occurs when fluoride-containing minerals and rocks come into contact with groundwater.[19–20]

Some processes that can treat excessive fluoride in water are coagulation, adsorption, electrochemical methods, and membrane processes. Adsorption and precipitation are the processes most commonly used in developing countries since electrochemical methods and membrane processes are expensive and usually require technology imported from out of the country. Some common adsorbents used are activated alumina, clay, limestone powder, and "bone charcoal." Some common precipitation chemicals include lime, calcium, magnesium salts, and alum.[15].

In our previous paper, we explored using calcium carbonate to adsorb fluoride from water. Calcium carbonate is an adsorbent of interest because it is naturally abundant and inexpensive and could decrease fluoride concentrations from 7 mg/L to drinkable levels (less than 1.5 mg/L F^-). However,

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the disadvantage was the large amount of calcium carbonate needed to bring fluoridated water down to permissible levels.[21] Therefore, further studies were performed to explore the possibility of defluoridating water using less material by adding a phosphate containing material to a calcium salt.

There have been several studies on defluoridating water using different calcium containing materials ("bone char", slack lime, $CaCl_2$, $Ca(NO_3)_2$, $CaSO_4$, cement paste).[22–23] Reardon and Wang[24] reduced fluoride concentrations from 10-25 mg/L down to below 2 mg/L by adding CO_2 in the water before treating it through two limestone columns in series. Influent pH was 4.97 which helped with dissolution of $CaCO_3$. Calcium phosphate systems have also been studied. He and Cao[25] studied different calcium phosphate systems (brushite, monocalcium phosphate, tricalcium phosphate, hydroxyapatite, calcium chloride, calcium hydroxide, calcium carbonate, bone char, potassium dihydrogen phosphate, calcium lactate, fluorhydroxyapatite), and found that if using only one material, tricalcium phosphate (87%), would have the best removal rate followed by hydroxyapatite (68%), followed by bone char (66.4%). The best combination of the materials would be bone char and monocalcium phosphate, which could defluoridate 100 mL of water from 10.4 mg/L F^- to 0.6 mg/L F^- with 300 mg of bone char and 23 mg of monocalcium phosphate. Adler and Klein[26] treated potable fluoridated water using tricalcium phosphate and determined that 1 kg of tricalcium phosphate could remove 6.05 grams of fluoride, and regeneration was possible by washing the adsorbents with sodium hydroxide followed by hydrochloric acid. Turner et al.[27] used potassium phosphate with calcite to defluoridate water. Adding 17 mg/L of potassium phosphate decreased fluoride concentrations by 20%. Adding 500 mg/L of potassium phosphate removed almost all the fluoride present. The calcite precipitated with phosphate to form fluorite, fluorapatite and hydroxyapatite. Gogoi et al.[28] studied defluoridation using limestone and phosphoric acid. By adding phosphoric acid, the adsorption capacity increased from 0.39 mg/g (limestone alone) to 1.10 mg/g. The mechanisms proposed were precipitation of fluorite and calcium phosphate hydroxide, and adsorption of fluoride with hydroxyapatite forming fluorapatite.

The goal of this paper is to find a calcium and phosphate system that could be used in an onsite defluoridation system for households that do not have access to water from a centralized water treatment plant. This system should have effective fluoride removal rates with a final concentration of fluoride less than 1.5 mg/L, be made from materials that are accessible and should avoid hazardous materials that would be dangerous for the local people. The system should also have a final pH within drinkable limits. Calcium phosphate systems for defluoridation is an important direction of research because it has the potential to be used as an effective, practical, and sustainable defluoridation system. Calcium phosphate systems have been shown to effectively remove fluoride from literature papers. Additionally, the solubility product of hydroxyapatite $Ca_5(PO_4)_3(OH)$ (2.91×10^{-58} at 25 °C) and fluorapatite $Ca_5(PO_4)_3F$ ($8.6 * 10^{-61}$ at 25° C) are so low compared to the solubility product of fluorite (CaF_2, $3.4 * 10^{-11}$ at 25° C), making the precipitants extremely insoluble and easy to precipitate without using much material.[29–31] 8 different calcium phosphate precipitation systems were analyzed using $CaCl_2$, $Ca(OH)_2$, $CaCO_3$ sources, and KH_2PO_4, NaH_2PO_4, and H_3PO_4 and tested for final fluoride concentrations and pH. Optimization experiments and cost analysis calculations were also performed for the most effective system.

