

Treatment of Fluoride Chemical Industry Wastewater for Defluoridation

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ABSTRACT: Effluent from industrial processes constitutes a major source of contamination of fluoride in water. Wastewater containing fluoride are commonly treated with lime or calcium salt along with aluminium salt to bring down the fluoride below 1.5 mg/L in the effluent to be discharged in water bodies. Fluoride react with calcium to form sparingly soluble calcium fluoride precipitate. The wastewater does not always behave ideally because of the presence of interfering anions. The studies on fluoride removal from wastewater generated from fluorine based chemical industries have been carried out by using lime and alum. The characterisation of waste generated from individual chemical unit were carried out to diagnose the exact nature of the problem. The treatability studies using lime followed by alum were conducted on mixed effluent collected in tank to bring down the fluoride below 1.5 mg/L in the effluent. The lime in combination with alum could bring down the fluoride concentration below 1.5 mg/L in treated effluent. A large variation was observed in effluent quality depending upon the different working units and quantity of effluent generated. The variation in alum dose to bring down the fluoride was due to change in effluent quality with respect to silica and fluoride concentration.

Keywords: Fluoride, Wastewater, Alum, Lime, Defluoridation, pH, Alkalinity.

INTRODUCTION

The high demand for water and landfill areas resulting from increased industrialization is a problem faced by entire global community. With rapid industrialization, the industrial discharge continues to grow and it needs the development of new treatment technologies that are efficient and cost effective. Effluent discharged from fluoride process industries constitutes a potential source of fluoride contamination of surface water bodies. The industries which produce fluoride bearing wastewater are aluminium, steel, enamel, pottery, glass, bricks, welding, refrigeration, oil refinery, plastic, pharmaceutical, tooth paste, automobile, chemical, single super phosphate, granular single super phosphate and other fertilizers (World Bank, 2002; Oyewale, 2005).

Chemical precipitation is widely used technology for removal of contaminants from wastewater. The precipitate formed captures contaminants and particles during formation and settles with sludge at the bottom (Tcnobanoglous and Burton, 1991).

In 1935, analysis of an effluent from lime softening plant showed lower fluoride concentration than influent, which led to lime precipitation experiments for

fluoride removal (Robosky and Miller, 1974). Wastewaters with fluoride are generally treated with lime or calcium salts sparingly supplemented with aluminium salt. (Rohrer, 1971, Zabban and Helwick, 1975). The Cheapest way to remove fluoride from wastewater is by adding lime or any calcium salt (Huang and Liu, 1999; Chuang *et al.*, 2002; Buffle *et al.*, 1985; Parthasarthy *et al.*, 1986).

Fluoride reacts with calcium to form sparingly soluble calcium fluoride and precipitates. Solubility calculation reveals that, when fluoride and calcium ions are in stoichiometric amounts, 8.18 mg/L of fluoride remains in solution and concentration may be lower due to common ion effect. However, it is observed that during defluoridation the fluoride concentration remained in treated effluent is generally higher than stoichiometric value. It is probably due to presence of interfering chemicals.

The studies deals with assessment of the quality of wastewater from fluoride chemical manufacturing industry and experiments to improve effluent treatment by reducing fluoride below 1.5 mg/L for discharge in receiving water bodies. The main fluoro-chemicals

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manufactured in the industry selected for study were sodium aluminium fluoride (cryolite), aluminium fluoride, hydrofluoric acid and brominated fluorocarbons. Other fluorine compounds such as ammonium fluoride, ammonium bifluoride, potassium titanium fluoride, potassium fluoborate, sodium fluoborate and sodium monofluorophosphate were also manufactured on a small scale. The total waste generated from industry was 1558 m³/day. The main wastewater generating units were cryolite, Aluminium fluoride and Hydrofluoric acid manufacturing units.

The effluent from cryolite plant is partially neutralised by passing over limestone pits. It then flows to Composite Effluent Collection Tank (CECT), which serves as equalisation chamber. The effluent from hydrofluoric acid, aluminium fluoride and other

fluoride chemicals manufacturing units are also collected in same CECT. The combined effluent is then treated with lime and subjected to conventional treatment of flocculation and sedimentation. The treated effluent contained fluoride above 1.5 mg/L, the limit stipulated by Pollution Control Board (PCB). The flow sheet of existing wastewater generating unit and the treatment units is depicted in Figure 1.

