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Significance of calcium containing materials for defluoridation of water: a review

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ABSTRACT

Removal of fluoride from groundwater for drinking purpose and from wastewater is a serious global problem. Though several defluoridation methods are available, each of them has certain merits and demerits. Precipitation and adsorption of fluoride are among the low-cost methods that have been used for years. Calcium materials have certain edges over other types of materials applied for precipitation and adsorption of fluoride. Hydroxyapatite (HAP), quick lime, slack lime, calcium chloride, limestone or calcium carbonate, calcium phosphate, calcium nitrate, calcium sulfate, etc. are among the calcium materials used for fluoride removal. In this paper, the significance of use of different calcium containing materials, their fluoride removal mechanism, and the prospects of application for the purpose have been critically reviewed. Considering easy availability, low cost, and high efficiency, HAP and limestone based processes may be potential clean choices for fluoride removal if the capacity and sludge disposal are adequately addressed.

Keywords: Defluoridation; Fluoride; Hydroxyapatite; Limestone; Groundwater

1. Introduction

Contamination of groundwater with fluoride through geological and anthropogenic activities is a serious worldwide problem because a long-term ingestion of drinking water contaminated with high concentration of fluoride leads to dental and skeletal fluorosis [1–5]. At present, more than 200 million people in more than 30 countries across the Globe are reported to be affected by fluorosis, the disease caused by long-term ingestion of fluoride-contaminated water [3]. Over 66 million people in India are estimated to be at risk because of the consumption of groundwater contaminated with F^- of concentrations higher than the limit of 1.5 mg/L prescribed by WHO (2011) in vast areas of the country [4,6]. The situation being alarming in the states of Assam, Andhra Pradesh, Gujarat, and Rajasthan [5,7–9]. Severe fluorosis is prevalent among the poor inhabitants in some of the areas of Assam where the F^- contamination has been recorded to be as high as 23.5 mg/L [7–9]. As an alternate fluoride free source of drinking water is not available, the people in some areas of Rajasthan, Andhra Pradesh, and Assam in the country are dependent on the groundwater despite contamination with F^-.

Detection of fluorosis and the reason behind this menace has become familiar from the starting of

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twentieth century and history of the development of fluoride removal technique from water was started in as early as 1934. Boruff described a method for defluoridation in which aluminium compounds were added to the F^- water leading to flocculation of aluminium–fluoride, which was then removed from the water by sedimentation and filtration [10]. He described addition of calcium hydroxide also for the treatment. This was the first report on a scientific attempt on F^- removal from water. Adler and his co-workers systematically studied the adsorption of F^- on tricalcium phosphate [11] and as the regeneration of calcium phosphate by NaOH lowered its capacity of F^- removal so regeneration process was improved on replacing HCl with CO_2 to neutralize the alkali [12]. Goodwin et al. achieved removal of F^- from an initial concentration of 5–0.42 mg/L in a pilot plant using tricalcium phosphate [13]. It was suggested that the F^- removal took place through adsorption and formation of fluoroapatite (FAP). These are the reported works during the starting period of the development of fluoride removal technique.

After that the reactions between calcium compounds and F^- solution received greater attention during 1950s, though not for the F^- removal process. Conversion of carbonate to fluorite was investigated for preservation of fossils by hydrofluoric acid treatment [14,15] and this technique was used for the improvement in identification and study of anatomy of shells [16]. In the same year, Trautz and Zapanta demonstrated the formation of 0.3 mm thick layer of fluorite on a large particle of calcite when it was immersed in 2% NaF solution for two months [17] and similar work was done to describe pseudomorphic replacement of (1011) plane of calcite by epitaxial growth of the (110) plane of fluorite using 1–50% HF [18–20]. Honjo and Minoura examined the use of ammonium bifluoride for cleaning of stone and use of HF to remove clay for preparation of nanofossils through replacement of calcite by fluorite [21].

The investigation on F^- removal from contaminated water also started simultaneously with the study of the causes of dental fluorosis. A related work on the reaction between powdered enamel and F^- solutions was studied with X-ray diffraction (XRD) technique by Wei and Forbes [22]. The main constituent of teeth and bone is hydroxyapatite (HAP), which has been proved to be a good adsorbent for F^- [22,23]. Fluoride ions replace hydroxide ions from HAP and forms harder FAP strengthening teeth and bones in the presence of an optimum quantity of F^-. However, on prolonged exposure to F^- in higher concentrations, e.g. >1.5 mg/L in drinking water, HAP is excessively converted into FAP making the teeth and the bones denser, harder, and more brittle. It causes dental fluorosis which slowly progresses to skeletal fluorosis.

The success on the evaluation of actual reactions occurring between F^- and calcium containing compounds and the developing knowledge about dental and skeletal fluorosis worked as an impetus for subsequent studies of the implementation of calcium containing compounds for fluoride removal by the scientist from the whole parts of the world. Since then numerous scientists from all parts of the world have been trying to find out simple, low-cost F^- removal methods based on different principles, viz. adsorption, coagulation/precipitation, electrochemical separation, electrodialysis, and hybrid processes of adsorption and dialysis [1,2,24–28]. Adsorption and precipitation/coagulation have importance in the F^- removal processes due to the availability of low-cost materials used, low-cost treatment processes, and user friendliness [24]. Several processes, based on these two principles, have been developed for defluoridation using calcium containing materials. From an examination of the works on this topic till date, it is clear that today's maximum research works on this subject are based on the research findings between 1930s and 1970s. Interestingly, the same materials which were used for F^- removal from water in that period are still used with a few exceptions of newly developed materials. The commonly used materials for F^- removal are mostly alum, quick lime, slack lime, limestone, charcoal, HAP, calcium phosphate, calcium sulfate, calcium chloride, etc. A significant novelty in the recent studies is that the materials are applied in different ways with the same principles.

Although many reviews on defluoridation techniques are available in the literature, the information about the use of calcium containing materials is not adequately addressed [1,24,25]. This review presents a detailed discussion of the available defluoridation techniques based on precipitation and adsorption of F^- using calcium containing materials with references to the mechanism of F^- removal, advantages and disadvantages, cost involvement, and suitability for application in India as well as other countries affected by fluorosis.

