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Modeling of particle growth: Application to water treatment in a fluidized bed reactor

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Abstract

Crystallization process in a fluidized bed reactor to remove fluoride from industrial wastewaters has been studied as a suitable alternative to the chemical precipitation, which generates large amounts of a water rich sludge that must be disposed of with increasing costs. The major advantage of this technology is the decrease of sludge formation, the simplification of the materials recovery procedures and the reduction of solid wastes.

Removal of fluoride by crystallization process has been carried out in a laboratory-scale fluidized bed reactor focused to the analysis of the influence of the supersaturation (S), the up-flow velocity (SV) and the amount and mean diameter of seed material (L_0) on the process efficiency, which are related to the crystal growth.

In the modeling, design and control of a fluidized bed reactor for water treatment it is necessary to study the particle growth kinetics. From the results obtained in this study, it has been proposed a growth model represented by the equation $G = 2.96 \times 10^{-5} L_0^{1.37} \mathrm{SV}^{0.5} S\,(\mathrm{m\,s^{-1}})$, which fits well the experimental data in the interval of variables studied.

Keywords: Crystallization; Fluidized bed reactor; Growth kinetics; Fluoride wastewater

1. Introduction

The common methods for fluoride removal from industrial wastewater involve chemical precipitation. The process generates large amounts of a water rich sludge, which requires dispose of with increasing costs. Due to the high water content and the low quality of the sludge, reuse of fluoride is not an economical option. Removal of fluoride in a fluidized bed reactor (FBR) by crystallization process has been studied as an alternative to the chemical precipitation [1–3].

The chemistry of the process is similar to the conventional precipitation. By dosing calcium hydroxide to the wastewater, the solubility of CaF_2 is exceeded and fluoride is converted from the aqueous solution to solid crystals. The main difference with the common precipitation lies on the fluidized bed reactor. The process is based on the crystallization of calcium fluoride upon seed material grains instead of mass precipitation in the liquid phase.

During the operation, the grains increase in diameter in the fluidized bed reactor and fluoride covered grains are removed form the bottom of the reactor and replaced by fresh seed grains. Fig. 1 shows SEM microphotographs of calcium fluoride pellets obtained in the crystallization process. The growth of granular calcium fluoride takes place by molecular growth and aggregation between the granular seed material and the formed calcium fluoride in the liquid phase (nucleated precipitation). The molecular growth and aggregation on the granular grains takes place while competing with discrete precipitation in the liquid phase (primary and secondary nucleation) and mineral layer abrasion. 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 from the top and form, together with the remaining fluoride in solution, the fraction of the fluoride that is not possible to recover in the reactor. The set-up of the reactor and streams is described in Fig. 2 .

In the modeling, design and control of a FBR for water treatment it is necessary to study the particle growth kinetics. The properties of the particles in a crystallization process depend mainly on the crystal growth rate and nucleation kinetics, which control the final properties of the solid product. The crystal growth is a complex mechanism that includes many factors

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Nomenclature

C	concentration (mg L^{-1})
G	overall linear crystal growth rate (m s^{-1})
j	crystal growth order referred to the supersaturation
K_g	overall crystal growth coefficient
L	particle size (m)
L_0	particle size (referred to the seed material) (m)
m	crystal growth order referred to the particle size
n	crystal growth order referred to the superficial velocity
S	supersaturation
SV	superficial velocity (m h^{-1})
t	time (s)
V	volume (m^3)
X	dimensionless conversion
X_F	dimensionless fines fraction
X_R	dimensionless efficiency

depending on different variables: dispersion, supersaturation, crystal size, solution velocity, admixtures, magnetic field, temperature, and pH [4].

This paper is focused on the study of the influence of the main process variables: amount and size of seed material, fluoride inlet concentration and superficial velocity in the reactor. In addition, it has been studied the influence of the main variables on the crystal growth and a model of crystal growth has been proposed for CaF_2 product.