Materials and methods

Materials

Fluoride solutions were obtained by diluting a 1,000 mg/L fluoride ACS reagent grade standard solution from Ricca Chemical Company, USA. Powdered ACS reagent grade calcium carbonate was purchased from Thermo Fisher, USA, Sigma Aldrich, USA and MP Biomedical, USA. Phosphoric acid (85% w/v H_3PO_4), HCl (0.1 M), and ACS reagent grade K_2HPO_4 were obtained from Thermo Scientific, USA. Samples were measured in 50 mL plastic Falcon tubes that were also obtained from Thermo Fisher Scientific, USA. Erlenmeyer flasks were used for samples greater than 50 mL. Eggshells and seashells were obtained from local stores, air dried and then ground to a powder using a blender. The approximate particle size of the calcium carbonates were 100 µm and obtained from material data sheets from the laboratories. DI water was used for all the experiments.

Instrumental analysis

A Burrell Scientific wrist action shaker model 75 was used to shake the samples for 1 hour. Fisher Scientific Thermix Magnetic Stirrer Model 120 MR was used to stir volumes of water greater than 50 mL. A Thermo Scientific Orion 3 Star pH portable meter was used to measure pH after 1 hour of shaking. TISAB II from Thermo Scientific was used to maintain high, constant ionic strength, adjust the pH, and complex interfering species. A Barnstead Thermolyne Labquake Shaker Rotisserie PAT.NO. 3,625,485 was used to shake the samples for approximately 15 minutes with TISAB II afterwards. Fluoride concentrations were determined using a Thermo Scientific Orion 420 A + basic pH/mV/ORP Meter and a Thermo Scientific Orion 9609 BNWP Ion Plus Sure-Flow Fluoride ion selective electrode. The electrode can detect down to fluoride levels of 0.02 mg/L F^- and the direct calibration method was used to obtain fluoride concentrations.[32]

Methods for calcium phosphate systems

Methods for calcium phosphate system 1: $CaCO_3$ with the addition of phosphoric acid

Two sets of experiments with $CaCO_3$ with the addition of phosphoric acid were performed. One set of sample tubes were all filled with 4 grams of $CaCO_3$ and the other set of Falcon tubes were all filled with 0.02 grams of $CaCO_3$.

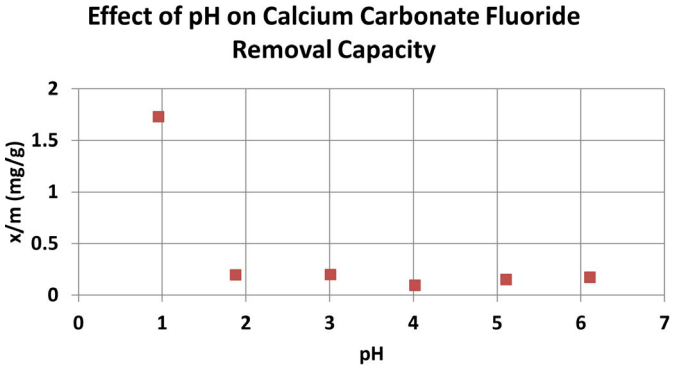

Figure 1. Effect of pH on fluoride adsorption capacity. Phosphoric Acid is added to the solution to lower pH. Adding phosphoric acid to the solution for a low pH (less than approximately 1.5), improves fluoride removal capacity for calcium carbonate significantly.

Increasing amounts of H_3PO_4 were then added to the Falcon tubes to lower pH. Tubes were shaken for one hour and pH of each sample tube was recorded. Final fluoride concentration was then recorded after the addition of TISAB. pH was plotted against adsorption capacity of fluoride (x/m) to determine if adding H_3PO_4 would improve defluoridation removal rates. Optimal pH to achieve optimal fluoride adsorption capacity was determined from the graph. Figure 1 shows the results for the set of Falcon tubes filled with 0.02 grams of $CaCO_3$.x/m (mg/g) values were calculated using the equation below:

$$x/m = (C_0 - C_t)V/m \quad (1)$$

where C_0 (mg/L) is the initial fluoride concentration, C_t (mg/L) is the concentration of fluoride at time t, V is volume of the solution (L), m is the mass of media used (g) and x is the mass of fluoride removed (mg).