2. Calcium materials for fluoride removal

The vast use of calcium materials for fluoride removal has been found to be in three ways—for precipitation of F^-, for both precipitation and adsorption, and combined with some other materials like aluminium compounds [11–13,26–32]. Fluoride ion is precipitated as calcium fluoride after reaction with quick lime, slack lime, calcium chloride, limestone or calcium carbonate, calcium phosphate, calcium nitrate, calcium sulfate etc. It also precipitates as FAP on reaction with HAP and adsorption of fluoride also takes place with HAP and limestone [30]. To discuss about these materials in a simpler way we have divided them as follows.

2.1. Defluoridation by apatite materials: HAP

It is a general perception that for every naturally occurring problem, people try to find out the remediation of the problem by applying the tricks hidden in the nature. Thus, F^- removal was also tried in a natural way in 1937 by using degreased bone as teeth and bone absorbs fluoride a lot [31]. The hydroxide group of the HAP of the degreased bones is replaced by anion exchange with F^-, forming FAP. The FAP was reconverted to HAP by treatment with NaOH. A controlled reaction between phosphoric acid and lime was found to give two products, namely calcium phosphate and HAP both capable of removing fluoride [32]. A similar removal process was reported where phosphate and calcium were added to F^- containing water to form FAP. The removal improved with increase in the pH above 10 by addition of $Ca(OH)_2$ [11].

Industrial fluoride containing wastewater was treated by Andco Environmental Processes Inc., by adding $CaCl_2$ and phosphate at a pH between 6.2 and 7.0 adjusted using solution of $Ca(OH)_2$ [33]. The chemical reactions occurring in these defluoridation processes were suggested to be as follows [11,34]:

$$NaF + 3H_3PO_4 + 0.5\,CaCl_2 + 4.5\,Ca(OH)_2 \rightarrow Ca_5(PO_4)_3F + NaCl + 9H_20 \quad (1)$$

$$Ca_5(PO_4)_3OH(solid) + NaF \rightarrow Ca_5(PO_4)_3F(solid) + NaOH \quad (2)$$

Duff contributed significantly to understand the chemistry of the formation of FAP from HAP and the stability of the different composition of the compounds formed during the course of the reactions under different conditions [35–37]. The works concluded that the conversion of HAP to FAP took place through the formations of different apatite compounds depending upon the system's pH, temperature, and the chemicals used as the source of F^-, e.g. NaF, KF, etc.

Fan et al. established the order of the F^- adsorption capacities of various materials as: HAP > Fluorspar > Quartz (activated using ferric ions) > Calcite > Quartz [30]. He and Cao found the defluoridation efficiency of the materials to be in the order: tricalcium phosphate, TCP (87.0%) > HAP (68.0%) > bone char, BC (66.4%). Combination of free phosphate with BC or HAP removed 95% F^- from high initial concentrations. Bone Char in combination with monocalcium phosphate showed the highest capacity for F^- removal [38]. High fluoride removal ability of HAP makes it a good choice for application in defluoridation. Badillo-Almaraz et al. found that HAP possessed a capacity as high as 100 mmol F^- subtractions per 100 g of HAP at pH 7.0 to 7.5 [39].

The capacity of HAP was found to increase with decrease in pH (below pH 7) and increase in surface area and more suitable for low initial concentration of fluoride [40]. The crystal structure of the apatite formed at high concentrations of fluoride was found to be hexagonal plate-like, while the apatite formed at low F^- concentrations was found to be dendritic or needle-like [41].

Manual stirring, continuous flow column test, and "fill mix and filter" method for field application of F^- removal by mixing the F^- containing water with Ca^{2+} and PO_4^{3-} ions and then bringing into contact with BC saturated with F^- showed 95–98% removal of F^-. This method has been claimed as one of the suitable low-cost and highly efficient field applicable F^- removal methods [42].

Nanomaterials are well known because of their enhanced properties. The decrease in the particle size causes increase in surface area which improves the adsorption properties of nanomaterials. HAP composite with chitin in nano form showed greater F^- removal capacity (2,840 mg/kg of F^-) than the single nano-HAP (1,296 mg/kg of F^-) [43]. If the treatment cost of F^- removal by HAP or nano-HAP can be made affordable for common people then defluoridation by using HAP will have a potentiality to be used worldwide. However, due to their nano size, nanoparticles may create new hazards for environment and human health if it is present in the water after treatment. Therefore, it should be separated from the water after treatment [44].

2.1.1. The mechanism of fluoride removal by HAP

The fluoride removal mechanism by HAP has been proved to be through precipitation of FAP and CaF_2 and surface adsorption or exchange of F^- with surface hydroxyl groups [40,45]. The mechanism of fluoride removal by Ca^{2+} and PO_4^{3-} ions and subsequent contact with bone char was suggested to be the saturated bones char catalyzed formation of FAP and formation of CaF_2 to some extent [42]. Lin has confirmed from an electrokinetic adsorption measurements and electron spectroscopy for chemical analysis study of HAP before and after treatment that FAP formed at the surface of HAP through adsorption followed by an F^-/OH^- exchange process at low concentrations of F^-. On the other hand, CaF_2 formed on HAP by a surface precipitation process at higher concentrations of F^- [45]. When HAP comes into contact with fluoride solution, at first F^- got adsorbed on the surface of HAP and then the adsorbed fluoride exchanged with OH^- group present in the apatite surface and slowly it starts to be exchanged with inner OH^- groups [46–54]. It was observed the fluoride incorporation into HAP occurs as a result of F^-/OH^- exchange reactions [30,55].