METHODOLOGY

During studies twenty four hours composite samples were collected from each chemical manufacturing unit and each stage of wastewater treatment for characterisation. The samples were analysed for physico-chemical parameters as per standard methods (APHA 1998) and results are presented in Table 1.

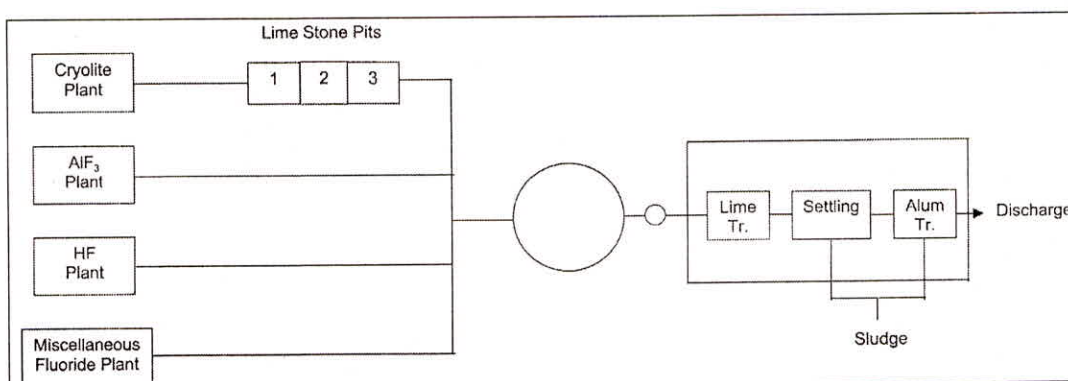


Fig. 1: Process and ETP Flowsheet of Fluoride Chemical Industry

Table 1: Average Effluent Quality at Various Plants and Different Stages of Wastewater Treatment

| Sl. No. | Parameters | Cryolite Processing | AlF ₃ Plant | HF Plant | Mixed Effluent | Effluent Neutralization Plant | Thickner |
|---------|---------------------------------------|---------------------|------------------------|----------|----------------|-------------------------------|-----------|
| 1. | pH | 0.9–1.1 | 1.1–2.8 | 2.3–2.9 | 1.6–2.0 | 6.5–11.0 | 6.9–7.5 |
| 2. | Conductivity (μm/cm) | | | | | | |
| 3. | Acid/alk. (CaCO ₃) | 165900–192760 | 372–13272 | 352–7505 | 234–15326 | 124–370 | 108–158 |
| 4. | Fluoride | 4900–16400 | 750–3050 | 400–1100 | 750–3350 | 22–40 | 7.8–16.8 |
| 5. | Sulphate | 46–1700 | 5–500 | 18–115 | 20–360 | 23–460 | 34–320 |
| 6. | Chloride | 70000–111000 | 580–5000 | 70–14500 | 580–19250 | 4700–6700 | 3700–6900 |
| 7. | Total Hardness (CaCO ₃) | 2900–3600 | 730–3000 | 350–3000 | 730–7100 | 3080–8400 | 2330–8300 |
| 8. | Calcium Hardness (CaCO ₃) | 20–90 | 20–340 | 20–80 | 340–2700 | 2590–5500 | 1670–4900 |
| 9. | Sodium | 5200–6000 | 23–44 | 32–34 | 26–850 | 44–315 | 30–315 |
| 10. | Potassium | 4–45 | 4–6 | 4–8 | 20–45 | 23–63 | 30–60 |
| 11. | Total Suspended Solids | 565–16198 | 218–245 | 363–2667 | 362–4681 | 80–10191 | 1–183 |
| 12. | Aluminium | 1500–1689 | 25–38 | 2.0–5.1 | 1516–1660 | 20–46 | 0.08–1.5 |
| 13. | Cadmium | 0 | 0.03 | 0.04 | 0.03 | 0.01 | ND |
| 14. | Iron | 2.8 | 0.14 | 2166 | 2121 | 0.17 | 0.10 |
| 15. | Manganese | 0.1 | 0.26 | 0.49 | 1.69 | 0.21 | 0.08 |
| 16. | Chromium | 0.01 | 0.04 | 0.18 | 0.13 | 0.10 | 0.10 |
| 17. | Copper | 0.09 | 0.02 | 1.98 | 0.10 | 0.02 | ND |
| 18. | Lead | 0.07 | 0.17 | 3.50 | 0.22 | 0.37 | 0.15 |
| 19. | Nickel | 0.04 | 0.13 | 0.33 | 0.29 | 0.13 | 0.05 |
| 20. | Cobalt | 0.06 | 0.19 | 0.30 | 0.26 | 0.25 | 0.21 |
| 21. | Zinc | 0.02 | 0.03 | 0.26 | 0.13 | 0.06 | 0.06 |