Additionally, isotherms for different brands of $CaCO_3$ (MP Biomedicals, Sigma Aldrich and Thermo Fisher) were compared with an isotherm of Thermo Fisher $CaCO_3$ plus H_3PO_4. Varying amounts of the $CaCO_3$ ($0.02 - 6$ grams) and 20 mL of various fluoride concentrations (5-10 mg/L) were added into Falcon tubes. For the Thermo Fisher $CaCO_3$ plus H_3PO_4 samples, 0.78 mL of phosphoric acid (85% w/v) was added to the samples to make the initial pH approximately 1. Fluoride concentrations were measured and adsorption capacity (x/m) of the different calcium carbonates and the calcium carbonate plus phosphoric acid system were calculated. x/m values were plotted against corresponding final concentrations of fluoride to see how much adding phosphoric acid to $CaCO_3$ improved fluoride adsorption capacity (Figure 2).

Experiments were performed to determine if adding phosphoric acid to all sources of $CaCO_3$, such as eggshells and seashells, would significantly increase fluoride adsorption capacity. Three sets of experiments were performed: one with $CaCO_3$, one with eggshells and one with seashells. Increasing amounts of $CaCO_3$, eggshells, and seashells (0-6 grams) were added into Falcon tubes as well as 20 mL of 5 mg/L F^-. 0.78 mL of phosphoric acid (85% w/v) was also added to bring the solutions to an initial pH of approximately 1. Final fluoride concentrations were measured and

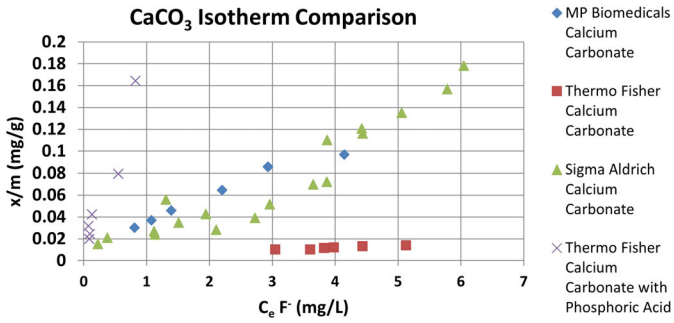

Figure 2. Calcium carbonate isotherm comparison for different brands of calcium carbonate. When adding phosphoric acid to the brand with lowest adsorption capabilities, the fluoride removal is greatly increased.

grams of eggshells, seashells and $CaCO_3$ were plotted against corresponding final concentrations of F^- (Figure 3).

Methods for Calcium Phosphate System 2-8: $CaCl_2$, $Ca(OH)_2$, limestone rock ($CaCO_3$), and KH_2PO_4, NaH_2PO_4, and H_3PO_4

Different calcium phosphate systems were compared and different calcium and phosphate containing materials were combined together: $CaCl_2$, $Ca(OH)_2$, limestone rock ($CaCO_3$), and KH_2PO_4, NaH_2PO_4, and H_3PO_4. Calcium phosphate combinations were put in Falcon tubes with 20 mL of 5 mg/L of F^- and shook for one hour. Final fluoride concentrations and final pHs were determined.

