

# Fluidized bed reactor for fluoride removal

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## Abstract

The common methods for fluoride removal from industrial wastewater involve chemical precipitation. This process generates large amounts of a water rich sludge requiring disposal with increasing costs. Due to the high water content and the low quality of the sludge, reuse of fluoride is not an economical option. The crystallization in a fluidized bed reactor offers an alternative to the conventional precipitation.

The influence of the supersaturation and recycling conditions in order to control the efficiency of the process was studied. A high supersaturation level decreases the fluoride removal efficiency due to the formation of small particles (fines). The main mechanism concerning the precipitation of calcium fluoride in a fluidized bed was established. Fines were produced by nucleation in liquid phase (homogeneous and secondary nucleation) in the reactor and the dilute fluoride tank, in order to decrease the amount of fines it is very important the control of the supersaturation.

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## 1. Introduction

The objective and principles of the environmental policy in the European Union (EU) consists of preventing, reducing and as far as possible eliminating pollution by giving priority to intervention at source and ensuring prudent management of natural resources, in compliance with the principle of pollution prevention. The goal is an integrated pollution control so that it is possible to reduce the emissions in order to promote the sustainable development. This concept aims to harmonize the economical, social and environmental dimensions of development strategies and it is now a key feature of policy making in the EU.

The Council Directive 96/61/EC set up EU legislation on Integrated Pollution Prevention and Control (IPPC) [1]. This was enacted in Spain in July 2002 under the Pollution Prevention and Control Law 16/2002 [2]. Installations detailed in the directive will be phased into the new regime on a sectoral basis up to the year 2007.

Furthermore, an important new feature to be remarked is the supplementing of permitting with voluntary environmen-

tal management systems, particularly ISO 14001 and EMAS, and with energy conservation agreements.

In accordance with IPPC Directive, the installations are operated in such a way that waste production is avoided. However, in case it is technically and economically impossible it should be disposed off avoiding or reducing any impact on the environment.

In this sense, fluoride wastewater is a typical effluent which neutralization is very important due to the hazardous effects. Fluoride is considered as a pollutant under regulation, therefore, it is necessary some treatment to reduce its concentration.

The method for fluoride removal from industrial wastewater generally involves a chemical precipitation process [3–5]. Several treatment methods to remove fluoride have been employed. Precipitation is the most common treatment technology. Fluoride is removed by adding an alkali compound such as lime or hydrated lime to adjust the wastewater pH to the point where the fluoride exhibits minimum solubility. Then the precipitated fluoride is removed by a proper solid–liquid separation technique such as sedimentation and filtration. The conventional fluoride removal process generates huge amounts of a water rich sludge, which has to be disposed off with increasing costs. Due to the high water

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### Nomenclature

$A$	crystal surface area
$b$	nucleation order
$B$	primary nucleation rate
$C_1, C_2$	constants
$(Ca^{2+})$	activity of calcium
$D$	secondary nucleation rate
$(F^-)$	activity of fluoride
$h$	nucleation order w.r.t. $N$
$j$	nucleation order w.r.t. $A$
$K_{sp}$	solubility product for calcium fluoride at the temperature under study
$SV$	linear velocity
$T$	temperature
$w_{F,dis in}$	flow of the component fluoride at the reactor inlet
$w_{F,dis out}$	flow of fluoride at the reactor out
$w_{F, fines}$	flow of fluoride as fines
$X$	conversion
$X_F$	fines fraction
$X_R$	efficiency
<i>Greek symbols</i>	
$\beta$	supersaturation ratio
$\gamma_s$	surface energy

content and the low quality of the sludge, reuse of fluoride is not an economical option.

Recently, several processes for fluoride removal from wastewaters have been developed. The fixed bed packed with granular calcite allows high efficiencies of fluoride removal without sludge generation [6,7]. However low effective conversion rates of calcite and formation of lumps in the fixed bed are obtained. Precipitate flotation [8] and other processes that involve recycle to reduce sludge and costs [9] are also used, but they are not able to recover the product.

Table 1  
Estimate costs and benefits evaluation

Type of costs	Costs <sup>a</sup> (USD/kg)	Remarks
Capital costs		Depending on capacity
Operating costs		
Depreciation	3–25	Depending on capacity
Chemicals	0.50–2.50	Depending on concentration
Energy	0.25	
Staff		1 h per day
Maintenance		3–5% of investment
Benefits		
Reuse	0–14.50	
Reduction of chemical waste	2–8	Depending on concentration in sludge
Saving on investment for precipitation plant	3–12	In the case of final treatment
Reduction of discharge fee	30–40	In the case of final treatment

<sup>a</sup> Per kilogram of recovered anion.