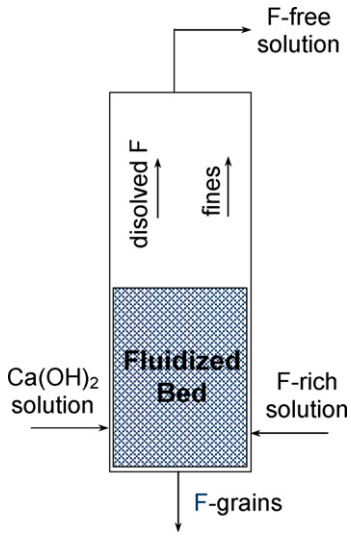

Fig. 2. Fluidized bed reactor.

2. Experimental

2.1. Laboratory-scale fluidized bed reactor

Two fluidized bed reactors have been used in order to study the influence of the main variables on the crystallization process and the crystal growth, respectively. The reactors consist of a methyl methacrylate cylindrical vessel (500 mm in height and a inner diameter of 36 mm; 350 mm in height and a inner diameter of 20 mm) partially filled with granular calcite in which the fluoride water and the calcium reagent solution are pumped upward through the reactor. The flow is such that the seed mate-

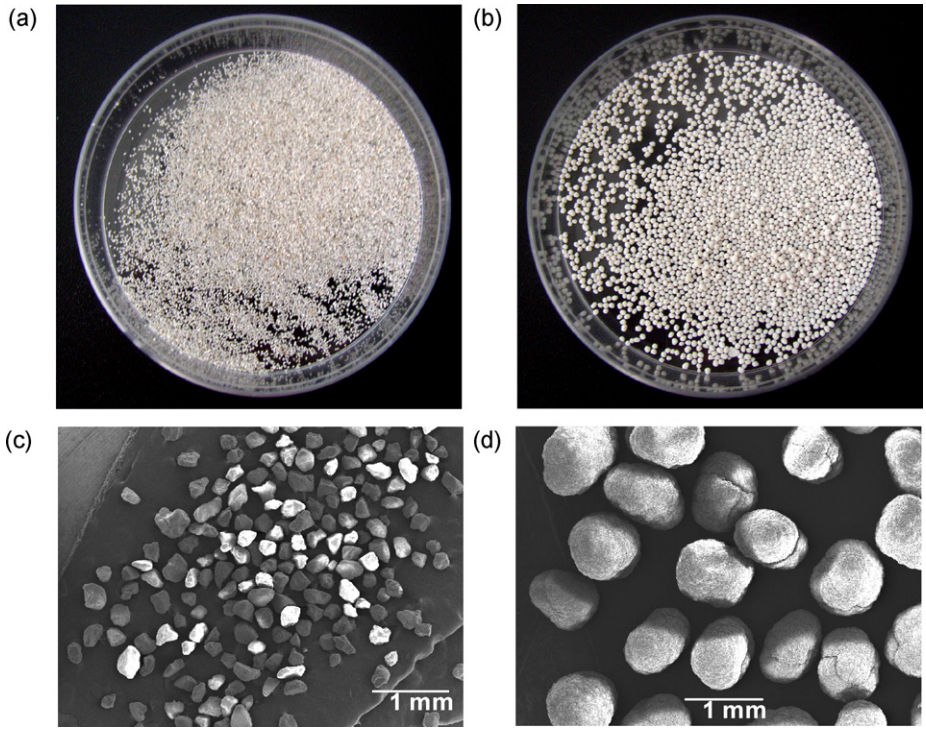

Fig. 1. Photography and SEM microphotography of (a and c) granular calcite and (b and d) pellets of calcium fluoride product.

rial will not settle down and flow out of the crystallization vessel.

The calcium reagent and fluoride solutions are injected into the fluidized bed reactor using different peristaltic pumps. The experimental facility is completed with several regulation valves and flowmeters.

2.2. Materials

The fluoride solution used as feed stream was obtained by diluting a concentrated hydrofluoric acid solution. Synthetic fluoride solutions in the range 80–500 mg L^{-1} were used in the experiments.