For calcium phosphate system 2 ($Ca(OH)_2$ and H_3PO_4), an increasing amount of $Ca(OH)_2$ ($0.4 - 5$ grams) and 0.78 mL of H_3PO_4 (85% w/v) were added into Falcon tubes. For calcium phosphate system 3 ($CaCl_2$ and H_3PO_4), an increasing amount of $CaCl_2$ (0.6-5.2 grams) and 0.78 mL of phosphoric acid (85% w/v) were added into Falcon tubes. For calcium phosphate system 4 (limestone and H_3PO_4), approximately 13 grams of limestone rock and increasing amounts of 85% w/v of H_3PO_4 (0.6 mL – 1.17 mL) were added into Falcon tubes. For calcium phosphate system 5 ($Ca(OH)_2$ and NaH_2PO_4), 2 grams of $Ca(OH)_2$ were added into Falcon tubes with increasing amounts of NaH_2PO_4 (0.46 g – 3 g). For calcium phosphate system 6 ($CaCl_2$ and NaH_2PO_4), 2 grams of $CaCl_2$ were added into Falcon tubes with increasing amounts of NaH_2PO_4 (0.55 g-3.3 g). For calcium phosphate system 7 (KH_2PO_4 with $CaCO_3$), increasing amounts of K_2HPO_4 ($0.1 - 3.3$ grams) were added into Falcon tubes with 2 grams of $CaCO_3$. Final fluoride concentrations were plotted against grams of K_2HPO_4 to analyze the effect of increasing dosage of K_2HPO_4 (Figure 4).

For calcium phosphate system 8 (KH_2PO_4 and $CaCO_3$ and HCl), there were two sets of experiments: one with samples of pH 1.88 and the other set of samples with pH 1.02. pH of the solution was lowered with the addition of 0.1 M HCl. To each set of samples, increasing amounts of K_2HPO_4 (0-0.55 grams) were added with the addition of 2 grams of $CaCO_3$. Final fluoride concentration was plotted against grams of K_2HPO_4 (Figure 5) to analyze the effect of increasing dosage of K_2HPO_4 (Figure 5).

Calcium phosphate system 5 ($Ca(OH)_2$ and NaH_2PO_4) was determined to be most effective in defluoridating water. Two set of experiments were performed to determine optimum dosage of each salt that would give effective

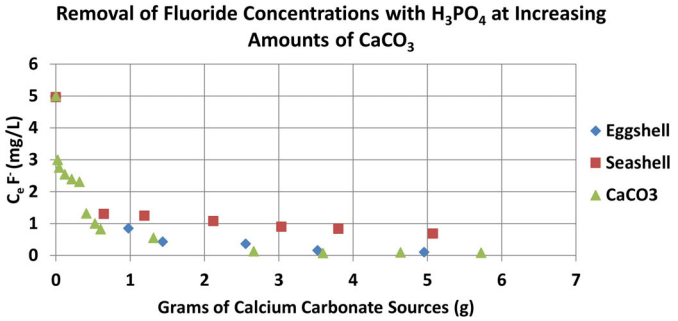

Figure 3. Fluoride removal with H_3PO_4 and increasing amounts of calcium carbonate, eggshells and seashells. Fluoride concentrations went down to drinkable limits for all three, showing that any source of calcium carbonate with the presence of phosphoric acid will remove fluoride significantly.

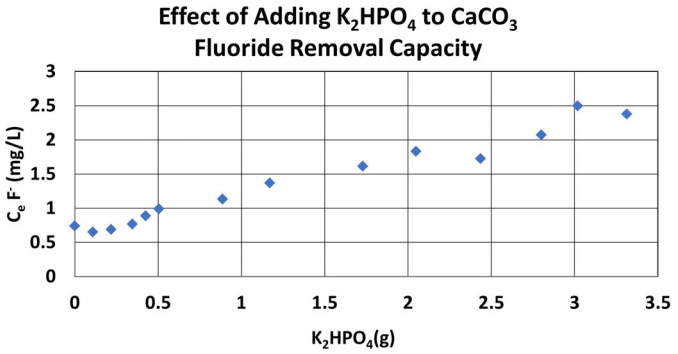

Figure 4. Effect of adding increasing amounts of K_2HPO_4 and 2 grams of calcium carbonate in fluoridated water. Amount of K_2HPO_4 (g) is plotted against equilibrium fluoride concentration (mg/L). As the amount of K_2HPO_4 increases, final equilibrium fluoride concentration increases. The presence of K_2HPO_4 does not help treat fluoride.

