

**REVIEW**

**Defluorination of Waste Waters**

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**INTRODUCTION**

Fluorine is widely distributed in nature and occurs in continental rocks of earth's crust. In the crustal abundance among the elements fluorine occupies 13th position. More than a hundred fluorine containing minerals have been identified. However, fluorine does not exist in elemental form due to its high reactivity attributed by atomic structure. Fluorine is a diatomic gas having an atomic number of 9 and atomic mass 19, is the most electronegative element and is much more reactive than oxygen and chlorine. Both metallic and non-metallic fluorides are known. Commercially, fluor spar or fluorite, cryolite, fluorapatite and calcium fluoride are important.

Fluorine and its compounds are extensively used in industries. Elemental fluorine is necessary in the preparation of many fluorides. Fluorine compounds play an important role in semiconductors, fertilisers, production of high purity graphite, electrolysis of alumina and in nuclear applications. Toxic wastes containing fluorine are generated in all industries using fluorine or its compounds. Prominent among these is aluminium smelter where fluorine gas is released into atmosphere and the contamination due to spent pot liners is not properly taken care of. While small scale units treat the wastes by lime, large scale industries have to use elaborate treatment techniques before discharging the effluents. In addition to the contribution from industries through air and water, fluoride is also released into subsoil water sources by the slow natural degradation of fluorine containing rocks.<sup>1-5</sup>

Fluoride is recognised as essential in human diet. Skeletal and dental problems can be prevented by maintaining a fluoride concentrations of 1 ppm in the dietary intake. However, when the fluoride concentration is above this level it leads to many bone diseases, mottling of teeth and lesions of the endocrine glands, thyroid, liver and other organs.

It is necessary to supplement diet with fluoride in low fluorine areas and it is essential to reduce the fluorine levels in areas where fluorine poisoning takes place by both natural and human activities. The present article gives a brief review of methods available for treatment of effluents with high fluorine content.

Fluorine forms sparingly soluble compounds with calcium and aluminium. It is also adsorbed by activated alumina and a few metal oxides. Certain inorganic and synthetic resins in their Al-form retain fluorine. Most of the industrial

processes for the removal of fluorine are based on these attributes and a few electrolysis methods.

### Treatment methods with lime and related compounds

Calcium, iron and aluminium fluoride are nearly insoluble in water at room temperature.<sup>6</sup> Treatment methods consist of using calcium salts alone or in combination with iron and aluminium salts. It is reported that removal of fluoride from water by calcium salts is not directly dependent on pH but is a function of formation of carbonate species from bicarbonate ions and therefore fluoride removal is more efficient at pH 5 to 7 than at higher pH of say 8–11.<sup>7</sup> However, Bespamyatnov *et al.* conclude that the efficiency of fluoride removal is dependent on several factors, like the composition of the waste water, the calcium compound used as reagent for precipitation of fluoride<sup>8</sup> etc. Not only precipitation but also flocculation or rapid settlement of calcium fluoride precipitate is essential for effective defluoridation. Moldavian groundwater has high (9.1 mg/L) fluoride content and by a simple treatment with calcium chloride (2 g/L) the fluoride concentration decreases to a manageable 5.9 g/L within 15 minutes.<sup>9</sup> Lime treatment combined with filtration over a bed of adsorbent pellets containing iron, phosphorus, calcium and magnesium compounds and a sand bed was claimed<sup>10</sup> to reduce fluoride from groundwaters in Japan to 0.44 ppm level.

Fluoride from waste waters usually requires a complex treatment for total precipitation as well as flocculation. Akasaki patented a method in which waste water containing fluoride was contacted with calcium fluoride or a mixture of limestone and calcium fluoride under slightly acidic conditions.<sup>11</sup> Some of the flocculation problems were overcome<sup>12</sup> by passing the calcium chloride or nitrate precipitated fluoride flocks over fluorite. Toshiyuki finds that addition of calcium fluoride seed crystals while using calcium and sodium chlorides as precipitating agents and addition of polyacrylamide flocculants is more efficient for defluoridation.<sup>13</sup> Calcium sulphate is itself sparingly soluble and the solid was used to remove fluoride from gas washing waste waters of aluminium plants, trash incinerating plants and metal plating plants. It was claimed<sup>14</sup> that when fluoride waste water was treated with calcium sulphate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) and the precipitate flocculated with iron or aluminium salts the effluent contained 7.9 mg/L fluoride. It appears that sulphate assists removal of fluoride in presence of calcium fluoride.<sup>15, 16</sup> In an alternate method Dergunova *et al.* described a method in which lime and sulphuric acid are used for removal of fluoride from waste waters.<sup>17</sup> After a critical appraisal, Seijiro observed that lime treatment was more efficient than iron salt addition. He<sup>18</sup> mentions that sulphate interfered in fluoride removal. Scaling is a problem in lime treatment for removal of fluoride<sup>19</sup> especially from flue gas desulphurisation waste water. This can be avoided by preliminary treatment with soda ash.

