Calcium fluoride recovery from fluoride wastewater in a fluidized bed reactor

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Abstract

In order to contribute to better resource efficiency and industrial waste management leading to a sustainable production and consumption pattern new processes must be developed, which should be operated in such a way that waste production is reduced or avoided.

Fluoride removal by precipitation generates huge amounts of a water rich sludge. Calcium fluoride is not recovered from the waste streams and it is not recycled due to the high water content and the low quality of the sludge. Crystallization process in a fluidized bed reactor (FBR) appears as an alternative technology to the conventional chemical precipitation process. In the crystallization process in a FBR silica sand is usually used as seed material, however silica is a deleterious impurity because it causes losses in the yield of HF and its content should be less than 1%.

In this paper, granular calcite has been used as seed material in order to obtain synthetic calcium fluoride. According to the composition (CaF$_2$ > 97%, SiO$_2$ < 1%), the synthetic calcium fluoride from the crystallization process in a FBR is able to be recycled as raw material for the manufacture of hydrofluoric acid leading to a reduction of raw materials consumption.

The crystallization process in a FBR to remove fluoride from industrial wastewaters contributes to an environmental friendly production, because it allows to reduce the waste production as well as to increase the recovery of materials.

Keywords:
Crystallization
Fluoride
Fluidized bed reactor
Wastewater
Recovery
Calcium fluoride

1. Introduction

Environmental regulations and efficient operation of wastewater treatment plants require fluoride removal and recovery from the effluent prior to discharge to the environment. The common treatment to remove fluoride from industrial wastewaters is chemical precipitation, which offers a cost-effective solution to several fluoride wastewaters sources (Saha, 1993; Yang and Smith, 1990). However, the low quality of the sludge (40–60% of CaF$_2$) prevents technical uses of precipitated fluoride (Aldaco et al., 2005a).

The Sixth Environment Action Programme of the European Community, “Environment 2010: Our Future, Our Choice”, identifies four environmental areas to be tackled for improvements. Among these objectives, the natural resources and wastes are considered as priorities in order to contribute to the sustainable development, which is now a key feature of policy making in the European Union. These objectives should be established achieving a significant overall reduction in the volumes of wastes based on waste prevention initiatives, giving preference to the recovery of waste streams (Decision No. 1600/2002/EC). In order to contribute to this
goal, it is necessary to develop environmentally sound waste recovery and treatment technology.

World fluorspar reserves in 2002 were estimated at 230 million tonnes, to be recovered from 375 million tonnes of ore. The worldwide consumption of “acid grade” fluorspar is currently about 4.5 million tonnes per year and this rate of consumption means that known reserves are estimated to be adequate to somewhat over 50 years supply.

The recovered fluoride as synthetic calcium fluoride may be reused as raw material or additive in several industrial applications. The percentage of CaF₂ determines the grade, which is related to the use. Ninety-eight percent of the fluorspar is consumed by two industries: the chemical industry, for the manufacture of hydrofluoric acid, and the iron and steel industry. Acid spar is used in the production of hydrogen fluoride and its derivatives. Deleterious impurities in acid spar are mainly silica, because it causes losses in the yield of HF and its content should be lesser than 1%. Other uses of fluorspar (manufacture of glasses, enamels, and welding fluxes) transform only small quantities of ores. Table 1 shows the composition of the calcium fluoride commercial grades.

Many alternatives have been developed for removal of fluoride from industrial wastewater. The packed fixed bed with granular calcite allows high efficiencies of fluoride removal without sludge generation (Sato et al., 1995; Yang et al., 1999; Reardon and Wang, 2000). However, the effective calcite conversion rate depends strongly on the superficial velocity in the reactor, and therefore important efforts should be made to increase the effective conversion rate of calcite when high flow rates are necessary to treat in the reactor. In addition, the formation of lumps in the fixed bed is an important drawback of the process (Yang et al., 1999).

Precipitate flotation (Huang and Liu, 1999) and other processes involving recycle to reduce sludge and costs (Toyoda and Taira, 2000) are also applied, but they are not able to recover fluoride as a valuable product.

The HARDTAC® process uses calcium chloride or lime as a source of calcium for the reaction with fluoride to form calcium fluoride, and it produces large particles (40–60 μm) by crystallization. The synthetic fluorspar is 85–89% CaF₂ with the balance being hydrated lime and calcium carbonate. However, this purity is low for acid grade fluorspar (Low, 2005). It has been developed a process for recovery of fluoride from a waste solution containing soluble fluoride in a fluidized bed crystallizer provided with a carrier. A water soluble sodium reagent and a water soluble aluminium reagent are added into the fluidized bed crystallizer to form crystallized cryolite (Na₃AlF₆) onto the carrier. Cryolite is in the form of crystals, which contain less than 10% water, and it is very convenient for re-utilization (Patent No. US 6,235,203). However, the fluoride content in the outlet solution is in the range 250–400 mg L⁻¹ and the treated effluent needs to be further purified by using a conventional process to fulfill wastewater discharge criteria (Aldaco et al., 2005b).