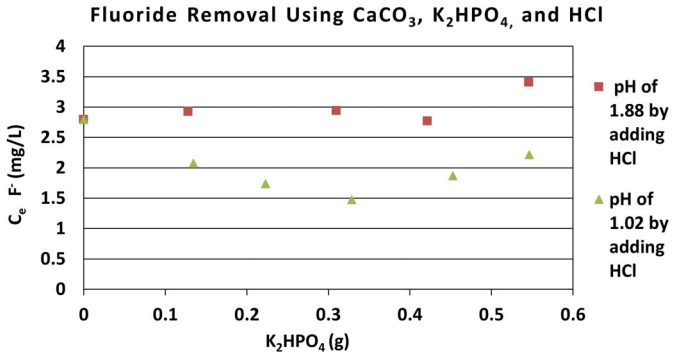

Figure 5. Final equilibrium fluoride concentration is plotted against grams of K_2HPO_4. $CaCO_3$, K_2HPO_4 and HCl were added in solution. Acidifying the solution with HCl is not effective in helping to decrease concentration of fluoride in solution.

defluoridation rates and appropriate pH of the water solution. 1 gram of monosodium phosphate was added into the first set of samples and 2 grams of monosodium phosphate were added into the second set of samples. Increasing amounts of slaked lime (0.46 g − 3 g) were added into each set of samples as well as 20 mL of 5 mg/L F^-. Final concentration of fluoride was measured after 1 hour of shaking and grams of slaked lime was plotted against final concentration of fluoride (Figure 6).

Experiments were performed to determine maximum amount of water 0.45 grams of slaked lime and 1 gram of NaH_2PO_4 could treat. Different volumes of 5 mg/L of

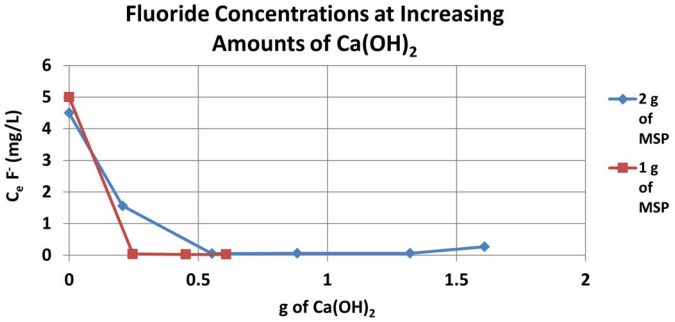

Figure 6. Concentration of fluoride at increasing amounts of $Ca(OH)_2$ with monosodium phosphate after 1 hr of shaking, showing near zero fluoride concentrations.

fluoride (100- 1,000 mL) were added into Erlenmeyer flasks as well as 0.45 grams of $Ca(OH)_2$ and 1 gram of NaH_2PO_4. A magnetic stirrer was used to stir the solution for one hour and final fluoride concentration was measured. Volume of water (mL) was plotted against fluoride removal ratio C/C_0 (Final fluoride concentration/Initial fluoride Concentration) and the volume where final fluoride concentration was 1.5 mg/L F^- was determined.

For calcium phosphate system 5, maximum initial fluoride concentration that could be treated was also determined. 20 mL of varying amounts of fluoride concentrations (10-100 mg/L) were put into Falcon tubes. 0.45 grams of $Ca(OH)_2$ and 1 gram of NaH_2PO_4 were added into the samples and shaken for an hour using a wrist shaker. Final fluoride concentration was determined and percentage removal was calculated by Eqn. 2. The maximum initial fluoride concentration 0.45 grams of $Ca(OH)_2$ and 1 gram of NaH_2PO_4 could treat down to less than 1.5 mg/L F^- was determined.

$$\text{Percentage fluoride removal} = \frac{C_o\ \left(\frac{mg}{L}\right) - C_e\ \left(\frac{mg}{L}\right)}{C_o\ \left(\frac{mg}{L}\right)} \quad (2)$$

Where $C_0 = \textit{initial fluoride concentration in } \left(\frac{mg}{L}\right)$

$C_e = \textit{final equilibrium fluroide concentration in } \left(\frac{mg}{L}\right)$

Results and discussion

Calcium phosphate system 1: $CaCO_3$ with the addition of phosphoric acid

Fluoride adsorption capacity increased dramatically as increasing amounts of phosphoric acid were added to $CaCO_3$, especially at initial pH ~ 1. At initial pH of 1.88, adsorption capacity was 0.12 mg/g. At initial pH of 0.96, adsorption capacity was 1.65 mg/g, a 13.75 times increase (Figure 1). After 1 hour of shaking, pH of the sample increased to ~ 6.5, which is within drinkable limits.[33] Gogoi et al.[28] used an initial pH of 1.6 in his experiments and found effective fluoride removal. Fluoride adsorption capacity would have increased even more if initial pH of approximately 1 was used.