A Langmuir adsorption isotherm analysis indicated that adsorption of F^- ion on HAP also hinders dissolution of the HAP. The adsorption increased with the duration of exposure to HAP and increased with decrease in pH [56]. An increase in the temperature increased the defluoridation by HAP [57]. However, crystal growth of FAP over HAP was found to be a complicated process at low supersaturation level and the surface hydroxyl groups are exchanged by F^- ions in this process [57]. Fan et al. described the uptake of F^- on HAP with pseudo-first-order and second-order ion-exchange mechanisms, whereas, the uptake on the other materials was through a pseudo-second-order surface adsorption [30]. Ca-deficient HAP which is a by-product of phosphate wastewater treatment had been used to remove F^- ions in presence of coexisting Ca^{2+}, Mg^{2+}, and Cl^- ions and it was found that the removal followed pseudo-second-order kinetics and the adsorption of F^- occurs mainly through ion-exchange [58]. The method was prescribed as applicable for treatment of high F^- contamination with a removal capacity of 85%. The adsorption of F^- was also reported to follow Freundlich isotherm with chemisorption taking place on heterogeneous surface [59].

2.1.2. *Advantages and limitations of the use of HAP*

The salient points regarding the advantages and the limitations of HAP as a material for F^- removal can be summarized below.

Advantages:

(a) HAP can remove F^- up to 95% by precipitation as FAP and CaF_2, and through adsorption.
(b) It possesses the highest capacity for adsorption of F^- compared to other common adsorbents, the order of decreasing capacity being: HAP > Fluorspar > Quartz (activated using ferric ions) > Calcite > Quartz.
(c) It works within acceptable pH range for drinking water and does not add any other contaminant to the water.
(d) Bone char, which contains HAP as the primary constituent, possesses remarkable F^- removal capacity in combination with monocalcium phosphate.
(e) The F^- removal capacity increases with increase in surface area and temperature and requires a small dose of the adsorbent.
(f) Nano-HAP composite with chitin has capacity of holding as high as 2,840 mg of F^- per kg of the adsorbent.

Limitations:

(a) The removal capacity is poor at high pH, i.e. above 7.5.
(b) The removal capacity decreases after regeneration.
(c) The formation of FAP is slow at high (above 5.5 mg/L) and low F^- concentrations (below 3.4 mg/L) [41].

2.2. *Quick lime, slack lime, $CaCl_2$, $Ca(NO_3)_2$, and $CaSO_4$ in F^- removal*

CaF_2 can be formed by the reactions of F^- containing water with different calcium compounds. Aluminium sulfate (alum) and calcium oxide (quick lime) can be added to the F^- water and mixed well to precipitate $Al(OH)_3$ [60]. This precipitate contains F^- which was thought to be due to co-precipitation of AlF_3. This method, known as Nalgonda technique had been applied in many countries, viz. India, Kenya, Senegal, and Tanzania; but due to some shortcomings, viz. increase in pH, insufficient F^- removal, addition of harmful aluminium to the treated water, etc. this application was brought to a halt [61,62].

A gas scrubbing technique was used for F^- removal as HF with subsequent further precipitation of F^- by lime [63]. F^- removal from sea water, saline groundwater, and distilled water amended with F^- were tried using CaO, MgO, and calcined natural dolomite in a wet scrubbing system [64]. The removal mechanism was suggested to be the precipitation of F^- as amorphous salt and insertion of F^- between the crystals of $CaCO_3$, $CaCO_3 \cdot H_2O$, $Mg(OH)_2$, and Mg_2SiO_4 which precipitated during the treatment process. Addition of lime to F^- wastewater was reported to remove F^- as insoluble CaF_2 [65]. However, addition of the strong bases requires subsequent pH correction.

Ferric chloride was used to precipitate iron cryolite from an initial F^- concentration of 1,000 mg/L [66]. The iron cryolite precipitates were separated from the water and the water was further treated with $CaCl_2$ to precipitate F^-. A removal of F^- up to only 10–15 mg/L was achieved on treatment of slightly acidic F^- containing water with CaO [66]. Addition of anhydrous $FeCl_3$ and $CaCl_2$ followed by addition of anhydrous $AlCl_3$ was employed for F^- removal whereupon an insoluble complex was obtained with constituents —Al^{3+}, Ca^{2+}, and F^-. Removal of F^- was achieved up to 1 mg/L by this method [67] but only after introducing another secondary contaminant, viz. aluminium.

A two step method of precipitation of F^- as CaF_2 by addition of $CaCl_2$ and PO_4^{3-} to a stream of F^- water followed by addition of CO_3^{2-} was developed by Fritts et al. [68]. Another two step defluoridation method was developed by Kust et al. where a solution containing CaF_2 was first treated with a Ca^{2+} source to form a first precipitate and then the first precipitate comprising the Ca^{2+} source was treated with the F^- containing wastewater to form a second precipitate [69]. Precipitation of CaF_2 using $CaCl_2$ followed by dispersed air floatation using surfactant was reported to remove F^- from wastewater to below 10 mg/L from an initial concentration of F^- in the wastewater of 742.3 mg/L [70]. Increase in molar ratio of $[Ca^{2+}]/[F^-]$ from 0.5 to 2.0 increased the removal efficiency and at $pH > 3$. This method was found to be highly beneficial for treatment of F^- containing industrial wastewater. Before electrocoagulation–flotation process was applied for F^- removal, F^- could be reduced to 10–15 mg/L using CaO, $CaCl_2$, and $Ca(OH)_2$ as precipitating agent where effective floatation process surfactant were used [71–74]. Removal of the surfactant from the treated water is however a difficult task.

$Ca(NO_3)_2$ was used to increase F^- adsorption ability of activated carbon, zeolite, and molecular sieves and it was found that the removal efficiency of the materials in fact increased over the virgin materials [75]. Seed generation method with SiF_6^{2-} and PO_4^{3-} where $CaCl_2$ and $Ca(OH)_2$ were used for Ca^{2+} supply was found to be suitable for treatment of wastewater containing high F^- level [76,77]. In this method, small portion of wastewater was first mixed with the calcium compounds and then it was mixed with the wastewater. Calcium containing reagents were used for F^- removal from wastewater also using fluidised bed crystallizers [78–80]. Krulik added calcium salts to F^- containing water for precipitation of F^- using programmable controller which measured the amount of Ca^{2+} needed for F^- elimination [81].