Chemical grade reactants (hydrated lime as calcium reagent (Ca^{2+})) and demineralized water were used. Several studies show the hydrated lime as an adequate source of calcium to the neutralization of fluoride containing wastewater [5,6]. In addition, the $Ca(OH)_2$ particles are likely to dissolve along the bed length, distributing the supersaturation more evenly throughout the bed [7]. Granular calcite ($CaCO_3$) was used as seed material in order to obtain synthetic calcium fluoride as a product able to be reused as raw material in the HF manufacture [8].

2.3. Experimental procedure

A typical run consists of adding about 70 g of sieved granular calcite as seed material and controlling the solution velocity so that the solids are uniformly suspended in the fluidized bed reactor. The experimental conditions in order to establish the influence of the variables on the calcium fluoride growth in a fluidized bed reactor are shown in Table 3. The superficial velocity in the reactor was in the range between 21 and 45 m h^{-1}. The seed size of granular calcite was between 0.25 and 0.60 mm. Finally, the supersaturation, through the fluoride inlet concentration in the reactor (50–300 mg L^{-1}), was between 6.4 and 38.5.

The seed material mass increases due to the precipitation of calcium fluoride upon the granular calcite. As result of this, the seed material increases in diameter. The duration of a run varies from 20 to 37 h, depending on the conditions of supersaturation and the superficial velocity.

During the experiments, samples of fluoride-coated calcite grains (pellets) were removed from the bottom of the reactor at different times. The pellets were air dried and the particle size was determined by Laser-Ray Diffraction (Mastersizer S, Malvern Instruments).

3. Results and discussion

3.1. Influence of the operation variables

A factorial design was carried out in order to determine the significant effects of the studied variables on the crystallization process.

The variables considered in this work and their corresponding values for each level (amount of seed material per reactor volume, superficial velocity and fluoride inlet concentration) are presented in Table 1. A factorial design 2^3 was conducted to combine the three factors with a central point for error estimation.

Table 1
Coded factor levels and real values for the experimental design

Factor	Low value (−)	Center value (0)	High value (+)
Mass/$V_{reactor}$ (kg m^{-3}) (A)	318	473	636
$C_{F,in\ reactor}$ (mg L^{-1}) (B)	150	175	200
SV (m h^{-1}) (C)	17	27	37

The responses include in the analysis were the dimensionless conversion (X), fines fraction (nucleation and abrasion processes) (X_F) and efficiency (precipitated fluoride upon seed material) (X_R), which are defined according to the following equations:

$$X = \frac{w_{F,dis\,in} - w_{F,dis\,out}}{w_{F,dis\,in}} \quad (1)$$

$$X_F = \frac{w_{F,fines}}{w_{F,dis\,in}} \quad (2)$$

$$X_R + X_F = X \quad (3)$$

where w_F is the molar flow (mol min^{-1}) of fluoride in the inlet stream (dis in), outlet stream (dis out) and fluoride as fines leaving the reactor (fines).

The values of the responses for the experimental runs carried out are summarized in Table 2, which also indicates the levels of the factors in each experiment.

From the values of the responses, the effects of the factors and interactions on responses were analyzed using the software STATGRAPHICS plus 5.1.

Fig. 3 shows the plots of the effects of the factors on the fluoride conversion in the crystallization process. From Fig. 3b and c it is possible to check that the studied variables present negligible influence on the fluoride conversion. The fluoride conversion increases from 85% to 95% when the fluoride inlet concentration increases. The conversion difference is related to the fluoride inlet concentration and the calcium fluoride solubility when the Ca/F ratio is in excess [3]. This negligible influence is in agreement with the Pareto chart shown in Fig. 3a, which was used to graphically summarize and display the relative importance of the studied variables.