An alternative option is to apply controlled crystallization in a fluidized bed reactor instead of conventional precipitation. The operating cost in the crystallization process are similar to the conventional precipitation. Nevertheless the derived benefits are important (reuse, reduction of chemical waste and reduction of discharge fee). Table 1 shows an estimate costs evaluation [14].

Continuous experiments in a fluidized bed reactor were carried out in order to study the influence of the supersaturation conditions and the recycle conditions.

## 2. Experimental section

### 2.1. Process and system description

The process is based on the crystallization of calcium fluoride upon seed grains in a fluidized bed using seed grains of silica sand.

The chemistry of the process is similar to the conventional precipitation. By dosing a calcium salt to the wastewater (e.g. lime, calcium chloride), the solubility of  $CaF_2$  is exceeded and fluoride is converted from the aqueous solution into solid crystal. Process includes the following reactions:



The reactor consists of a vessel partially filled with suitable seed material in which the fluoride water is pumped upwards direction through the reactor at a velocity that ensures the fluidization of the pellets.

The fluoride-covered grains are removed from the bottom of the bed and replaced by fresh seed grains.

Simultaneously to the precipitation upon the grains (heterogeneous nucleation or “nucleated precipitation”) nucleation in the liquid phase (homogeneous and secondary nucleation or “discrete precipitation”) and mineral layer abrasion take places. Fig. 1 shows the nucleated and discrete precipitation.

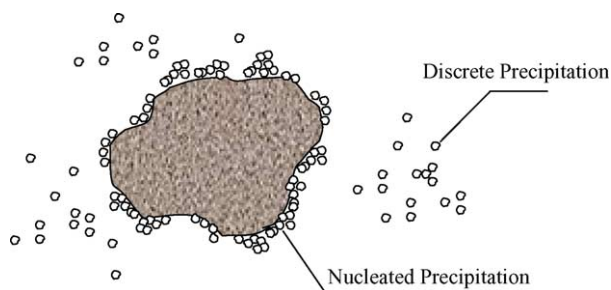


Fig. 1. Nucleated and discrete precipitation.

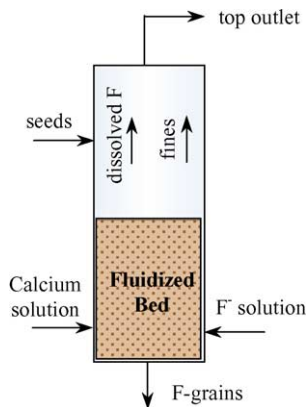


Fig. 2. Schematic representation of the fluidized bed reactor.

The nucleation in the liquid phase and abrasion of the grains in the fluidized bed lead to small particles (referred to as “fines”), which leave the reactor at the top and form, together with the remaining fluoride in solution, the fraction of the fluoride that is not recovered in the reactor [10]. The scheme of the reactor and streams is indicated in Fig. 2.

The efficiency of fluoride removal is calculated by measuring the concentration of both fines and dissolved fluoride in the outlet stream. The dimensionless conversion ( $X$ ), fines fraction (nucleation and abrasion processes) ( $X_F$ ) and efficiency (precipitated fluoride upon sand) ( $X_R$ ) are defined as [10]:

$$X = \frac{w_{F,dis in} - w_{F,dis out}}{w_{F,dis in}} \quad (3)$$

$$X_F = \frac{w_{F,fines}}{w_{F,dis in}} \quad (4)$$

$$X_R + X_F = X \quad (5)$$

Fig. 3 shows the fluidized bed reactor circulation system.

Recycle ratio is required to obtain a fluoride concentration to prevent primary nucleation. In addition, another recycle is necessary in order to obtain the appropriate calcium dosage.

### 3. Materials and methods

The reactor was filled with sand with a diameter of 0.15–0.30 mm and density of 2.56 g cm<sup>-3</sup>. The static

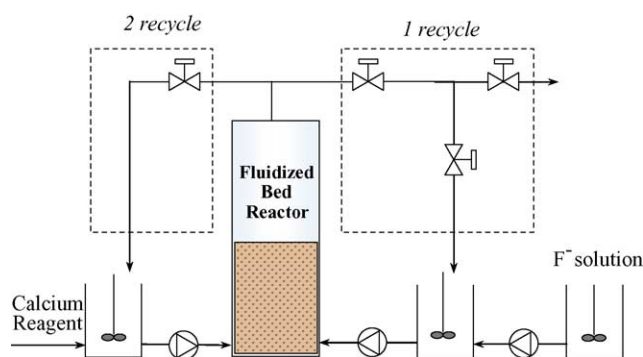


Fig. 3. Schematic diagram of the experimental setup.

height of the packed sand in the reactor was  $0.20 \pm 0.01$  m.