In Figure 2, isotherms of different brands of $CaCO_3$ are shown. Thermo Fisher $CaCO_3$ had the worst adsorption

capacity values. Adsorption capacity values were below 0.02 mg/g for all equilibrium fluoride concentrations. However, when adding phosphoric acid to the Thermo Fisher $CaCO_3$, adsorption capacity values increased dramatically. At an equilibrium fluoride concentration of 0.8 mg/L, adsorption capacity was ~0.03 mg/g for the better performing calcium carbonates (MP Biomedical and Sigma Aldrich). For the phosphoric acid and Thermo Fisher calcium carbonate system, adsorption capacity was ~ 0.16 mg/g, a 5.3 times increase.

There was effective fluoride removal when adding phosphoric acid to other forms of $CaCO_3$ as well (seashells and eggshells). This is significant because in a previous paper[21], it was determined that using sources of $CaCO_3$ solely, especially eggshells and seashells, removed fluoride effectively only with high amounts of $CaCO_3$. Seashells were not able to defluoridate water below 1.5 mg/L F^-. Using granular $CaCO_3$ and H_3PO_4 reduced fluoride concentrations from 5 mg/L to 0.01 mg/L; using eggshells and H_3PO_4 reduced fluoride concentrations to 0.02 mg/L; using seashells and H_3PO_4 reduced fluoride concentrations to as low as 0.7 mg/L (Figure 3).

Gogoi and Dutta[34] explained the mechanism of the phosphoric acid and limestone system ($CaCO_3$) according to the following proposed mechanisms:

$$CaCO_3(s) + 2H_3PO_4 \rightarrow Ca^{2+} + 2H_2PO_4^- + CO_2^- + H_2O \quad (3)$$

$$CaCO_3(s) + 2H_2PO_4^- \rightarrow Ca^{2+} + 2HPO_4^{2-} + CO_2^- + H_2O \quad (4)$$

$$Ca^{2+} + F^- \rightarrow CaF_2(s) \quad (5)$$

$$5Ca^{2+} + 3HPO_4^{2-} + 4OH^- \rightarrow Ca_5(PO_4)_3OH(s) + 3H_2O \quad (6)$$

$$Ca_5(PO_4)_3OH(s) + F^- \rightarrow Ca_5(PO_4)_3F(s) + OH \quad (7)$$

Dissolution of $CaCO_3$ is increased by adding phosphoric acid, increasing the amount of Ca^{2+} (Eqn. 3; Eqn. 4). Saturation of the solution occurs, and CaF_2 and $Ca_5(PO_4)_3OH$ hydroxyapatite (HAP) precipitants form (Eqn. 5; Eqn. 6). Fluoride also adsorbs to HAP and displaces OH^- to form $Ca_5(PO_4)_3F(s)$ fluorapatite (FAP) (Eqn. 6). The sorption is an ion exchange physical adsorption and is a significant mechanism of fluoride removal in the phosphoric acid, calcium carbonate system.[35]

Calcium phosphates systems 2-8: $CaCl_2$, $Ca(OH)_2$, limestone rock ($CaCO_3$), and KH_2PO_4, NaH_2PO_4, and H_3PO_4

