

# Selective Fluoride Removal

By Kedar Oke, Dr. Stefan Neumann, & Beryn Adams

Fluoride concentrations of less than one milligram per liter can easily be achieved by utilization of a new adsorption method based on a regenerable aluminum doped chelating resin. A case study illustrates practical aspects of the implementation and lab data gives more technical background on important parameters for process design.

## Introduction

Fluorides are found in the waste discharges from process streams in a number of industries. Significant amounts of fluoride come from the following industries: semiconductor, photovoltaic, glass manufacturers, electroplating, steel and aluminum, pesticides and fertilizer. The fluoride concentration in untreated effluent can vary over a large range, and the allowable level for discharge depends on the place of disposal. When there is any risk of fluoride seeping back to water supplies, a limitation of around one ppm fluoride is typical. Apart from treatment of industrial waste streams, the other main application of fluoride removal is the treatment of potable water supplies to reduce the fluoride content to 1 ppm or less.

High levels of fluoride are generally reduced by adding calcium salts, causing precipitation of  $\text{CaF}_2$ . However due to certain rest-solubility and kinetic effects the fluoride concentration after precipitation is normally 7–15 mg/L, higher than the acceptable limits. Since pollution control boards typically require an effluent limit of 1 mg/L fluoride, these saturated  $\text{CaF}_2$  solutions must undergo further treatment. There are two known treatment processes:

- 1) Adsorption on activated alumina
- 2) Removal by selective ion exchange resin

In this article we will be focusing on removal of fluoride by a fluoride selective ion exchange resin.

## Principle Of The Process

The fluoride selective ion exchange resin is a chelating resin loaded with aluminum ions. The functional group of the resin is an amino-methyl-phosphonic-acid-group, or AMPA-group. The phosphonic acid group has a high tendency to bind aluminum. This strong binding force can be deduced from the fact that aluminum-phosphate has a low solubility in water. The AMPA-resin was chosen as the most suitable resin for this application since it tightly binds the aluminum, resulting in low leakage of aluminum during operation. The theoretical structure of the AMPA functional group loaded with aluminum-chloride is shown below in Figure 1.

It is significant that the aluminum ion is connected with two binding arms towards the AMPA-group, while the third binding arm of the aluminum core is attached to one chloride ion. In contact with fluoride containing solutions the chloride is exchanged by fluoride. Other ions such as sulfate or nitrate do not interact with the aluminum ion since their affinity to aluminum is very low (this can be deduced from the high solubility of aluminum sulfate and aluminum nitrate in solution).

One liter of Lewatit MonoPlus® TP260 can be doped with approximately 1.1 mole of aluminum. Supposing every aluminum ion absorbs one fluoride ion, the maximum theoretical uptake (total capacity) of fluoride is about 21 g/L. As usual, operating capacities experienced under operating conditions are significantly lower than this.

After exhaustion of the resin, the regeneration can be carried out using aluminum chloride solutions (a solution of  $\text{AlCl}_3$  or  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ). The  $\text{Al}^{3+}$  will form several complexes with fluoride in solution, such as  $[\text{AlF}]^{2+}$ ,  $[\text{AlF}_2]^+$ ,  $[\text{AlF}(\text{OH})]^+$ ,  $[\text{AlF}_4]^-$  and others. These compete with the fluoride fixed on the functional group of the resin. Due to effects of mass action and shift of equilibrium the fluoride is extracted from the resin

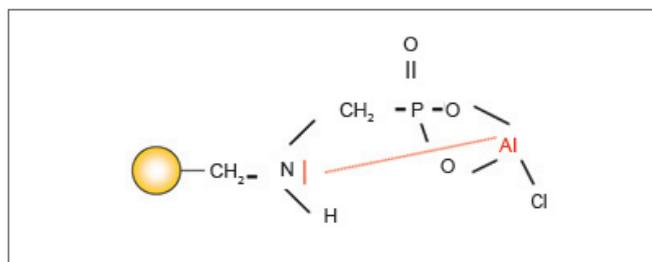


Figure 1: Functional Group Of The AMPA-Resin Lewatit MonoPlus® TP 260 After Loading With Aluminum-Chloride