However, it can be seen in Table 2 that a quite wide range of efficiency values of fluoride recovery as CaF_2 product ($25.0\% < X_R < 75.0\%$) is reached. In this sense, it is necessary to analyze the influence of the main operation variables in order to maximize the efficiency of the process and therefore the recovery of fluoride as pellets of calcium fluoride.

As can be seen in Fig. 4, the factor with the greatest effect on the efficiency of crystallization process is A (amount of seed material per reactor volume). In addition, AB interaction (amount of seed material and fluoride inlet concentration), B (fluoride inlet concentration), C (superficial velocity) and AC interaction (amount of seed material per reactor volume and superficial velocity) are also important.

Table 2
Design matrix and values of the responses

Exp. no.	Variables			Responses		
	Mass/$V_{reactor}$ (kg m^{-3})	$C_{F,in\ reactor}$ (mg L^{-1})	SV (m h^{-1})	x	x_F	x_R
AF-1	+	−	+	0.87 ± 0.02	0.14 ± 0.02	0.75 ± 0.02
AF-2	−	−	+	0.90 ± 0.07	0.56 ± 0.03	0.34 ± 0.03
AF-3	−	+	−	0.93 ± 0.01	0.67 ± 0.04	0.26 ± 0.03
AF-4	+	+	−	0.87 ± 0.03	0.30 ± 0.05	0.56 ± 0.04
AF-5	+	−	−	0.90 ± 0.03	0.19 ± 0.03	0.72 ± 0.04
AF-6	−	+	+	0.93 ± 0.02	0.49 ± 0.05	0.44 ± 0.05
AF-7	−	−	−	0.92 ± 0.02	0.67 ± 0.05	0.25 ± 0.02
AF-8	+	+	+	0.92 ± 0.03	0.42 ± 0.04	0.50 ± 0.03
AF-9	0	0	0	0.92 ± 0.02	0.57 ± 0.02	0.35 ± 0.03

The positive effect of the factor A could be explained assuming that the crystallization process arises from aggregation of fines formed by homogeneous nucleation in the liquid phase on the granular calcite surface and by molecular growth, i.e., Ca^{2+} and F^- ions feed in the fluidized bed reactor nucleate directly onto the granular calcite surface [9]. Thus, the maximum process efficiency is reached when high surface area of the seed material is used in the fluidized bed reactor, which suggests surface control.