Masamba et al. used natural gypsum ($CaSO_4.2H_2O$) and calcined gypsum for defluoridation of drinking water [82]. It was observed that 400°C calcined phase of gypsum gave the highest defluoridation capacity of 67.80% compared to raw (uncalcined) gypsum, and 200, 300, and 500°C calcined phases, due to the production of less crystalline $CaSO_4$ at that particular temperature. Fluoride, along with phosphate was also separated from fertilizer plant acidic wastewater containing H_3PO_4, HF, and/or H_2SiF_6 in an efficient way by addition of lime [83]. Increase in initial concentration of F^-, temperature and adsorbent dose increased the rate of F^- removal [84]. Precipitation of F^- by these methods leads to the formation of very fine particles of CaF_2 which were difficult to separate out from the water. Flotation and coagulation techniques were applied with surfactant and $FeCl_3$ as coagulant to separate these particles. Kagne used bleaching powder $[Ca(ClO)_2]$ for F^- removal which worked in moderate and high pH and the maximum removal was observed within 1 h [85]. A dose of 100 g/L of the powder was needed for the 90% removal of fluoride from initial concentration of 5 mg/L at pH 6.7. The removal mechanism was suggested to be the precipitation of fluoride by lime, which formed after the addition of bleaching powder to the water [85].

2.2.1. Mechanism of fluoride removal as CaF_2 by the above Ca-compounds

The main reaction occurring during the F^- removal processes by using the materials mentioned in section 2.2. is:

$$CaX_2 \text{ or } CaY + F^- \rightarrow CaF_2\downarrow \quad (3)$$

where X and Y are monovalent and bivalent anions. Precipitation of F^- as CaF_2 by addition of Ca^{2+} is a slow process when the initial concentration of F^- is low but the precipitation is fast at higher concentration of F^-. Interestingly, this process is accelerated by addition of seeds of CaF_2 in a concentration of 20 mg/L which is attributed to the enhancement of nucleation of CaF_2 in presence of the supplied CaF_2 seeds [86]. The precipitates of CaF_2 could be settled down easily also using a coagulating agent, viz. polymeric aluminium hydroxide. Heat treated quick lime showed good F^- removal ability which was due to precipitation and chemisorption following first-order kinetics of adsorption. Kinetic studies of adsorption of F^- onto plaster of Paris [$CaSO_4.1/2H_2O$] revealed that it followed first-order kinetics involving a three stage mechanism in the process external surface adsorption, intraparticle diffusion, and final equilibrium [87]. Bilinski suggested that, during defluoridation with CaO, MgO, and calcined natural dolomite in a wet scrubbing system, the removal mechanism is the precipitation of F^- as amorphous salt and insertion of F^- between the crystals of $CaCO_3$, $CaCO_3 \cdot H_2O$, $Mg(OH)_2$, and Mg_2SiO_4 which precipitate during the treatment process [64]. On the other hand, during F^- removal by gypsum, the removal of F^- was thought to take place through an ion-exchange mechanism [82].

2.2.2. *Advantages and limitations of the application of the Ca-compounds*

Advantages:

(a) Quick lime and slack lime can remove up to 98% of F^- from water.
(b) $CaCl_2$ is useful for industrial wastewater, which have high initial concentration of F^-.
(c) Since these materials remove fluoride mainly through precipitation of CaF_2, stoichiometric amount of these salts can be used for this purpose.
(d) These are low-cost chemicals and therefore the overall treatment cost is low.

Limitations:

(a) Although quick lime and slack lime are highly efficient, they make the water alkaline requiring additional pH correction.
(b) $CaCl_2$ can remove F^- only up to 10–12 mg/L from high fluoride industrial wastewater.
(c) $Ca(NO_3)_2$ and $CaSO_4$ leave nitrate and sulfate ions, respectively, in the treated water.

2.3. *Limestone/calcite for F^- removal and the mechanism of removal*

Grayson first observed the reaction of $CaCO_3$ with HF which resulted in precipitation of CaF_2 [88]. Since then research in this direction was continued by many workers [14,15,18,46,88–93]. The CaF_2 produced in this reaction possessed molecular volume of 33% smaller than that of $CaCO_3$ in calcite due to which the replacement reaction left 33% additional porosity in fluorite, which facilitated the diffusion of F^- ions into and of CO_3^{2-} ions out of the particles [18]. The involved reactions were described as follows:

$$2F^- + CaCO_3(s) = CaF_2(s) + CO_3^{2-} \tag{4}$$

$$2F^- + Ca^{2+} \rightarrow CaF_2 \tag{5}$$

$$K_{sp} = [F^-]^2[Ca^{2+}] = 3.5 \times 10^{-11} \tag{6}$$

The rate of the reaction between calcite and NH_4F was found to depend on the concentration of F^- ion and surface area of calcite [89]. A similar study was carried out by Duff by reacting calcite with 1.0, 0.1, and 0.01 M solutions of NaF at 25˚C [46]. A mixture of crystalline $CaCO_3$ with NH_4F, KF, and NaF when heated for several hours above 80˚C formed fluorite which was found to be a pseudomorph of calcite crystals as evidenced by XRD and electron microscopic techniques [90]. The course of the reaction involved penetration of F^- into the body of the grains of $CaCO_3$ forming polycrystalline CaF_2. These studies showed the rate of the reaction between F^- and $CaCO_3$ to be very slow and established CaF_2 as the product of the reaction, significantly contributing to the development of F^- removal processes.

A methodical study of limestone in the field of F^- removal was reported in 1979 [93]. The size and shape of the original limestone particles were found to remain unchanged after conversion to fluorite. The reaction rate was affected by the some cations present in the wastewater. Initially the rate was independent of F^- ion concentration but at higher concentration of F^- the probability of formation of CO_2 increased hindering the diffusion process of F^- through newly formed CaF_2 layer and the reaction with the untreated limestone. Temperature is reported to increase the rate of the conversion of $CaCO_3$ to fluorite [93]. Calcite was applied by many researchers for reducing F^- from industrial wastewater containing HF and a mixture of HF and NH_4F, however these works were aimed at getting low F^- water to satisfy wastewater discharge criteria and not to get potable water [94–96]. Surprisingly, it was found difficult to decrease the amount of F^- to the discharge level of wastewater from a lower initial concentration (<50 mg/L) than from higher initial F^- concentration. This was suggested that supersaturation of F^- and Ca^{2+} could not be achieved at lower initial concentration of F^- (<50 mg/L) the ionic product $[F^-]^2[Ca^{2+}]$ being equal to 3.5×10^{-11}. A series of three limestone columns only could lower the F^- level to 10–20 mg/L from wastewater containing NH_4F [97,98]. In fixed bed calcite treatment for defluoridation also, the effluent F^- concentration had a correlation with the effluent Ca^{2+} concentration. Since the extent of dissolution of Ca^{2+} from calcite is related to the pH, an effluent F^- concentration below 10 mg/L could be obtained by adjusting the initial $[H^+]/[F^-]$ ratio in the wastewater [99].