The synthetic fluoride wastewater used in the feed was obtained by diluting a more concentrated fluoride solution. Fluoride wastewaters of 300–2000 mg l<sup>-1</sup> were treated.

Chemical grade reactants and demineralized water were used. The temperature in the fluidized bed was  $20 \pm 2$  °C.

The calcium reagent and fluoride solutions were injected into reactor using two peristaltic pumps. The samples were taken from the effluent of the reactor at regular time intervals. pH measurements were conducted by a pH meter.

The concentrations and flow rates of the feed and outlet streams were measured. Dissolved fluoride was analyzed by specific fluoride ion electrode and fluoride contained in the fines was calculated from the filtered solids with a filter of 0.45 μm.

The experimental planning is listed in Table 2 that details the concentration and flow rates of the inlet streams to the reactor (calcium reagent and fluoride solutions), and the linear velocity (SV).

### 4. Results and discussion

The supersaturation has an important effect on the process related to the nucleation mechanism, to the fines formation and the efficiency of the process. The degree of saturation can be defined as a ratio of the ion activity product to the solubility product as

$$\beta = \frac{(Ca^{2+})(F^{-})^2}{K_{sp}(CaF_2)} \quad (6)$$

At a given pH and overdose of calcium, the supersaturation depends only on the fluoride concentration of the wastewater. Fig. 4 reveals the effect of the inlet fluoride concentration referred to the supersaturation on the fines generation according to the experiments showed in Table 2. From this figure, it is checked that high supersaturation improves the homogeneous nucleation and therefore the generation of fines [11–13]. Fluoride concentration at the bottom of the reactor has to be kept below a critical value in order to prevent discrete precipitation. Fluoride concentration of 100 mg l<sup>-1</sup> implies 10% of

Table 2  
Experimental conditions

Exp. no.	$C_{F,in}$ ( $\text{mg l}^{-1}$ )	$(\text{Ca/F})_{in}$ (-)	$C_{F,in}$ reactor ( $\text{mg l}^{-1}$ )	$F_{F,in}$ ( $\text{ml min}^{-1}$ )	$F_{Ca,in}$ ( $\text{ml min}^{-1}$ )	$F_{recir,F}$ ( $\text{ml min}^{-1}$ )	$F_{recir,Ca}$ ( $\text{ml min}^{-1}$ )	SV ( $\text{m h}^{-1}$ )
SM.1	200	1.0	100	250	250	–	–	30
SM.2	300	1.0	150	250	250	–	–	30
SM.3	600	1.0	300	250	250	–	–	30
SR1.1	300	1.1	150	250	250	–	–	30
1R1.1	2000	1.1	136	34	200	266	–	30
2R1.1	2000	1.1	136	34	200	266	200	30

finer while with a concentration of  $300 \text{ mg l}^{-1}$  the fines become 50%. This is in good agreement with the primary nucleation kinetic equation [12]:

$$B = C_1 \exp \left[ -\frac{C_2 \gamma_s^3}{T^3 (\ln B)^2} \right] \quad (7)$$

The primary nucleation rate is therefore highly non-linear related to the solution supersaturation, being negligible for low values of  $\beta$  but increasing rapidly once some critical supersaturation is achieved. Besides, heterogeneous nucleation, i.e. induced by other surfaces, may require significantly lower supersaturations than homogeneous nucleation. In practice, fluoride concentrations smaller than  $150 \text{ mg l}^{-1}$  in the reactor should be employed.

In the case of a concentrated wastewater (2000 ppm in this case) a recycle ratio is applied to dilute the fluoride concentration in the feed stream of the reactor. Consequently, the effluent concentration is low and it is possible to control the supersaturation in the reactor according to the considerations previously made. A second recirculation is required in order to feeding the calcium reagent with water of process itself. The objective in both cases is the saving of water.

The study of two recirculations has been carried out. In both cases, the dimensionless streams parameters defined by Eqs. (3)–(5) as a function of time in the fluidized bed has been studied.