All values except pH and Conductivity are expressed in mg/L

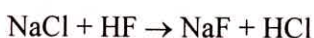
The studies were carried out with mixed effluent from CECT as well as final lime treated effluent to bring down the fluoride below 1.5 mg/L. Treatability studies were carried out with various batches of lime treated effluent to see the variation in alum dose due to variation in fluoride concentration and interference of anions present in the effluent.

Lime, alum and Polyaluminium Chloride (PAC) were used in isolation and combination for the treatment of mixed effluent. During studies the doses of lime, alum and PAC were 2.5–8.5 g/L, 1.25–8 g/L and 4 g/L respectively. The sequential treatment with lime and alum as well as lime and PAC was also investigated.

The effluent was stirred for 1 min. after adding chemicals and was allowed to settle for 24 h. Aliquots were withdrawn at regular intervals of 1, 2, 4, 8 and 24 hours for estimation of fluoride. Ammonia, sodium carbonate and sodium hydroxide were used individually in three sets to neutralize the mixed effluent to pH 7 and fluoride concentration was determined after settling. The settling characteristics of lime treated mixed effluent were studied by adding 6 g/L of lime in effluent and supernatant was drawn to see the suspended solids as turbidity and residual fluoride at definite interval of time. The supernatant after 24 h. settling was further treated with alum to reduce the fluoride upto 1.5 mg/L or less. Lime and sodium bicarbonate were used to maintain the alkalinity required for precipitation of aluminium hydroxide during alum treatment of the effluent obtained after lime treatment.

RESULTS AND DISCUSSION

The effluent characterisation indicated that the wastewater generated from cryolite manufacturing unit showed low pH 0.9–1.1 with acidity 165900–192760 mg/L as CaCO₃ aluminium 1500–1689 mg/L and fluoride 4900–16400 mg/L and silica 2.0–4.0 mg/L (Table 1). The acidity in effluent was due to the presence of hydrochloric acid generated during the manufacturing process as per following reaction,



Some acidity may also be contributed by the residual hydrofluoric acid. The analysis of effluent of cryolite plant after passing through lime stone pit showed acidity 350–32785 mg/L. and fluoride 920–3800

mg/L. The decrease in acidity was due to partial neutralization of acid while passing through the limestone pit and decrease in fluoride concentration was because of precipitation of fluoride as calcium fluoride during neutralisation. It was observed that the concentration of silica in cryolite plant effluent was increased from 1–3 mg/L to 120–240 mg/L after passing through lime stone pit. The silicates present in the limestone react with residual hydrofluoric acid present in effluent to form soluble silicates and enter into the effluent after passing through the limestone pit. After neutralization the effluent goes to common effluent collection tank. The wastewater from aluminium fluoride and hydrofluoric acid manufacturing unit showed pH 1.2–2.8 and 2.3–2.9 with acidity 750–3050 and 400–1100 mg/L respectively. The fluoride and aluminium observed was 750–3050 mg/L and 25–38 mg/L in aluminium fluoride plant effluent and 400–1100 mg/L and 2.0–5.1 mg/L. in HF plant effluent. The effluent generated from these units also flows to CECT. The mixed effluent of CECT showed 750–3350 mg/L fluoride 1500–1660 mg/L of aluminium and pH 1.6–2.0. The aluminium concentration in mixed effluent is mainly through the cryolite plant effluent. The silica concentration observed was 95–120mg/L. It was observed that the quality of mixed effluent varied with the flow rate of wastewater from individual production units, which in turn depend upon the rate of the production of chemical. The concentration of fluoride, acidity and silica was mainly influenced by working of cryolite plant. The effluent of CECT was treated with lime in neutralization plant. The settled effluent after lime treatment had fluoride and silica 7.8–16.8 mg/L and 55–95 mg/L respectively (Table 1). The pH and alkalinity of treated effluent was 6.9–7.5 and 108–158 mg/L.