Limestone filtration alone cannot reduce fluoride concentration to below 4 mg/L. However, fluoride removal by limestone was achieved Reardon and Wang to below 2 mg/L from initial concentration of 10–25 mg/L by passing CO_2 through the water before filtering through a two columns series system [100]. After equilibrating with CO_2, the pH of the influent water became 4.97 due to the formation of carbonic acid [H_2CO_3], which helped in dissolution of limestone to generate Ca^{2+} as follows:

$$CO_2 + H_2O \leftrightharpoons H_2CO_3 \tag{7}$$

$$H_2CO_3 \leftrightharpoons H^+ + HCO_3^- \tag{8}$$

$$H^+ + CaCO_3 \rightarrow HCO_3^- + Ca^{2+} \tag{9}$$

The free Ca^{2+} produced reacted with F^- to precipitate CaF_2. The effluent from the first column having pH 6.53 and Ca^{2+} = 8.07 mg/L was adjusted to pH 8.42 and Ca^{2+} = 0.58 mg/L after passing the water through a second column. The advantage of this method is that no chemical is required for this process except CO_2 gas and the process does not need column regeneration [100].

Treatment of semiconductor industry wastewater using fluidised bed reactor was reported, where excess F^- was removed by precipitation using $CaCl_2$, $Ca(OH)_2$, etc. [79,80,101,102]. After this treatment 10–20 mg/L F^- remained in the treated water which could be removed using granular $CaCO_3$. The removal was found to be better at low pH since pH determined the dissolution of $CaCO_3$ [103]. Fluorite precipitation created new surfaces of limestone which increased the number of adsorption sites increasing the adsorption of F^- along with the precipitation [104]. It was found from a saturation index (SI) calculation of fluorite using Eq. (10) that precipitation was the main mechanism of fluoride removal where adsorption of F^- also aided the F^- removal simultaneously:

$$SI_{\text{fluorite}} = \log\{([Ca^{2+}][F^-]^2)/K_{sp}\} \tag{10}$$

where, K_{sp} is the solubility product of CaF_2 in $(mol/L)^3$ and $[Ca^{2+}]$ & $[F^-]$ are molar concentrations in mol/L before reaction. $SI_{\text{fluorite}} < 0$ indicates the adsorption to be the dominant mechanism and $SI_{\text{fluorite}} > 0$ indicates precipitation to be the main mechanism since it reaches the supersaturation level of F^- and Ca^{2+} necessary for precipitation. The precipitation of fluorite dominates at lower pH and lower surface area (or particle size greater than 850 μm), whereas the adsorption of F^- dominates at higher pH and higher surface area (or particle size 150–300 μm) [103,104]. Injection of CO_2 directly into the calcite column for purification of groundwater contaminated with Spent Pot Lining waste from aluminium industry was reported to be effective at removing fluoride up to about 99% giving neutral effluent pH, whereas in equilibration of CO_2 with the influent solution method gave alkaline effluent [104,105].

Nath and Dutta added organic acids, viz. acetic, citric, and oxalic acid to the influent F^- water to increase Ca^{2+} activity *in situ* in crushed limestone reactor [26–28]. These acids were chosen because they are of low cost and not only nontoxic but are also common food additives or are present in different food items. Fluoride could be removed to below 1.5 mg/L from initial concentration of 10 mg/L retaining the pH of the effluent within the acceptable range for drinking water. The affect of other anions present in the water was found to be insignificant. SI_{fluorite} calculation and XPS study indicated the removal to take place mainly through precipitation though there was a significant but a relatively slower adsorption of F^- on the limestone particles [26]. It has been shown from a detailed XRD, IR, and thermal analysis that the used limestone from this acid-enhanced limestone defluoridation (AELD) can be reused after rinsing off the precipitates formed on the surface [106]. The limestone after the AELD process exhibits almost similar morphological properties with the original limestone which suggests the suitability of the used limestone for its normal use as raw material for cement manufacturing, reducing the sludge disposal problem of the defluoridation process.

A recent study on the influence of PO_4^{3-} on F^- removal by limestone has revealed that fluoride and PO_4^{3-} are removed together from water by limestone as fluorite, FAP, and HAP [107]. It has been reported that a small amount, viz. 17 mg/L of PO_4^{3-} can reduce the F^- removal by 20% and 500 mg/L of PO_4^{3-} can completely hold back fluoride removal. The study of removal of these two anions together from wastewater using calcite showed the highest phosphate adsorption capacity of 40.65 mg/g of calcite to be at pH 6.5. Both adsorption and precipitation governs the removal of phosphate and fluoride. The precipitates of brushite and HAP were characterized. The mechanism of F^- removal was suggested to be through fluorite (CaF_2) precipitation as well as adsorption onto brushite and HAP while F^- was found to inhibit the precipitation of PO_4^{3-} [108].

2.3.1. *Advantages and disadvantages of the use of limestone*

Advantages:

- (a) Limestone has the capacity of removing fluoride from lower initial concentration to the allowed discharge level of wastewater as well as to the WHO guideline level for drinking water.
- (b) Injection of CO_2 directly into the calcite can remove ~99% of F^-.
- (c) The replacement of calcite by fluorite leaves 33% additional porosity in fluorite, which facilitates the diffusion of F^- ions into the limestone for adsorption.
- (d) Addition of edible acids to the influent water to limestone column removes F^- to below 1.5 mg/L retaining the pH within the acceptable range for drinking water.
- (e) Limestone defluoridation have the potential for field applications due to high efficiency, cost effectiveness and user friendliness. The easy availability of limestone in most of the fluoride affected areas is an added advantage.