For calcium phosphate system 2 ($Ca(OH)_2$ and H_3PO_4), fluoride concentrations could be reduced from 5 mg/L to 0.1 mg/L. However, as amount of slaked lime increases greater than 3 grams, fluoride removal decreases rapidly because of the rapid increase of pH (~ 12.6). There is less dissociation of slaked lime, leading to less Ca^{2+} dissolution in solution and less HAP, CaF_2, and FAP precipitant formation. For calcium phosphate system 3 ($CaCl_2$ and H_3PO_4 system), fluoride concentrations decreased from 5 mg/L to 0.15 mg/L, but the resulting pH was too low and not suitable for human consumption (~0). The pH decreased very rapidly probably due to the formation of HCl. For calcium phosphate system 4 (limestone and H_3PO_4), fluoride removal capacity increased as phosphoric acid amounts increased. Fluoride concentrations decreased from 5 mg/L to 0.3 mg/L. For calcium phosphate system 6 ($CaCl_2$ and NaH_2PO_4 system), with increasing amounts of NaH_2PO_4, fluoride concentrations decreased from 5 mg/L to 0.02 mg/L and then increased to 0.1 mg/L. The increase of fluoride concentration is probably due to the formation of calcium hydrogen phosphate $CaHPO_4$ (solubility product 1.25 $*10^{-7}$ at 25 °C) or calcium phosphate (2 $*10^{-29}$ at 25 °C) , which would mean less fluorapatite and calcium fluoride precipitate formation[31,34]. Even though fluoride concentrations were well below drinking water limits (1.5 mg/L F^-), this system would not be practical because pH is very low ~2 due to the formation of HCl.

For calcium phosphate system 7 (KH_2PO_4 and $CaCO_3$), as amount of KH_2PO_4 increased, final fluoride concentration decreased from 5 mg/L to 0.8 mg/L and then increased to 2.5 mg/L. Adding increasing amounts of KH_2PO_4 did not help to defluoridate water and did not improve removal because the pH was too high (10.3 – 10.4). There was not enough dissolution of $CaCO_3$ into solution and concentration of Ca^{2+} to make $Ca_5(PO_4)_3OH(s)$ and CaF_2 precipitants (Figure 4). For calcium phosphate system 8 (KH_2PO_4 with $CaCO_3$ and HCl), HCl was added to decrease pH and cause more dissociation of $CaCO_3$. Fluoride removal did not improve probably because the counter effect of adding KH_2PO_4 increased pH too much. 0.13 grams of KH_2PO_4 increased pH from 1.02 to pH of ~6 rapidly. With increasing amounts of KH_2PO_4, final fluoride concentration decreased from 2.8 mg/L to 1.5 mg/L and then started to increase again (Figure 5).

Best results were found from calcium phosphate system 5 ($Ca(OH)_2$ and NaH_2PO_4). As amount of NaH_2PO_4 increased, final fluoride concentrations decreased. Increasing the amount of $Ca(OH)_2$ didn't help with decreasing final fluoride concentrations and at a certain point even hindered fluoride removal (Figure 6). In order to obtain a solution with neutral pH of~ 7, the amount of $Ca(OH)_2$/amount of NaH_2PO_4 should equal to approximately 0.45.

With 0.45 g of $Ca(OH)_2$ and 1 g of NaH_2PO_4, fluoride concentrations decreased from 5 mg/L F^- to as low as 0.003 mg/L F^-. Slaked lime easily dissociates in water which leads to Ca^{2+} dissolution and quick formation of $Ca_5(PO_4)_3OH(s)$ (HAP) precipitates. Not much material is needed to form HAP, since the solubility product of HAP is so low (~2.91* 10^{-58} at 25 °C).[29–31] Additionally, adding NaH_2PO_4 will maintain pHs lower than, for example, K_2HPO_4 because H_2PO_4 exists dominantly in the 2.12- 7.21 range, ensuring more dissociation of slaked lime and more Ca^{2+} ions in solution.[32] A significant advantage of this system is that it uses no hazardous materials, such as concentrated acids.

Table 1. Percentage of Fluoride Removed at Increasing Initial Fluoride Concentrations with 0.45 g $Ca(OH)_2$ and 1 g of monosodium phosphate.