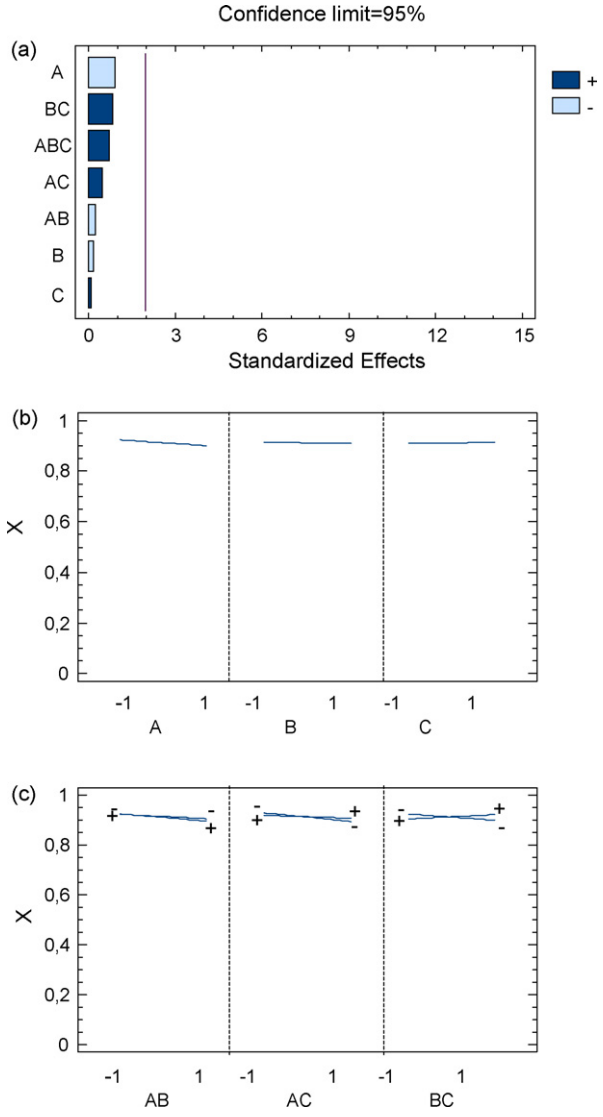

Fig. 3. Pareto chart (a), individual (b) and interactions (c) for the effects on the fluoride conversion.

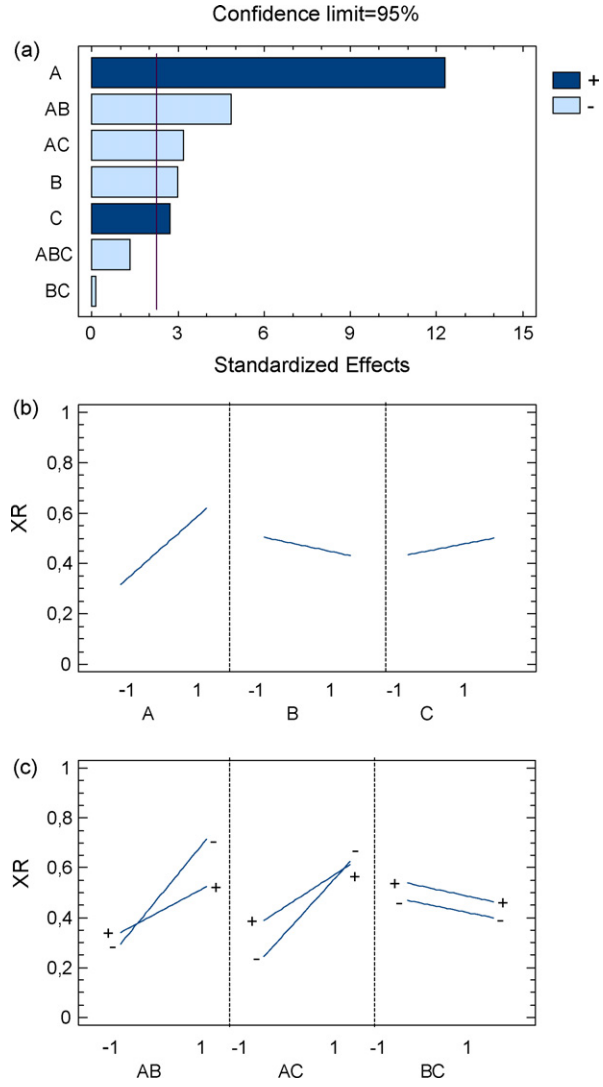

Fig. 4. Pareto chart (a), individual (b) and interactions (c) for the effects on the process efficiency.

Table 3
Overall linear growth rate (G) of pellets of calcium fluoride in a fluidized bed reactor as a function of the supersaturation (S)

Run no.	L_0 (mm)	$C_{F,in\ reactor}$ (mg L^{-1})	S (−)	SV (m h^{-1})	G (m s^{-1})	R^2
CG-1	0.30–0.35	150	19.2	33	8.78×10^{-10}	0.981
CG-2	0.55–0.60	150	19.2	33	2.25×10^{-09}	0.980
CG-3	0.25–0.30	150	19.2	33	8.15×10^{-10}	0.987
CG-4	0.45–0.50	150	19.2	33	1.36×10^{-09}	0.982
CG-5	0.30–0.35	50	6.4	33	2.56×10^{-10}	0.989
CG-6	0.30–0.35	300	38.5	33	1.86×10^{-09}	0.956
CG-7	0.30–0.35	150	19.2	21	8.19×10^{-10}	0.996
CG-8	0.30–0.35	150	19.2	45	1.16×10^{-09}	0.990

Particle size (L_0) and superficial velocity (SV). $M_{calcite}/V_{reactor}$ 409 kg m^{-3}; $(Ca/F)_{in}$ 1.1.