According to a Japanese patent<sup>20</sup> acidic waste water of pH 2 and 600 ppm fluoride was treated with lime water at pH 10 and after flocculating the precipitate with an organic flocculant the supernatant liquor was further treated with aluminium sulphate at pH 7 to get an effluent with 9.1 g/L fluoride. In yet another process for treatment of waste water, from dry distillation of coal or petroleum

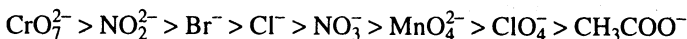
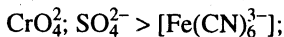
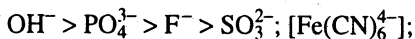
combustion gas scrubbing, iron compounds replaced aluminium nitrate to reduce the fluoride content from 280 ppm to 4 ppm.<sup>21</sup> In either case calcium fluoride flocks are adsorbed on hydrated iron or aluminium hydroxides. Hoshimoto and Nakajima claim that ferric salts are required to adjust the oxidation-reduction potential of the system.<sup>22</sup> In order to avoid excessive corrosion problems while using iron chloride or sulphate Gu and colleagues used a non-ionic polyacrylamide water flocculant.<sup>23</sup> Use of polyacrylamide flocculants is also reported by Li *et al.*<sup>24</sup> For treatment of fluorite mine water containing 470–1000 mg/L fluoride, Xue *et al.*<sup>25</sup> first treated the waste water with aluminium sulphate and then stirred the slurry with lime and finally used polyacrylamide derivatives to precipitate the fluoride sludge. A similar procedure was reported for treatment of waste waters from ore flotation.<sup>26</sup> Bulusu and colleagues claim<sup>27–30</sup> that fluoride is removed as aluminium fluoride than as calcium fluoride. Based on this principle they developed the now famous Nalgonda technique for removal of fluoride from drinking water sources in many parts of India. Fluoride levels are brought down to 0.9 to 1.2 ppm by the Nalgonda technique. The method was shown<sup>31</sup> as not reliable due to certain analytical errors in the determination of fluoride using ion-selective electrode since the ion-selective electrode does not respond to soluble aluminium fluoride. The role of sulphate as calcium sulphate or activated calcium sulphate/fluoride is not known in defluoridation. Hitachi<sup>32</sup> developed a process using sulphuric acid treated calcium fluoride for the removal of fluorides from semiconductor processing plants. Petrova and Tubolkin<sup>33</sup> used decalcified pyrolytic carbon as adsorbent after preliminary removal of fluoride with milk of lime and an adsorbent.

Jacobus reported<sup>34</sup> use of inert bed material to retain the precipitated calcium fluoride in a fluidised bed reactor. The inert material is changed after it is saturated with the calcium fluoride.<sup>35</sup> While defluoridation with calcium compounds is widely used there is not much information on the methods for disposal of the waste sludge.<sup>36</sup> Recovery and recycling of fluoride is reported.<sup>37</sup> The waste water containing silica<sup>38</sup> is treated with calcium compounds at pH 4.2–8.5 and the formed silico-calcium fluoride is used for recovery/recycling of fluoride. Lime and alumina based processes were described for treatment of waste containing organic matter and fluorine<sup>39</sup>; waste water from fertiliser manufacture,<sup>40</sup> solder etching waste water<sup>41</sup> and others were available in patent literature.<sup>42–45</sup> A multiple stage process of removal of fluoride by calcium-magnesium chlorides was patented by Roger *et al.*<sup>46</sup> Spent potline leachate of aluminium smelters contains fluorine and cyanide. Fluoride is removed by lime treatment and cyanide oxidation methods.<sup>47, 48</sup> When borofluorides are present in the effluent water it is necessary to first decompose these at high temperature (> 60°C) for removal of fluoride with lime alumina treatment.<sup>49</sup>

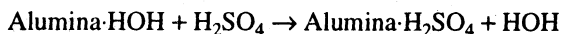
### Treatment methods with alumina

Lime or lime alumina treatment is used for treatment of industrial effluents containing very high fluoride concentration. Due to the limitation of the solubility of calcium fluoride, the treated water still contains 4 to 11 mg/L of fluorine. This water may be satisfying the limits for discharge of effluents, but is not suitable

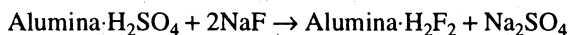
for potable water where fluoride concentration is to be within 1.5 mg/L. Activated alumina functions as an anion exchanger and the order of preference for various anions can be expressed<sup>50</sup> as:



Activated alumina is prepared by treating alumina with sulphuric acid:



When acidic alumina is contacted with fluoride it replaces the sulphate ion:



Fluoride loaded alumina can be converted back to sulphate form:



Two defluoridation plants are under operation using activated alumina in South Africa and Schoeman and Leach gave a detailed account of their operation.<sup>51</sup> Barbier and Mazounie<sup>52</sup> studied the adsorption of fluoride on activated alumina beds for effective removal of fluoride from drinking water. The same regeneration technique was reported. The ion exchange capacity of activated alumina is further improved by maintaining the pH at 4–5 with aluminium sulphate.<sup>53</sup> Komandenko<sup>54</sup> states that ion exchange of fluoride by activated alumina is dependent on pH. In a variation of the method for preparing active alumina Matsumoto<sup>55</sup> found advantage in precipitating aluminium *in situ* from aluminium sulphate by using sodium aluminate or sodium hydroxide or sodium carbonate. The same effect was also achieved by neutralising sodium aluminate with sulphuric or hydrochloric acid. The method was based on operation in a multi-tank separation system working at different pH values. The treated water contained 0.61 ppm fluoride. The effect of particle size, pH and interference from other ions normally present in water sources was investigated by Schoeman *et al.*<sup>56–59</sup> They report that smaller particles have higher adsorption capacity; bicarbonate and hydroxide interfere while sulphate, phosphate and silicate have little effect at pH of 4–5. The method of *in situ* precipitation of aluminium hydroxide from aluminium sulphate for the adsorption of fluoride poses problems of separation of fluoride-loaded aluminium hydroxide. One method recommended was by froth flotation.<sup>60</sup> The other method is to use a coagulant.<sup>61–63</sup> In the presence of sodium chloride under controlled conditions of precipitation, cryolite is formed from neutralisation of aluminium sulphate in fluoride waters<sup>64</sup> and this effectively removes the fluoride.

### Electrolysis

Aluminium fluoride is formed in water containing fluoride when electric current is passed between electrodes of aluminium. A few investigations were

carried out to evaluate the method for defluoridation. Aluminium consumption was least at a pH of 6.4–6.7 and presence of bicarbonate is beneficial.<sup>65</sup> Ming and coworkers studied several experimental parameters of this method, like: ratio of fluoride to aluminium, pH, effect of agitation. They<sup>66</sup> claim that bacterial count also was reduced and the method was more efficient than activated alumina process. Prisyazhnyuk reported<sup>67, 68</sup> the use of parallel plate duralumin electrodes or graphite cathode and aluminium anode for defluorination of drinking water to achieve 48–72% removal of fluoride from raw water with 4–15 mg/L fluoride at a current density of 6–8 mA/cm<sup>2</sup>. Theoretical aspects of electrolysis were discussed by Wang *et al.*<sup>69</sup>

### Ion-exchange

Both anion and cation exchange processes were reported in literature for defluoridation of contaminated water. In both the processes the basic reaction is between aluminium and related elements with high affinity for fluorine and fluoride ion of waste waters.

*Anion exchange:* With silicic acid fluoride forms  $\text{SiF}_6^{2-}$  and when such a complex is passed over an anion exchanger the bed life is claimed to have increased without adversely affecting the efficiency.<sup>70</sup> Hitachi Company claims that an effluent with < 2 ppm fluoride<sup>71</sup> is obtained by passing a synthetic solution of 1000 mg/L fluoride along with aluminium, iron, sodium and zirconium sulphates at 1–2 times equivalent amount of fluoride over a bed of anion exchanger.

*Cation exchange:* Most of the cation exchange resins are based on aluminium exchanged aminomethylenephosphonic acid. Zhang *et al.*<sup>72</sup> described a method for synthesis of such resin with a capacity of 9.297 mg/mL. The resins are selective<sup>73</sup> for fluoride and can be regenerated. Kanamoto studied the adsorption characteristics of La(III) loaded chelating resin containing phosphonomethylamino groups. It is reported<sup>74</sup> that the optimum pH to avoid leakage of lanthanum is 3.5 and there is no interference from chloride, nitrate and sulphate. The treated resin can be regenerated with dilute alkali repeatedly without significant loss of efficiency. Sulphostyrene group of ion exchange resins in their aluminium form are useful in defluorination. Gel-type KU-2X8 and KU-23<sup>75–77</sup> and Agrion C-100<sup>78</sup> resins belonging to this class were used for defluoridation.

### Miscellaneous

Several adsorbents like metal oxides, activated charcoal and fly ash are reported for defluorination of industrial and drinking water. A few are listed here.

