

FLUORIDES REMOVAL TECHNOLOGY

PATENT 2003 A 02590



Fluoride removal in drinking water and in wastewater has been subject of many publications and studies, that have better progressively developed the aspects of toxicity on the man and on the environment.

The manufacturing firms of fertilizers, of **aluminium and glass**, traditionally have to tackle this problem and other activities as **electronic production, surface treatments of copper and aluminium and stainless steel** produce wastewater with a strong presence of Fluoride ion

TREATMENT METHODS

An outline of the applicable systems of treatment to the drinking water containing Fluorides is reported both on the USEPA and AWWA sites www.awwa.org reporting Best Available Technology in synthesis:

- 1) ABSORPTION on Activated Granular Alumina (pH 5,0–6,0) and following washing and regeneration
- 2) Reverse Osmosis
- 3) ED and EDR (Reverse Electrodialysis)
- 4) ABSORPTION on Bone Char

These techniques, applicable for the elimination of Fluorides in low concentrations, have relevant costs of investment and a complex management, justifiable therefore to big water flow treatments. Companies and Organizations have studied systems of precipitation of the Fluoride ion in sedimentation plants, suitable for small and medium flow dimension waste water production.

A wide literature is available on methods of precipitation of the Fluorides with salts of Calcium, Aluminum and Iron, that exploit the lower Products of Solubility of the correspondents fluorinated salts.

The treatment of water containing Fluorides, has been traditionally realized with Lime in alkaline pH range.

The reaction is :



The addition of an anionic poly-acrylamide (High Molecular Weight) allows the agglomeration of the flocks and a quick clarification

The fundamental problem that exists using this technique, arises from the low solubility of the Calcium Hydroxide (around = 0,07%) that therefore requires an excess of reagent to get a complete precipitation. For against, the solubility of the Calcium Fluoride ($K_{sp} = 4 \cdot 10^{-11}$) doesn't obtain a complete removal of the Fluorides as required by the discharge Limits.

Using Iron salts (II) (Sulfate) to get the formation of $(\text{FeF}_6)^{3-}$, the results aren't totally satisfactory.

The study on the formation of Aluminum complexes with the Fluorine has been developed (Garrison Sposito: The Environmental Chemistry of Aluminium—CRC Press—1989).

Experimental trials confirmed the ability of absorption of Fluoride ions on the Aluminum Hydroxide matrix due to the dimension of the ion F^- - that is similar to the ion OH^- -

Experimental trials carried out with PAC or PASS and Alum not always obtained reproducible results

INTECNA's method, allows to carry out the reaction in more reduced timing and to obtain removal performance higher than 98 %

INTECNA's PATENTED product **HYCOR FL** is a mixture of precipitated Aluminium Oxide and re-dissolution of a complex Aluminium salt at pH value < 1

METHOD DESCRIPTION

INTECNA's method for Fluorides removal is suitable for potable water production and for wastewater treatment.

The method provides the following two steps :

1.- LIME PRETREATMENT (WHEN AND IF NECESSARY)

The usual treatment with **cheap** lime in slurry allows to treat concentrated flows (Fluorides > 1500 ppm) rising from washing or process wastewater where Hydrofluoric Acid (or Ammonium Fluoride) has been used.

Such treatment obtains residual Fluoride content in the range of 25 – 60 ppm depending on contact time, reaction conditions etc.

2.- HYCOR FL TREATMENT

Limpid water from pre-treatment step has been treated as follows :

- Mixing of HYCOR FL in a well stirred reactor for a reaction time of 3 – 5 minutes

- pH adjustment in a second reactor with Lime slurry until pH value of 7,5 – 7,8

- Anionic Polymer solution (HYCRAM A 760) addition to allow a formation of big flocks

- Sedimentation in a final settling tank

Method is a conventional sedimentation process and HYCOR FL characteristic is his capacity to form complexes with **Fluoride having Solubility Product (K_{sp}) 1000 times lower than Calcium Fluoride.**