The influence of the fluoride inlet concentration has been analyzed in terms of the supersaturation in previous works related to the nucleation mechanism [1,3]. High supersaturation values increase the fines formation related to the calcium fluoride nucleation in the liquid phase. Fluoride concentration at the bottom of the reactor has to be kept below a critical value in order to prevent fines formation and to increase the process efficiency. From a technical point of view, a fluoride concentration lower than 150 mg L^{-1} needs to be introduced in the reactor in order to favor the efficiency of the process.

The influence of the superficial velocity must be analyzed based on the AC interaction plot shown in Fig. 4c. As can be seen in Fig. 4c, the highest process efficiency was obtained when the crystallization process is carried out at the high level of the factor A (amount of seed material per reactor volume) and the low level of the factor C (superficial velocity).

The mineral layer abrasion of the pellets in the fluidized bed reactor [8,10], the fines elutriation, the increase of the fluidized bed porosity when the superficial velocity increases [11] have been assumed to be the causes of the process efficiency reduction. As the superficial velocity increases, the expansion ratio of the fluidized bed increases, decreasing the surface area of the seed material per reactor volume and increasing the porosity of the fluidized bed. In these conditions, the efficiency of the process is lower.

3.2. Modeling of crystal growth of calcium fluoride

From the analysis of the influence of the operation variables on the crystallization process, the surface area of the seed material, the fluoride inlet concentration and the superficial velocity show effects statistically significant on the efficiency of the process and therefore, these variables may be significant on the crystal growth [12–14]. In this sense, in order to obtain a model that takes into account the main variables that influence on the crystallization process, a general model of particle growth has been proposed.

The experimental conditions and the overall linear crystal growth rates of the calcium fluoride for several runs are shown in Table 3. The crystal linear growth rate G has been determined as the ratio between the size increment between two given instants and the elapsed time. Three important remarks may be noted: (i) G varies from about 8.19×10^{-10} to 1.16×10^{-9} m s^{-1} as the solution velocity increases from 21 to 45 m h^{-1}; (ii) G raises from 2.56×10^{-10} to 1.86×10^{-9} m s^{-1} when the supersaturation increases from 6.5 to 38.5; (iii) G varies from 8.15×10^{-10} to 2.25×10^{-9} m s^{-1} as the particle size of the seed material varies from 0.25–0.30 to 0.55–0.60 mm. The increase of the

