TREATMENT OF AQUEOUS EFFLUENTS FOR FLUORIDE REMOVAL

Introduction

The treatment of fluoride bearing effluents is an area of increasing concern, as fluoride content in drinking water has become a part of the public and regulatory agenda. Industrial operations, such as petroleum refineries, aluminum smelters, and rapidly growing semi-conductor production facilities, generate effluents that are high in fluoride content and require treatment prior to their discharge into the public streams.

In recent years, a considerable amount of work has been done to remove the fluoride species from these effluents. As these effluent streams may contain residual amounts of hydrofluoric acid, they may also require pH adjustment to meet regulatory specifications before they can be discharged.

Precipitation of Fluoride:

While Reverse Osmosis, Ion Exchange and Molecular Sieves can be used in the removal of the fluoride species from effluents, they have various limitations. Along with these processes being expensive for the removal of high concentrations of the fluoride species that are usually encountered in the industrial streams, they are also adversely affected by solid contents in the effluent streams. However, these processes may still be used for the final polishing of the treated effluent.

Precipitation of fluoride species into a chemically stable form is an option that has become a common practice in the industry. Fluorides of alkali earth metals have low solubility. Their respective solubility in water is given in Table 1.

Table 1
Water Solubility of Alkaline Earth Metal Fluorides*

	Solubility (g/100 ml water)
BaF_2	0.12
SrF_2	0.011
MgF_2	0.0076
CaF_2	0.0016

** CRC Handbook of Chemistry and Physics, 65th Edition, CRC Press*

As can be seen in Table 1, among the alkali earth metal fluorides, CaF_2 is least soluble in water. Consequently, removal of fluoride from the effluents by converting it into CaF_2 has become the most widely used method of treatment. MgF_2 is considerably less water soluble than BaF_2. Its solubility is comparable to SrF_2. However, it is many times more soluble than CaF_2.

Due to high solubility of BaF_2, use of Ba electrolytes is not considered even an option for the removal of fluoride from the effluents. Strontium (Sr) or magnesium (Mg) electrolytes can be used for removing the bulk of fluoride species from the effluents, but they would still leave a considerable concentration of fluoride in the treated effluent. Because of the high cost of strontium electrolytes its use is not a viable economic option.

Precipitation of Fluoride with Hydroxides and Chlorides:

Lime Vs Magnesium Hydroxide: Lime [$Ca(OH)_2$] and magnesium hydroxide [$Mg(OH)_2$], respectively, are good source of calcium (Ca) and magnesium (Mg). Solubility of lime in water is much higher than magnesium hydroxide (0.185 g/100 ml Vs 0.0009 g/100 ml). Magnesium hydroxide, with its extremely low solubility, will require addition in large quantities in order to remove the fluoride species from the effluents. Consequently, while it could be used for the pH neutralization, its use for the removal of fluoride becomes highly restrictive. Lime, on the other hand, apart from being an effective additive for pH neutralization, due to its higher solubility than magnesium hydroxide, its addition to the effluent would provide larger available interactive cationic species for fluoride uptake than what magnesium hydroxide would provide. Nevertheless, MgF_2 is much more soluble than CaF_2 (Table 1), which makes magnesium hydroxide less effective for the removal of fluoride from the effluent streams.

Lime Vs Calcium Chloride: Lime and calcium chloride ($CaCl_2$) are both used in the industry for the treatment of fluoride containing effluents. A chemical comparison between these additives is given in Table 2. It is noted that while lime contains higher concentrations of the calcium species than calcium chloride (54.05% Vs 36.36%), its solubility is much lower (0.185 g/ 100 ml Vs 74.5 g/100 ml). Consequently, when lime is added to the effluent, there is a significantly lower concentration of calcium species in the system that is available for interaction with the fluoride ions.

Table 2
Available Calcium Species from Lime and Calcium Chloride for the Removal of Fluoride in the Effluents

	Stoichiometrically Available Ca (wt%)	**Water Solubility* (g/ 100ml)**
$CaCl_2$	36.36	74.5
$Ca(OH)_2$	54.05	0.185

** CRC Handbook of Chemistry and Physics, 65th Edition, CRC Press*

Lime has been frequently used for the treatment of these streams with duel objectives. First, its alkalinity is able to increase the pH of the effluent; and second, the calcium content of lime reacts with the fluoride ions and form chemically stable calcium fluoride precipitate. However, as lime has low water solubility (0.185 g/100 ml water), it requires a large volume to adequately precipitate the fluoride species. Such treatments, particularly for the treatment of streams with high fluoride contents, render undesirable effects. First, it increases the pH to a level above the permissible discharge limit; and second, sparsely soluble lime particles become the major constituent of the precipitated sludge. This in addition to increasing the sludge volume, due to its high alkalinity, may also require treatments prior to its disposal.

Concluding Remarks:

Precipitation of the fluoride species into a chemically stable form is the most effective option for the removal of fluoride from effluent streams. Calcium chloride, due to the low solubility of calcium fluoride precipitate that it forms, is superior to barium, strontium and magnesium electrolytes. Calcium chloride is also preferred to lime due to its higher solubility and the lower ratio of additive to effluent that is required. The benefits of using calcium chloride over lime are summarized below:

- Small volume required per unit fluoride removal
- Better rate of fluoride removal
- Ease of dispensing and monitoring of the additive
- Better materials handling
- Better control on the pH of the treated effluent
- More cost effective

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