Disadvantages:

- (a) Management of a huge quantity of solid sludge is necessary.
- (b) It requires relatively longer treatment time, since conversion of calcite to fluorite is a slow process.

2.4. *Fluoride removal by cement and related materials*

Cement paste, viz. cured mixture of cement and water from waste concrete recycling process, was reported to be an economical and viable substitute for lime to remove fluoride, nitrate, and phosphate from wastewater [109]. The feasibility of application of some other but similar materials, viz. hydrated cement, alumina cement granules (ALC), etc. was also investigated. Cement paste was found to possess a high capacity for F^- removal which is comparable to that of lime. It could also remove F^- much better and faster than raw cement. 92.6% of F^- was removed by 1% dose of the cement paste powder from 100 mg/L F^- containing wastewater, whereas the removal efficiencies of raw cement and lime were reported to be 47.3 and 96.4%, respectively. A column of cement paste was found to remove F^- from 1,150 mg/L immediately to the level of less than 15 mg/L and the F^- removal capacity of the cement paste column was 0.149 g F^- [110]. However, the cement paste slurry worked within moderate and higher range of pH and the pH of the treated water became higher. Such a column is reported to be useful for treatment of mixed hydrofluoric acid wastewater and for simultaneous removal of F^-, PO_4^{3-}, SO_4^{2-}, and NO_3^-. The hydrates of calcium present in cement paste are readily soluble portlandites. Whereas calcium silicate hydrate, formed by of the reaction between the silicate phases of Portland cement and water, releases Ca slowly [110]. The reaction involved is:

$$2Ca_3SiO_5 + 7H_2O \rightarrow 3CaO.2SiO_2.4H_2O + 3Ca(OH)_2 \tag{11}$$

A remarkable observed removal of F^- from 407 mg/L to below 0.5 mg/L was suggested to be due to the highly elevated concentrations of Ca^{2+} generated in the system. The PO_4^{3-} present in the water was removed completely by precipitation of amorphous calcium phosphate, which adsorbs the remaining F^- [109]. The defluoridation by hydrated cement does not produce any chemical sludge and works in a wide range of pH between 3 and 10. The defluoridation capacity of the adsorbent was appreciable in acidic range which has been attributed to presence of alumina. An observed sharp drop in defluoridation capacity at highly alkaline pH is due to a competition between OH^- and F^- ions [111].

Studies on use of ALC for removing F^- from water showed that a dose of 2 g/L of ALC could bring down fluoride concentrations in water from 8.65 mg/L to below 1.0 mg/L under optimum conditions [112–114]. The maximum adsorption capacity was found to be 2.27 mg/g at a flow rate of 4 mL/min. ALC exhibits two phases of sorption of F^-: an initial rapid uptake phase followed by a slow and gradual phase. An inner-sphere complex of F^- with ALC has been suggested to be formed through a chemisorptive ligand exchange reaction.

2.4.1. *Advantages and disadvantages of the use of cement paste and related materials*

Advantages:

- (a) Cement paste has higher capacity of F^- removal than raw cement and can simultaneously remove phosphate, sulfate, and nitrate.
- (b) Cement paste works within neutral and alkaline range of pH and its F^- removal

capacity is comparable to that of lime.

(c) Hydrated cement posses 99.8% fluoride removal capacity, works in a wide range of pH, and does not produce any chemical sludge.

(d) ALC possess good F^- removal capacity from lower initial F^- concentration.

Disadvantages:

(a) The pH of the water increases after treatment using cement paste needing a pH correction.

(b) The defluoridation capacity of hydrated cement is good only in acidic pH.

(c) ALC cannot remove much F^- from higher concentrations.

3. Effect of other ions in fluoride removal by calcium containing materials

Fluoride is referred to as a "*difficult to remove*" inorganic contaminant of water since the removal of this ion is affected by many factors like pH of the treatment system, presence of the other ions, the process of removal, the materials chosen for the removal, etc. Among these factors, the influence of other organic or inorganic ions like, Na^+, K^+, NH_4^+, CH_3COO^- (acetate), $C_6H_5O_7^{3-}$ (citrate), $C_2O_4^{2-}$ (oxalate), PO_4^{3-}, SO_4^{2-}, Cl^-, Br^-, NO_3^-, HCO_3^-, SiF_6^{2-} can affect defluoridation through precipitation, adsorption, electrochemical, ion-exchange, and nanofiltration techniques [70–72,76,84,99,115–117]. These ions compete with F^- in the precipitation and adsorption processes involving Ca-compounds depending on pH and concentration of the particular ion in the water.

The fluoride precipitation reaction was significantly delayed by the presence of high concentrations of SiF_6^{2-} in electronic industry wastewater [76]. A high pH resulted in a low F^- removal efficiency from $SiF_6{}^{2-}$ which was found to be greatly improved by aging. The precipitation process can be accelerated by controlling the reaction pH at a low value, viz. at less than pH 9 [76].

The inhibition by PO_4^{3-} on F^- removal was not only through competition for Ca^{2+}, but also through retardation of the crystal growth of CaF_2 by the earlier precipitation of $Ca_3(PO_4)_2$ at pH greater than 9 [76]. By lowering the pH to 4, precipitation of $Ca_3(PO_4)_2$ can be prevented which improved F^- removal but still a reckonable quantity of PO_4^{3-} is also removed simultaneously [99,107]. Below pH 4, the residual F^- increases because of dissolution of CaF_2 in that pH range [76].