The results of the parameters defined in Eqs. (3)–(5) (conversion, fines fraction and efficiency) as a function of time are shown in Fig. 5, working under conditions: no recycle, 1 and 2 recycles.

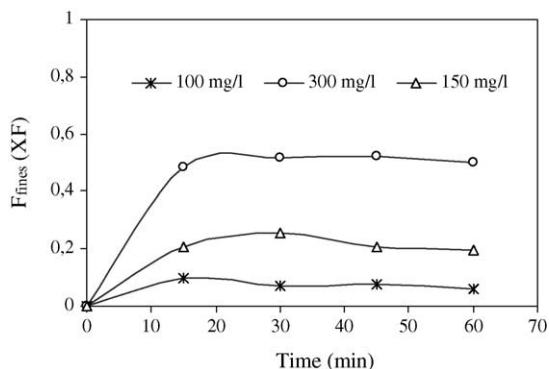


Fig. 4. Dimensionless fines generation in the fluidized bed as a function of supersaturation.

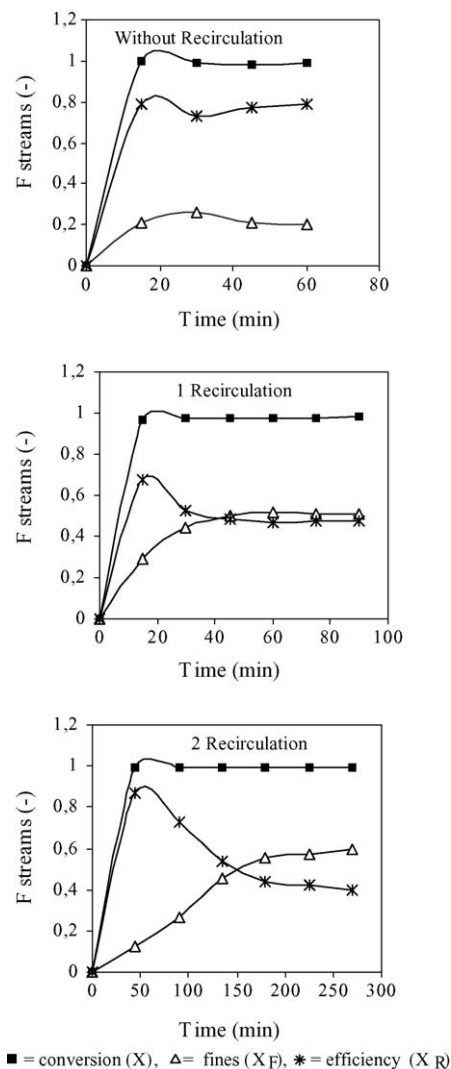


Fig. 5. Dimensionless fluoride streams in the fluidized bed as a function of time.

The process conversion ( $X$ ) is the same in all the studied case for  $\text{Ca/F}$  molar ratio equal to 1.1. However, the fines fraction ( $X_F$ ) and therefore, the efficiency ( $X_R$ ) of the process are different. In steady state, with 1 and 2 recirculations, the fluoride removal efficiencies are 48 and 39%, respectively, while without recirculation the efficiency is about 80%.

The local supersaturation ratio is significantly higher in fluoride dilution tank due the recycled calcium excess nec-

essary to obtain an appropriate fluoride concentration in the effluent. This seems to be the cause of the homogeneous nucleation and greater degree of fines formation.

In addition, the recycled fines could be the reason of additional fines formation by secondary nucleation, and therefore, the heterogeneous nucleation in the reactor is lower than without recirculation. The occurrence of secondary nucleation depends on the presence of solute crystals in the solution. Three operation variables have importance on secondary nucleation: the supersaturation, the magma density referred to the material being crystallized and the fluid mechanics interactions. These effects can be expressed through the relation [12]:

$$D \propto \beta^b A^j N^h \quad (8)$$

The supersaturation control and the minimization of the recycled fines are necessary in order to avoid the discrete precipitation and consequently to achieve a high fluoride recovery in further investigations.

## 5. Conclusions

A high supersaturation level decreases the fluoride removal efficiency due to the formation of fines.

The main processes that involve the precipitation of calcium fluoride in a fluidized bed in viable technical conditions were established. Fines were produced by nucleation in liquid phase (homogeneous and secondary nucleation) in the reactor and dilute fluoride tank.

It is not possible to obtain efficiencies higher than 40% in viable technical conditions when it is necessary to dilute the influent through recycle stream. So it is very important to control the supersaturation degree in the fluidized bed reactor.

## Acknowledgements

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