*Metal oxides:* Hydrated titanium dioxide has very good affinity for fluoride, phosphate and sulphate.<sup>79</sup> Zirconium or cerium hydrous oxide impregnated resins have shown good characteristics for adsorption of fluoride.<sup>80, 81</sup> Blackwell and Carr<sup>82</sup> studied the adsorption characteristics of porous microparticulate zirconium oxide and ascribe the strong adsorption of fluoride on these surfaces to the presence of Lewis acid sites. Fluoride ion coordinates strongly with these sites on zirconium oxide and forms a surface whose composition is pH and ionic strength dependent. Fluoride can be desorbed with alkali and this treatment does

not harm the zirconium oxide particles. A mixture of rare earth and alkaline earth compounds is found effective for removal of fluoride by Inoue *et al.*<sup>83</sup>

**Activated carbon:** Aluminium sulphate granulated activated carbon is reported by Slipchenko *et al.* for defluorination of groundwater to make it suitable for drinking purposes.<sup>84</sup> Similar studies were reported using coconut shell carbon by Arulnathan and coworkers.<sup>85</sup> In these cases it is interesting to note that the aluminium sulphate impregnated active carbon is used and is reported to be superior to untreated active carbon. Treatment with untreated active carbon however is less expensive even though the adsorption capacity is far less than treated samples.<sup>86</sup> The active carbon may be providing additional surface sites for improving the adsorption of fluoride on activated alumina formed *in situ*. Different grades of bone charcoal have different affinity for fluoride. Mwaniki<sup>87</sup> concluded from batch tests that fluoride removal capacity follows the order: black grade > grey grade > white grade. Black grade can be used to treat drinking water. Phosphogypsum is a waste generated in superphosphate manufacture and contains a mixture of calcium sulphate and phosphate. This waste has been proposed as a reagent for defluorination of waste water either alone or in combination with lime.<sup>88</sup>

**Clays and other minerals:** Bentonite group of clays are known adsorbents for anions. Perhaps some aluminium sites available on the surface may be responsible for removal of fluoride by bentonite<sup>89</sup> and colloidal soils.<sup>90</sup> Semicalcined dolomite is reported for treatment of drinking water for the removal of manganese, phosphate and fluoride.<sup>91</sup> In some of the calcium minerals like shell rock, calcium oxide is available in a free form and such minerals can be used for removal of fluoride.<sup>92</sup> However serpentinite<sup>93</sup> is to be activated with hydrochloric acid. The residue from alum manufacture contains aluminium and metal sulphates. Nair and coworkers<sup>94</sup> investigated this residue for the removal of fluorine from polluted water; they find addition of calcium compounds is required for better results. Activated natural zeolites of Inner Mongolia possess ability to remove fluorine from water. Wu and coworkers<sup>95</sup> and Li *et al.*<sup>96</sup> investigated different aspects of this adsorption. Coal ash or fly ash from coal fired power plants is advocated for removal of fluoride from waste waters. Flue gas desulphurisation waste water containing 290 mg/L fluoride is treated with fly ash to reduce the fluoride content to 10 mg/L.<sup>97</sup> Chaturvedi and coworkers studied the different parameters affecting fluoride adsorption on fly ash and report that low concentration, high temperature and acidic pH favour fluoride removal.<sup>98</sup> Fly ash-lime combination could be useful to reduce fluoride from 20–100 mg/L to <10 mg/L.<sup>99</sup>

**Others:** Different types of reactors are used for defluoridation. Bhargava and Killedar<sup>100</sup> studied the efficiency of moving media reactor and extended the studies with fish bone charcoal.<sup>101</sup> Sludge from sewage was reported to remove fluoride under separate aerobic and anaerobic operations.<sup>102</sup> Reverse osmosis technique was reported as useful for removal of arsenic and fluoride in ground water.<sup>103</sup>

## Conclusions

Fluoride level in drinking water has been given wider importance than any other naturally occurring inorganic constituent. The fluoride entered in the body is absorbed completely and rapidly distributes throughout the system. The release of fluoride in environment is through different channels like air, soil and water, out of which water is the major contributor. Therefore, maintenance of an optimal fluoride concentration in drinking water is essential. Several indigenously prepared adsorbents have been chemically treated and tested for their ability to remove fluoride from ground, drinking and waste waters. Use of calcium and aluminium salts for defluoridation of ground drinking waste waters seems to be much economical, simple and environmentally safe. The fluoride precipitated as  $\text{CaF}_2$  and  $\text{AlF}_3$  are not classified as toxic materials because of their low solubility in water. The ion-exchange and electrolysis methods are also given equal importance for the treatment of waste water.

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