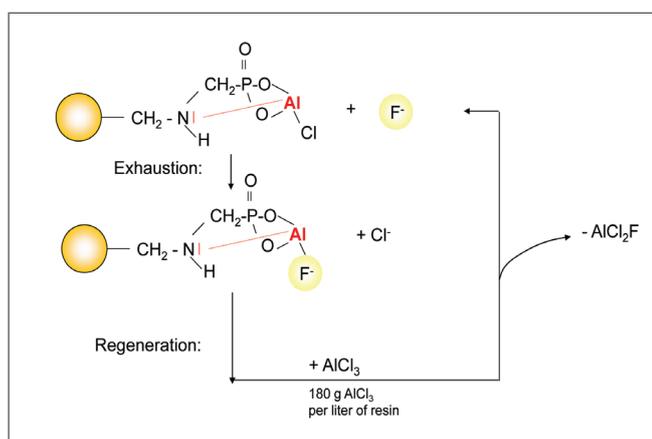


Figure 2: Reaction Scheme Of The Selective Fluoride Removal By Aluminum Doped Lewatit MonoPlus® TP 260

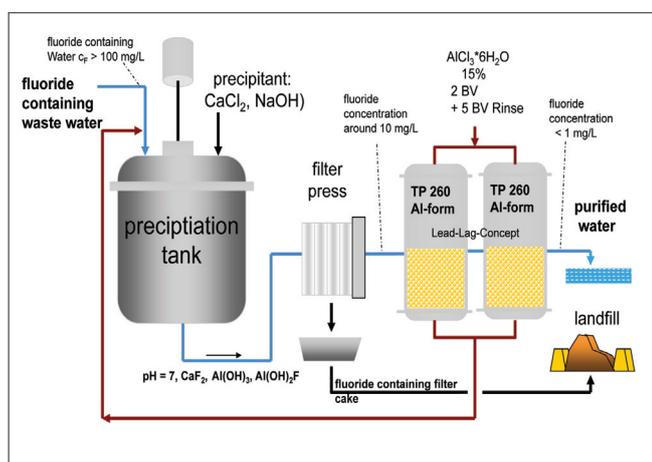


Figure 3: Principle Of Using Fluoride Selective Resin As A Polishing Filter Unit Behind  $\text{CaF}_2$  Precipitation

and exchanged by chloride. Hence after the treatment with the  $\text{AlCl}_3$  solution the resin is still in the aluminum loaded form with a chloride-ion connected to it.

After this operation, the spent regenerant solution containing aluminum salt and fluoride can be treated by precipitation. Usually this is done by adding milk of lime into the weakly acidic waste water: the aluminum will precipitate as aluminum hydroxide, while fluoride will form  $\text{CaF}_2$  and  $\text{Al}(\text{OH})_2\text{F}$ . The precipitated solids can be filtered and sent to landfill.

In case the ion exchanger is used as a polishing filter behind a lime precipitation unit, the spent regenerant can be discharged into this unit and no extra spent regeneration treatment unit is required. Hereby the excess aluminum coming from the ion exchanger unit can support the performance of the precipitation unit and partially substitute the chemical dosage required there.

The whole operating cycle is schematically depicted in figure 2. The concept of a precipitation unit followed by the ion exchanger as a polishing filter is shown in figure 3.

## Case Study

### Technical Equipment / Plant Concept /Performance

A unit containing Lewatit MonoPlus® TP 260 resin has been installed in a major chemical manufacturing company in Gujarat, India. It has been reliably treating the full effluent stream of a production facility for more than a year and is still operating successfully. The plant has consistently maintained the fluoride level in the treated effluent to less than 1 mg/L. A photo of the plant is given in figure 4.