The mixed effluent collected from CECT during treatability studies was kept for settling for 24 h without any treatment. The aliquot analysed after 1, 2, 4, 8 and 24 showed reduction in fluoride from 1240 mg/L to 980 mg/L at 24 h. The undissolved particles of fluoride chemicals, used in the manufacturing process contribute for fluoride concentration in the effluent. As the mixed effluent was acidic and contained aluminium, experiments were conducted for neutralization to pH 7 by using lime ammonia, sodium carbonate and sodium hydroxide separately. It was observed that, after neutralization, fluoride concentration was reduced after one hour settling from 1240 mg/L to 110 mg/L, 130 mg/L, 112 mg/L and 106 mg/L respectively. The fluoride concentration in

lime treated effluent was 8.3 mg/L, 100 mg/L, 110 mg/L and 106 mg/L after 24 h of settling in Ammonia, Sodium carbonate and sodium hydroxide treated effluent respectively. In lime neutralization the reduction in fluoride was due to formation of calcium fluoride precipitate which is insoluble in water. The significant reduction after 24 h in lime treated effluent was due to settling of suspended calcium fluoride particles. During neutralization with ammonia, sodium carbonate and sodium hydroxide, the aluminium present in effluent reduces the fluoride by coprecipitation, adsorption and complex formation and this reduction depends upon the concentration of aluminium remained in the effluent during manufacturing process. During neutralization aluminium was reduced from 1650 mg/L to 0.2 mg/L. When lime was added in combination with alum and PVC, the minimum residual fluoride achieved was 6.3 and 24.5 respectively (Figure 1). The further increase in alum or PAC did not influence the removal of fluoride from the effluent and minimum concentration of fluoride 1.5 mg/L could not be achieved. When lime and alum or PAC was added in combination, the fluoride in effluent reacted with calcium, which is more reactive, than aluminium form calcium fluoride and does not form any complex with aluminium. As per solubility product the solubility of calcium fluoride is approximately 19.00 mg/L and the fluoride ions remaining in the effluent were from soluble calcium fluoride and were nearly 8 mg/L. The variation in soluble fluoride concentration depends upon the concentration of other interfering ions present in the effluent (Roher, 1971). When the effluent was treated in two stages i.e. the lime treatment followed by alum, the fluoride in lime treated effluent reacts with alum and precipitate out by

adsorption, coprecipitation and complex formation. The minimum concentration achieved was 0.4 mg/L, when lime was used to maintain the alkalinity and 0.12 mg/L with sodium bicarbonate in II treatment stage.

The studies carried out by varying the lime concentration from 2.5 g/L to 7.9 g/L indicate that addition of 6.5 g/L of lime reduce fluoride from 1240 mg/L to 6.7 mg/L and increase in pH from 2.4 to 7.8. There was no further significant reduction in fluoride concentration with the increase of lime above 6.5 g/L but there was increase in residual fluoride with increased dose of lime. Further increase of lime resulted in higher pH but no significant decrease in fluoride. The change in pH and fluoride concentration is shown in Figure 2. Settling studies on mixed effluent at 1200 mg/L fluoride with lime showed 96.4% fluoride reduction in 2 hours which further increased to 99.2% with 24 h settling. Residual fluoride levels after 2, 8, 24 and 28 h of settling were 40, 24, 9 and 7.5 mg/L respectively (Figure 3).