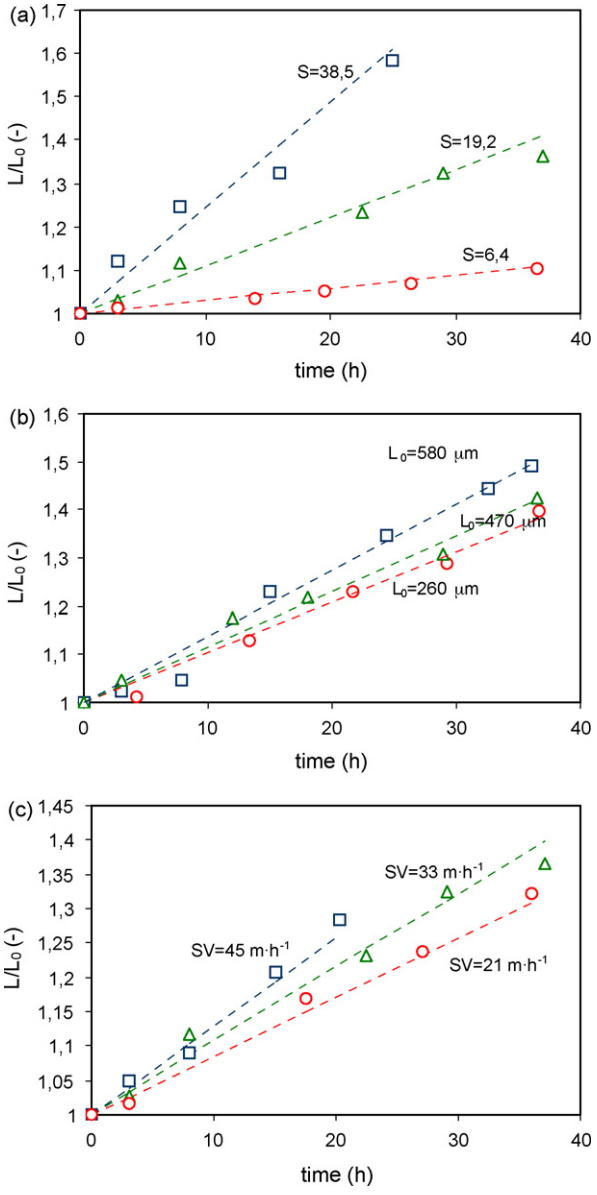

Fig. 5. Influence of the supersaturation (a), particle size (b) and superficial velocity (c) on the dimensional particle size of the pellets as a function of time.

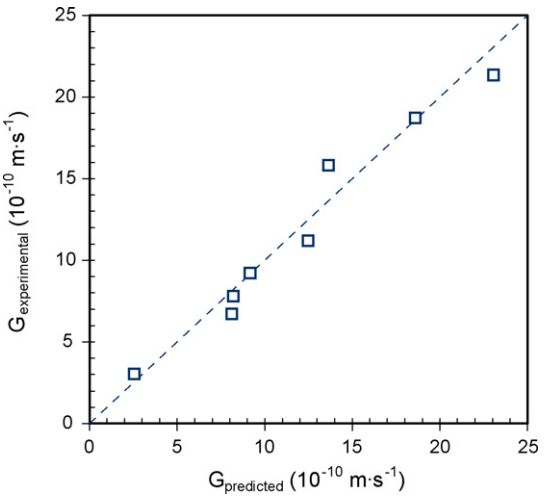

Fig. 6. Parity graph for predicted values of overall linear growth rate by the proposed semiempiric model of crystal growth of calcium fluoride in a fluidized bed reactor.

superficial velocity in the reactor, the supersaturation and the particle size of the seed material implies the rise of the particle size of the calcium fluoride pellets in a FBR. Fig. 5 shows the dimensionless particle size of the pellets as a function of time when the supersaturation, the particle size of the seed material and the superficial velocity change.

A general model has been fitted according to the following equation:

$$G = \frac{dL}{dt} = K_g L_0^m SV^n S^j \quad (4)$$

The growth rate data given in Table 3 have been fitted to Eq. (4) to calculate the overall crystal growth coefficient K_g, and the growth rate orders m, n and j, referred to the particle size, the superficial velocity and supersaturation, respectively, which define the overall linear crystal growth of calcium fluoride in a fluidized bed reactor as:

$$G = 2.96 \times 10^{-5} L_0^{1.37} SV^{0.49} S^{1.01} \quad (5)$$

The correlation between the experimental and the predicted values of G is shown in Fig. 6. The correlation coefficient of the fitting was 0.969, which indicates the well-correlated data.

4. Conclusions

A parametric study of the removal of fluoride by crystallization in a fluidized bed reactor was made. The main influence of the variables concerning the recovery of fluoride in a fluidized bed reactor was established. The conversion of fluoride depends only on the overdose of calcium. The amount of seed material, related to the specific surface area, is the most important variable in the process, since the process is governed by the precipitation of calcium fluoride upon seed material.

The increase of the superficial velocity in the reactor, the supersaturation and the particle size of the seed material imply the rise of the linear growth rate of the calcium fluoride in a fluidized bed reactor.

It has been found a crystallization model for the CaF_2 production based on the statistically significant effects studied in the parametric study. The model is useful in the design, operation and control of fluidized bed reactors for water treatment.

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