The concept of the plant comprises initial precipitation of the fluoride with  $\text{CaCl}_2$  followed by filtration. The filtrate is polished with the ion exchanger. The effluent stream flow is around  $1.5 \text{ m}^3/\text{h}$ . The  $\text{CaCl}_2$  precipitation process reduces the fluoride content from around 100 mg/l down to 8 – 18 mg/l.

Fluoride feed concentration: 9 mg/L; feed pH = 5.8; specific flow rate 5 BV/h; salt background (TDS) high due to precipitation upstream but not determined.

In this plant there is a single ion exchange filter, containing 300 liters of resin. A representative filtration curve is shown in figure 5. It can be concluded from the curve that the break through of fluoride at 1 ppm occurred after 286 BV, which equals 57 hours of operation. With an influent fluoride concentration of 9 mg/l, the operating capacity of the filter is therefore about 2.6 grams of fluoride adsorbed per liter of resin.

After break through the filter is regenerated by pumping 3 BV of a 5.5%  $\text{AlCl}_3$  solution down through the bed at 5 BV/h. The operation is followed by a 10 min upstream rinse at 10 m/h linear velocity and a final rinse by 2.5 BV of clean water at 5 BV/h.

The ion exchange wastewater (comprising spent regenerant, backwash and final-rinse water) is discharged into a cone shaped tank equipped with an agitator, pH control and  $\text{CaCl}_2$ ,  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$  dosage. Fluoride and aluminum are precipitated

and the suspended particles are settled. The sludge is then thickened and finally dewatered in a filter press.

The user of the plant takes advantage from the following benefits:

- Able to safely meet the pollution control board norms for waste water discharge
- Synergism with the upstream precipitation unit: no additional waste stream generated, as the spent regenerant from the ion exchanger is treated using the existing on-site process
- Regenerable adsorber material that can stay in place for several years

## Results Of Lab-Tests On Ion Exchange Based Fluoride Removal

Complementary laboratory tests were conducted during the development of this technology for selective fluoride removal. This generated interesting data and in particular gave insights into the influence of fluoride-concentration, pH and salt content of the feed solution on the operating capacity.

Figure 6 demonstrates operating capacities as a function of feed concentration under two different salt background conditions. As usual the operating capacity increases with increased feed concentration, which is normal for adsorption processes. Secondly, it was found that operating capacities are higher in cases where the salt content in the feed is higher. This is a quite unexpected result since typically the operating capacity decreases with higher concentration of competing ions.

We propose the explanation that higher salt concentrations in solution increase the proportion of aluminum ions (shown in Figure 1) having one binding leg attached to a dissolved ion, making it available for exchange of fluoride (according to the scheme given in Figure 2). If there is less salt in the background the aluminum ion in the complex tends more to coordinate to the resin functional groups with all three binding legs. In that configuration the aluminum seems to have a lower tendency to adsorb fluoride.

Figure 7 shows the effect of pH on the operating capacity measured under low salt background conditions. Here it was



Figure 4: Fluoride Selective Ion Exchanger Operated At A Major Chemicals Manufacturing Company In Gujarat, India

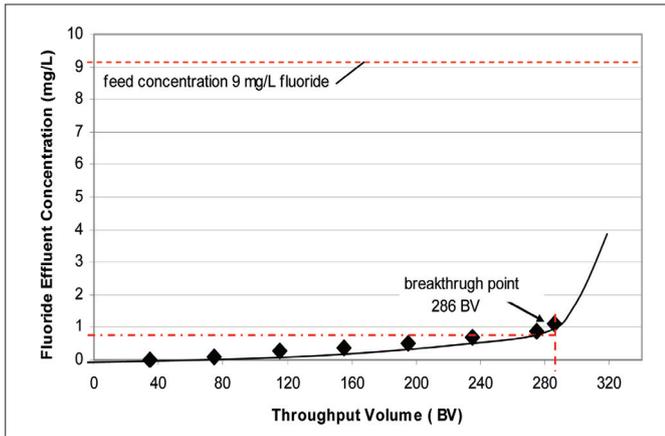


Figure 5: Original Filtration Curve Generated From Data Measured At The Gujarat Reference Plant.

found that the operating capacity is highest under weakly acidic conditions (pH = 4) and decreases roughly by 50% in weakly alkaline conditions (pH = 10). Hence it can be concluded that slightly acidic to neutral conditions in the feed water are favorable for the process.