The supernatant obtained after lime treatment was treated with alum (Bulusu and Nawlakhe 1979). The lime and bicarbonate were added separately to supplement the alkalinity. Lime and bicarbonate were added after addition of alum dose and pH was maintained between 6.5 and 7.00. The alum dose required to bring down residual fluoride level from 7.5 to 1.5 mg/L was 1500 mg/L. The residual fluoride upto 0.4 mg/L could be achieved with alum dose of 2000 mg/L with lime. The residual fluoride with same alum dose along with bicarbonate was 0.12 mg/L (Figure 4). The treatability studies conducted on various batches of thickener sample showed large variation in alum dose required for different batches to

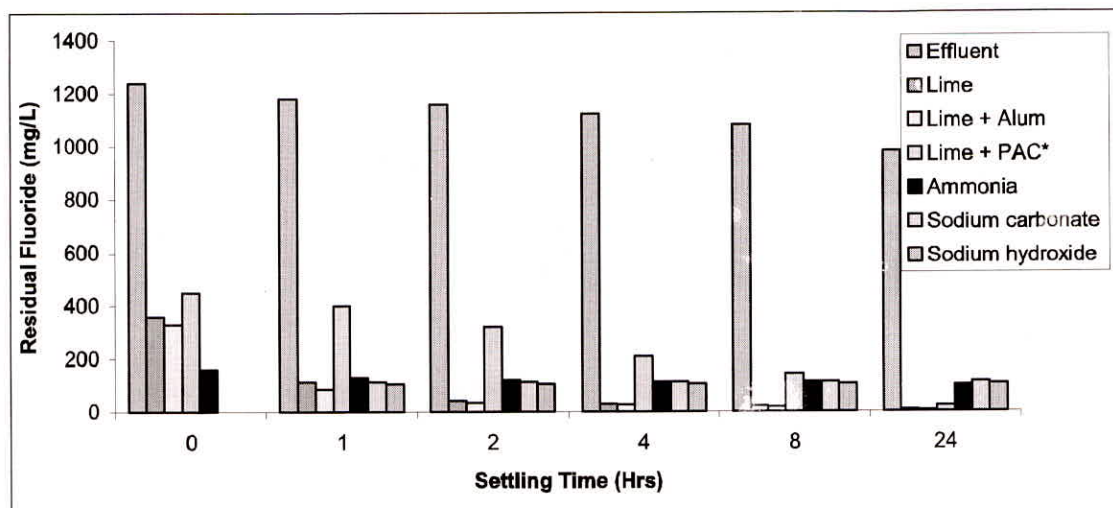


Fig. 2: Treatability studies on fluoride removal at various settling time

reduce the fluoride below 1.5 mg/L (Figure 5). For same fluoride concentration 12.8 mg/L, the alum required to reduce the fluoride to 1.6 mg/L for two different batches was 1500 mg/L and 2000 mg/L. Similarly it was also observed that the alum dose of 1500 mg/L was sufficient to bring down fluoride below 1.5 mg/L, when fluoride in thicker effluent was 16.5 mg/L. This was because of variation in concentration of silica in effluent. The silica concentration in these batches of lime treated effluent was 85 mg/L, 95 mg/L and 65 mg/L. Silica has adverse effect on removal of fluoride from water and the dose of alum increases with increase in silica concentration in effluent (Nawalkhe *et al.*, 1975, Joshi and Nanoti, 2003). This silica is introduced in effluent when effluent from cryolite manufacturing unit passed through lime pit for neutralization. The variation in silica depends upon the dissolution of silica from limestone pit during partial neutralization of cryolite unit wastewater and in turn depends upon the concentration of residual hydrofluoric acid in wastewater, quality and quantity of limestone exposed to contact with wastewater, flow rate and contact period of effluent.