The amount of residual F^- increased from 4.01 to 14.42 and 19.87 mg/L when SO_4^{2-} was added to the concentrations of 100 and 500 mg/L with an initial fluoride concentration of 630 mg/L [70]. In fluoride removal from wastewater by using lime and electrochemical technique, the interference by the anions was reported to follow the order: $PO_4^{3-} > SO_4^{2-} > Br^- > Cl^-$ [71]. Similar trend was observed when laboratory-prepared F^- water was used for the removal process by using lime alone [84]. Na^+, K^+, Cl^-, CH_3COO^-, NH_4^+ ions also have adverse effect on fluoride removal process, though they are less pronounced in comparison to SiF_6^{2-}, PO_4^{3-}, and SO_4^{2-} [76]. The process of F^- removal from industrial wastewater using granular calcite also affected by the presence of PO_4^{3-} and SO_4^{2-}. A concentration of 300 mg/L of SO_4^{2-} gave an increase of residual F^- concentration by 50%. The inhibiting effect of PO_4^{3-} was more profound than that of SO_4^{2-} and addition of 29 mg/L PO_4^{3-} resulted in an increase of effluent F^- concentration from 6 mg/L to more than 30 mg/L [99].

The effect of other ions on AELD technique showed that even in the presence of the ions 96–90% F^- was removed when 0.1 M citric acid was added to the F^- water before the limestone treatment. Similarly, in case of 0.1 M acetic acid and oxalic acid, 90–82% and 95–80% of F^- removal was found, respectively, in presence of the ions [26–28]. The removal capacity of the limestone decreased with increase in the amount of the ions which followed the same order, i.e. $NO_3{}^- < Cl^- < Br^- < SO_4^{2-} < PO_4^{3-}$.

Thus, it can be summarized here that the influence of the other ions on fluoride removal process by using calcium compounds is an important factor which depends on the pH of the treatment system and the concentrations of the ions. The effect of these ions can be controlled by maintaining suitable pH range through process optimization for the treatment process. It is also interesting to note the smaller effect of the competing ions on enhanced limestone defluoridation by using acetic, citric, and oxalic acid.

4. Effect of pH on fluoride removal by calcium containing materials

The pH of the solution is one of the most important parameters that govern the removal of F^-in both precipitation and adsorption process using Ca-containing materials [26–28,59,76,99,100,104]. Generally, adsorption of F^- was found to be better at low pH (below 4) which may be attributed to the presence of a large number of H^+ ions at these pH values, which neutralizes the negatively charged OH^- ions on adsorbed surface thereby reducing hindrance to the diffusion of F^- ions. In case of natural materials like fishbone charcoal containing calcium at higher pH values, the reduction in adsorption may be due to plenty of OH^- ions causing increased hindrance to diffusion of F^- [118–121]. In the case of HAP, which possesses a high F^- adsorption property, the maximum sorption of F^- ions was found in the equilibrium pH range between 5.0 and 7.3 [59]. Precipitation of F^- as CaF_2 needs a pH greater than 2, since below this pH CaF_2 starts to dissociate again and above pH 6 the precipitation continues more efficiently [122]. According to another report, the F^- removal efficiency of the Ca^{2+} is not much affected above pH 4; however, at pH less than 4 dissolution of CaF_2 occurs which increases the effluent F^- concentration [76]. In precipitate flotation process of F^- removal by using Ca^{2+} it was observed that when pH was 3 or more, the amount of residual fluoride was 9.7 mg/L from an initial concentration of 742.3 mg/L; while at pH 2, the amount of residual fluoride was 91.5 mg/L [70].

A considerable decrease in the reactivity of F^- is observed with cement paste slurries when pH was lowered below 4.7 [110]. The cement paste retains a substantial removal capacity for F^- in the mid or high pH, viz. from 7.0 to 11.5 regions where the cement hydrates play an important role in immobilizing aqueous F^-. In the F^- removal process by granular calcite, the pH is the main factor for dissolution of calcite and liberation of Ca^{2+}, which precipitates F^-. Yang et al. formulated a logarithmic relation in between the effluent F^- concentration and pH of the water [99]. In acid-enhanced limestone defluoridation process, addition of 0.1 M acetic, citric, and oxalic acid to the water before the limestone treatment, pH of the water was 2.89, 2.06, and 1.36, respectively and after defluoridation the pH comes within the range of 6–7 [26–28].

Thus, summarizing the discussion it can be said that the effect of pH factor on fluoride removal is negligible when $CaCl_2$ and lime are used as the source of Ca^{2+} or HAP as the absorber, which works in a large pH range of 4–11. However, a pH of less than 4 can give good defluoridation when limestone or calcite is used for the F^- treatment. The initial pH should be acidic; otherwise, the dissolution of calcite will also take a long time increasing the treatment time of the defluoridation process [26–28,99,100,104].

5. Cost, efficiency, and safety parameters of defluoridation by calcium materials

Calcium is a naturally abundant element, which is found in 3.65% in the Earth's crust mostly as calcium carbonate [123]. The main sources of calcium carbonate are the rocks as marble, limestone, dolomite, etc. distributed all over the world and the main component of shells of marine organisms, snails, pearls, and eggshells. HAP, which is found in nature, is the main constituent of teeth and bone of human as well as animals. Calcium sulfate is also naturally abundant as gypsum. Calcium carbonate is a low-cost chemical due to its high natural abundance and therefore, many other calcium containing chemicals, viz. $CaCl_2$, $Ca(OH)_2$, $Ca(NO_3)_2$, etc. are produced from it at low cost.

The performance of the calcium containing chemicals, viz. $CaCO_3$, $CaCl_2$, $Ca(OH)_2$, $Ca(NO_3)_2$, $Ca_5(PO_4)_3(OH)$ etc. on defluoridation from industrial wastewater and groundwater have been assessed by many researchers [26–28,59,76,99,100,104,118,119]. These Ca-containing materials do not require any pretreatment and are less expensive in comparison to other adsorbent materials, viz. aluminium compounds, laterite [124], activated carbon prepared from *Morringa indica* bark [125], carboxymethylated starch-based hydrogels loaded with Fe^{2+} [126], Neem (*Azadirachta indica*) bark, and Kikar leaves (*Acacia arabica*) [127].