### Conclusion & Outlook

The plant experience referenced has been very successful and as a result other factories are investing in resin based treatment to solve their wastewater problems. In the near future

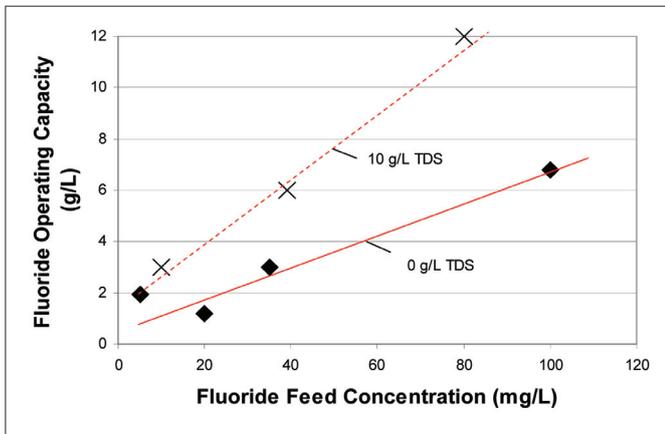


Figure 6: Effect of feed concentration on operating capacity under two different operating conditions: With 10 g/L total dissolved solids (TDS) in the background and with demineralized water background (0 g/L TDS). Specific Velocity (SV) = 10 BV/h, 1.3 moles of  $Al^{3+}$  doped per liter of resin Lewatit MonoPlus® TP 260, feed pH = 3.6; salt mixture for TDS background containing 50% p.w. NaCl and 50%  $Na_2SO_4$ .

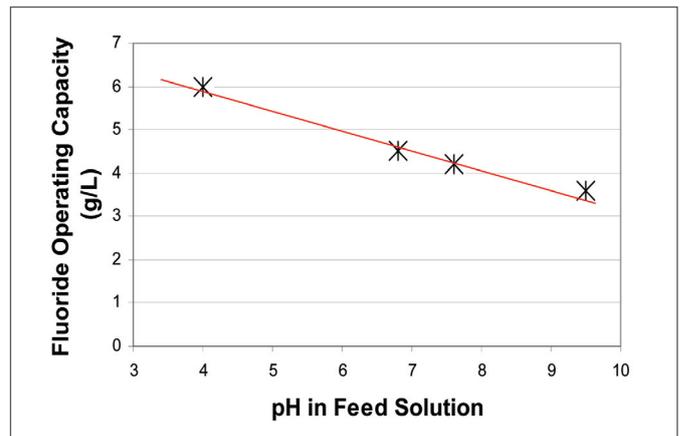


Figure 7: Effect of pH on fluoride operating capacity. SV = 10 BV/h, 1.2 moles of  $Al^{3+}$  doped per liter of resin Lewatit MonoPlus® TP 260, concentration of fluoride in feed = 127 mg/L, demineralized water background

more projects utilizing this process will be commissioned in India. Further work is planned to investigate reducing aluminum consumption during regeneration. While already an economically attractive process, this should lead to reductions in operational cost as well.

Further Laboratory work is underway to adapt the process to make it suitable for potable water applications. As Lewatit MonoPlus® TP 207 has approval for use with drinking water; it is used in place of Lewatit MonoPlus® TP 260. The application method and performance is comparable when using Lewatit MonoPlus® TP 207, leading to very optimistic expectations about the potential. The initial aluminum leakage of the freshly regenerated column can be successfully removed by a polishing column behind the fluoride selective filters.

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