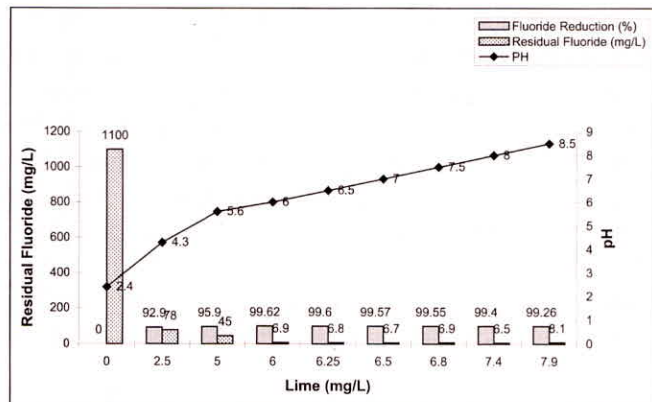


Fig. 3: Effect of lime dose on pH and fluoride in mixed effluent

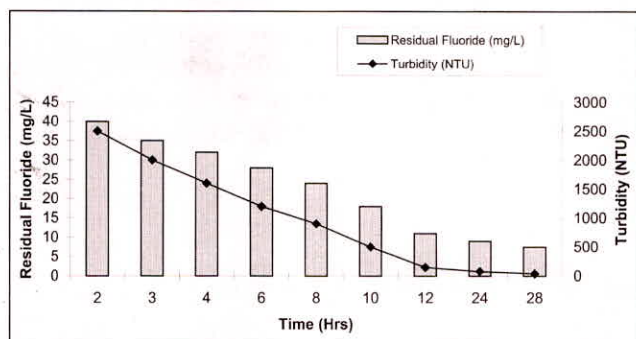


Fig. 4: Settling characteristic of mixed effluent after lime addition and its effect on fluoride reduction

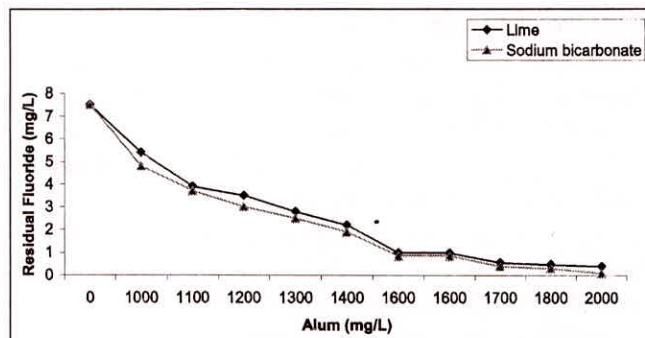


Fig. 5: Effect of addition of alum with lime/sodium bicarbonate on fluoride reduction

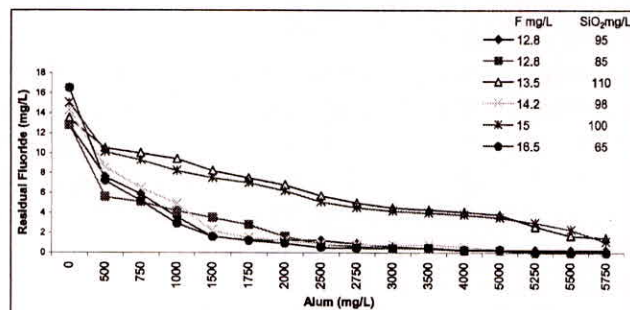


Fig. 6: Reduction in fluoride with alum at different silica concentration in lime treated effluent

It is a common practice to use lime for treatment of effluent in various industries. There is no significant difference in residual fluoride when alum was used separately with lime and bicarbonate to maintain the alkalinity in two stage treatment. The alum in combination with lime in two stage treatment could reduce the residual fluoride concentration to 1.5 mg/L and below. The dose of alum varies with the change in effluent quality with respect to fluoride and silica.

CONCLUSIONS

The study indicated that the treatment of effluent having high concentration of fluoride with lime-alum combination is very much effective to bring down the fluoride level to permissible level of 1.5 mg/L and the precipitation of calcium fluoride is governed by the kinetics of precipitation process. The dose of alum and lime is to be decided with the concentration of fluoride and silica in wastewater to bring down fluoride level within permissible level.

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