C_0 F^- (mg/L)	C_e F^- (mg/L)	% of Fluoride Removed
10	0.036	99.64
20	0.021	99.90
40	0.017	99.96
60	0.017	99.97
100	0.017	99.98

With 0.45 g of $Ca(OH)_2$ and 1 g of NaH_2PO_4, initial fluoride concentrations up to 100 mg/L or more could be reduced to near zero concentrations (~0.02 mg/L F^-) (Table 1). He and Cao's best calcium phosphate system could defluoridate 100 mL of water from 10.4 mg/l F^- to 0.6 mg/l F^- with 300 mg of bone char and 23 mg of monocalcium phosphate.[25] Calcium phosphate system 5 performed better than He and Cao's system in that it has shown to decrease fluoride concentrations from significantly higher concentrations to significantly lower concentrations. With 0.45 g of $Ca(OH)_2$ and 1 g of NaH_2PO_4, a volume of approximately 337 mL of water with an initial concentration of 5 mg/L F^- could be treated down to less than 1.5 mg/L F^-(Figure 7). For a single person to drink 2 liters of defluoridated water a day, it would take 5.93 grams of monosodium phosphate and 2.67 grams of slaked lime. For a family of four to drink 8 liters of defluoridated water a day, it would take 23.72 grams of monosodium phosphate and 10.68 grams of slaked lime.

It is not possible to generally predict costs because the cost of the chemicals varies by location. However, a rough estimate can be calculated. Fawell et al.[10] gave an estimate of $0.86/kg of monosodium phosphate and $0.06/kg of lime. For a single person to drink 2 liters of defluoridated a day, it would cost roughly US$0.005 for MSP and US$0.00016 for lime. For a family of four to drink 8 liters of defluoridated water a day, it would cost roughly US$0.02 for MSP and US$0.00064 for lime.[10,36]

Conclusion

Out of the different calcium phosphate systems, two systems were found to be the most effective in defluoridation: calcium carbonate with the addition of phosphoric acid and monosodium phosphate with the addition of slaked lime. Adding phosphoric acid increased calcium carbonate adsorption capacity by 5 times and any source of calcium carbonate could be used, even waste products like eggshells and seashells. However, there would need to be a significant amount of phosphoric acid and initial pH would need to be really low to have optimal removal rates (pH ~1.5 or less). Best fluoride removal rates came from using $Ca(OH)_2$ and NaH_2PO_4 with final fluoride concentrations decreasing from 100 mg/L F^- to 0.02 mg/L F^-, a 99.98% removal. Slaked lime easily dissociates in water as Ca^{2+} and can quickly form $Ca_5(PO_4)_3OH(s)$ because of the low solubility product of HAP. Additionally, adding NaH_2PO_4 will keep pHs low enough because H_2PO_4 exists dominantly in the 2.12- 7.21 range. A neutral pH could be attained when the ratio of the amount of slaked lime to the amount of monosodium phosphate was approximately 0.45.

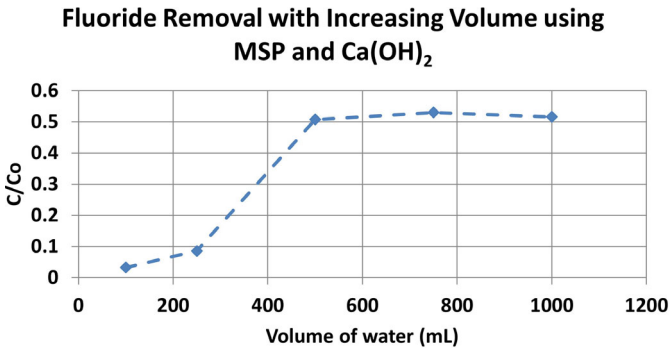

Figure 7. Removal rate of fluoride using 0.45 g of $Ca(OH)_2$ and 1 g monosodium phosphate at increasing water volumes. Fluoride concentration at 1.5 mg/L at approximately 377 mL of water.

For a single person to drink 2 liters of defluoridated water a day from an initial concentration of 5 mg/L, it would take approximately 5.93 grams of monosodium phosphate and 2.67 grams of slaked lime. For a family of four to drink 8 liters of defluoridated water a day, it would take approximately 23.72 grams of monosodium phosphate and 10.68 grams of slaked lime. The significant advantage of this system is that it uses no hazardous materials, such as acids. Further studies include finding minerals that naturally contain monosodium phosphate, determining if this slaked lime, monosodium phosphate system will also treat other contaminants simultaneously, and assembling a household sized defluoridation unit.

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