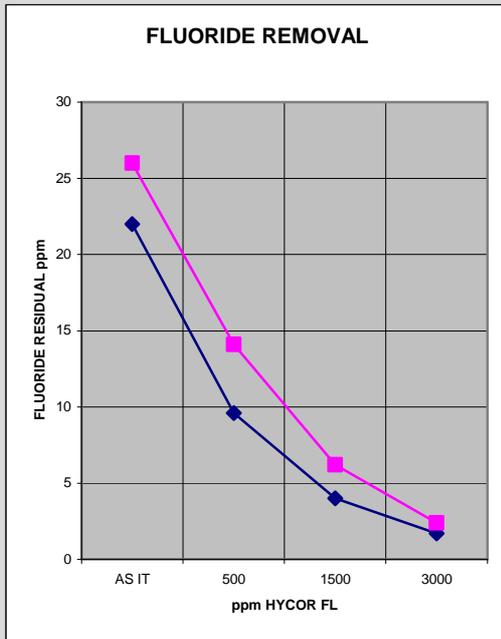
Sometimes starting Fluoride content is in the range 80 – 130 ppm, (for example in Wheels production wastewater). In such case, lime pre-treatment is not required. In these plants, HYCOR FL has been used directly on wastewater flow (composed by alkaline and acidic flow) and dosage point has been done in acidic flow.



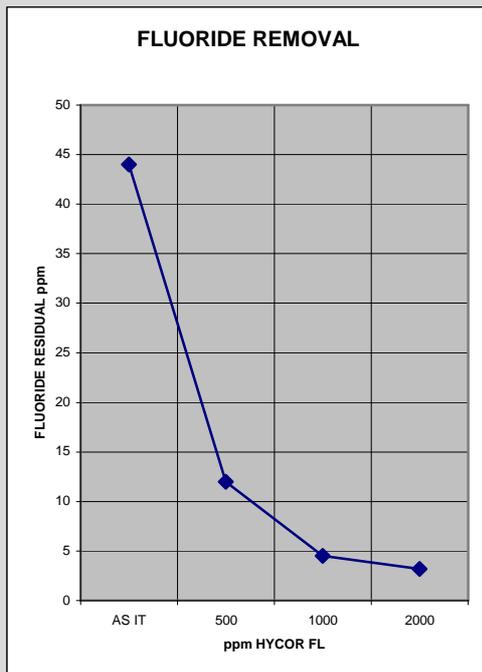
Typical sludge aspect of HYCOR FL treated wastewater



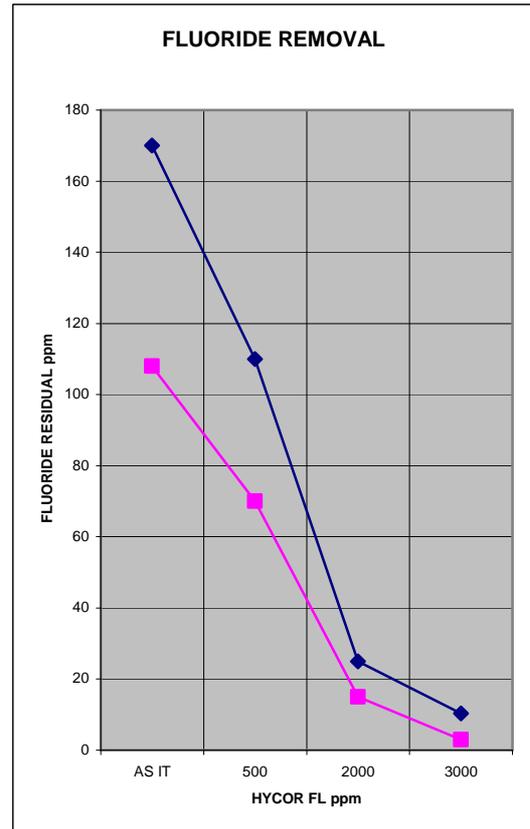
CASES HISTORIES



1.- STAINLESS STEEL SURFACE TREATMENT



2.- GLASS INDUSTRY



3.- ALUMINIUM SURFACE TREATMENT

TREATMENT BENEFITS

1. The described method is suitable to treat wastewater containing Fluorides in the range of 50 – 100 ppm to allow a residual selective removal until final value < 2 ppm
2. The method is a simple sedimentation plant and does not affect water quality, because does not increase other parameters
3. The investment cost is very acceptable and the treatment cost is lower when compared with other technologies
4. Sludge production is acceptable and the quality improved the efficiency in press filtration by obtaining a final dry content more than 40 %