All of these Ca-compounds defluoridate water through precipitation and adsorption. Both these processes are known to be cost effective in comparison to reverse osmosis, nanofiltration, and ion-exchange. That is why the research related to the defluoridation by Ca-compounds, which started during 1930s, is still an active area of research and new methods based on them are still coming up. The F^- removal capacity of these compounds is impressive. In F^- containing industrial wastewater purification, $CaCl_2$ can bring down the fluoride level from 742.3 mg/L to below 10 mg/L [70]. Another report claimed that on addition of a stoichiometric quantity of Ca^{2+} to 640 mg/L F^- containing water, the amount of F^- decreased to 13.43 mg/L, which further decreased by coagulation with polyaluminium chloride [77]. Hundred grams of HAP was found to subtract 100 mmol F^- at pH 7.0 to 7.5 [39]. Limestone can bring down the F^- concentration from initial 10–15 mg/L to below 1.5 mg/L in the presence of organic acids [26–28]. These examples indicate that the Ca-materials are highly efficient in bringing down the F^- from higher and lower initial concentration from industrial wastewater as well as groundwater.

Aluminium compounds have been extensively used for defluoridation of drinking water but the residual aluminium is suspected to cause Alzheimer disease [128] and therefore, from the safety point of view also calcium containing materials are preferable to the aluminium compounds.

Table 1
Comparison table of different fluoride removal methods

F^- removal technique	Efficiency in terms of F^- removal	Working pH	Need of power/Energy	Handling	Situation wise use	Difficulties faced	Sludge	Cost*	References
Adsorption	Moderate up to 90%	<7	Optional	simple	Rural/urban	Highly depends on pH, efficiency depends on the capacity of the adsorbent, regeneration of the adsorbent decreases efficiency	Large liquid and solid sludge	Low	[25,30]
Precipitation	High 85–90%	Non-specific	Optional	simple	Rural/urban	Lime, calcium and magnesium hydroxide increases the pH of water, it is difficult to obtain equilibrium fluoride concentrations less than ~0.42 mM because of solubility restriction	Small solid sludge	Low	[84,104]
Precipitation/adsorption	High 97–99%	~4	Optional	simple	Rural/urban	Pre-acidification of water is necessary for better result, large amount of limestone is needed	Large solid sludge	Low	[26–28,104]
Coagulation/precipitation	Moderate 67–82%	Non-specific	Optional	simple	Rural/urban	Use of lime increases pH up to 11–12, use of aluminium sulfate as coagulant increases residual aluminium in excess of 0.2 mg/L in treated water, which is dangerous and the sulphate ion concentration increases above permissible limit of 400 mg/L	Small solid sludge	Low	[1,72,73,130]
Reverse Osmosis	High up to 90–98%	pH dependent	Required	Tricky	Urban	It removes all the ions present in water so remineralization is required, after treatment disposal of backwash water is a problem, high detention time, efficiency is reduced in presence of other ions	Large liquid sludge	High	[131,132]
Nanofiltration	High up to 90–98%	Non-specific	Optional	Tricky	Urban	Efficiency is reduced in presence of other ions	Large solid sludge	High	[133–135]
Electrodialysis/Electrocoagu–lation	High up to 90–98%	pH dependent	Required	Tricky	Urban	Efficiency is reduced in presence of other ions	Large liquid sludge	High	[136–138]
Ion-Exchange	High up to 90–98%	pH dependent	Optional	Tricky	Urban	Regeneration of resin required	Large liquid and solid sludge	High	[139–141]

*Cost aspects are hardly discussed quantitatively in the literature.

6. General remarks

Another major factor to be taken into consideration, while choosing a defluoridation technique, is the location specificity [1]. If a material has a high potential for removing F^- and is readily available at a particular place, the material obviously gets the priority. In this respect, locally available abundant materials like limestone, gypsum, dolomite, etc. can be most suitable provided they can be efficiently used for defluoridation. Most of the minerals capable of defluoridating water are readily available in the nature throughout the world. As an example, limestone or dolomite is almost evenly distributed in all or around all F^--affected areas of India which can be utilized for defluoridation [4,7,8,25,129].

Different fluoride removal methods can be compared in terms of their efficiency, energy requirement, situation wise use, difficulties faced during operation, and the cost factor which is presented in the Table 1. The table also presents an overview of the present techniques of defluoridation, their merits and demerits and includes the usefulness of each method in context to the use in rural/urban areas, cost-effectiveness, power requirement, sludge production, efficiency etc. It is clear from the table that in terms of cost, toxicity, safety, and efficiency in defluoridation and user friendliness, the Ca-compounds have great potential in fluoride removal from water.

In context to India and other developing countries which comprise a lot of rural areas, it is difficult to choose a fluoride removal method since modern techniques always need power supply. Therefore, traditional methods like precipitation, coagulation, and adsorption are highly applicable in those areas since they can be run without using power and also of low cost. The quantity of sludge management is important. Adsorption and precipitation methods usually produce large sludge of used material but low reject of wastewater unlike reverse osmosis. Though HAP, limestone, or other similar materials are highly efficient in fluoride removal the amount of the used materials cannot be ignored. If the used materials can find some other applications, these materials may be promising.

7. Conclusions

- The potential calcium materials for defluoridation purpose are mainly HAP, lime, calcium hydroxide, calcium chloride, bleaching powder and plaster of Paris, limestone, cement paste, hydrated cement and ALC. Each of the methods has certain advantages and disadvantages.
- HAP is an efficient defluoridating agent. In-situ production of HAP from low-cost materials may be an even better defluoridation technique. With proper sludge management, defluoridation by HAP has a high potential for application.
- Limestone, which is a low-cost material and almost evenly distributed in the nature in all F^- affected areas of India, when used along with CO_2 or acids can be highly effective in F^- removal. In addition, these methods have high F^- removal ability, due to combined precipitation and adsorption. This can be another highly potential defluoridation method provided that the low capacity of limestone is addressed adequately.
- If the management of the associated large quantity of sludge are addressed well, HAP and limestone methods may provide viable alternatives to use of alumina and reverse osmosis for defluoridation of groundwater in India and elsewhere.
- Defluoridation by using other calcium compounds are either less efficient or require further treatment of the water for correction of pH, removal of secondary contaminants, large sludge management, etc.
- There are scopes for further improvement of the capacity of HAP and limestone through modification of the processes and optimization of physico-chemical parameters.

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