A method to remove fluoride from wastewater in a fluidized bed reactor using silica sand as seed material has been developed by DHV Raadgevend Ingenieursbureau (Patent No. US 6,106,509). An advantage of the process is the ability to produce highly pure, nearly dry calcium fluoride pellets. However, silica content in the product reduces the HF efficiency because the silicon tetrafluoride gas formed in the manufacture of HF is lost, and the operation of washing in a plant vent scrubbing is often troublesome. Therefore, the silica content prevents technically the reuse of the calcium fluoride from the crystallization process as raw material in the HF manufacture.

Fluidized bed reactors have been used in different water and wastewater treatment processes. The pellet reactor has been reported in water softening of drinking water (van Houwelingen and Nooijen, 1993), phosphate removal (Seckler...
et al., 1996a–c; Battistoni et al., 2001, 2002) fluoride removal (Aldaco et al., 2006; Giesen, 1998; van den Broeck et al., 2003), and heavy metal recovery from wastewaters (Zhou et al., 1999; Chen and Yu, 2000; Guillard and Lewis, 2001).

The process of the development is similar to that of conventional precipitation. By dosing calcium ions to the fluoride wastewater, the ion product (Ca²⁺ and F⁻) exceeds the solubility product (CaF₂), which is formed in the homogeneous liquid phase according to the following reactions:

\[
\begin{align*}
H^+ + F^- & \leftrightarrow HF, \\
Ca^{2+} + 2OH^- & \leftrightarrow Ca(OH)_2, \\
Ca^{2+} + 2F^- & \leftrightarrow CaF_2 \, (s).
\end{align*}
\]

Crystallization of calcium fluoride in the FBR can be carried out over a wide pH range (pH = 2–14). Nevertheless, control of the process pH can be used to prevent co-crystallization of other components in the wastewaters (Giesen, 1998).

The process is based on the crystallization of calcium fluoride upon seed material instead of mass precipitation in the liquid phase. During the operation, the grains increase in diameter and the fluoride-covered grains are removed from the bottom of the reactor and replaced by fresh seed grains.

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.

High supersaturation implies primary nucleation. Therefore, it is very important to control the supersaturation in the FBR by means of a fluoride inlet concentration lower than 150 mg L⁻¹ (Aldaco et al., 2006).

Wastewaters with a fluoride concentration of 10–100 000 mg L⁻¹ are possible to be treated in the FBR. In the case of low fluoride content no recycle or small recycle ratio is required, while at high fluoride content a big recycle ratio is required in order to control the supersaturation at the bottom of the reactor. Increasing the recycle ratio in the reactor improves the efficiency of the process avoiding primary nucleation. However, the recycle of fines may be the origin of the new fines formation by secondary nucleation in the reactor, decreasing the efficiency of the process. The use of a sand filter bed improves the efficiency of the process when recycling of the effluent is necessary (Aldaco et al., 2006).

This paper reports the development of a crystallization process in a fluidized bed reactor using granular calcite as seed material in order to obtain synthetic calcium fluoride from fluoride wastewater that may be used as raw material for the production of hydrofluoric acid. In these conditions, the crystallization in a FBR could be considered a cleaner technology and its application in the fluorine industry could contribute to the sustainable development.

2. Materials and methods

2.1. Laboratory-scale pellet reactor

The reactor consists of a methyl methacrylate cylindrical vessel with a height of 500 mm and a diameter of 20 mm partially filled with a seed material (silica sand or granular calcite), where the fluoride solution and the calcium reagent are pumped upward through the reactor at a velocity that ensures the fluidization of the pellets so that the cementing of grains is prevented.

The fluidized bed reactor is provided with two inlet nozzles at the bottom. The main nozzle (6 mm in diameter) is located vertically at the symmetry axis of the reactor. The fluid velocity of the fluoride solution through this nozzle is in the range between 0.035 and 0.062 m s⁻¹. The fluoride inlet concentration to the reactor \((C_{F, \text{in reactor}})\) and the fluoride concentration at the bottom of the reactor \((C_{F, \text{bottom reactor}})\) are 250 and 150 mg L⁻¹, respectively, and therefore, recycle ratio is not necessary under the operational conditions of this work.

The calcium solution is pumped into the reactor through a secondary nozzle (6 mm in diameter) placed horizontally at the wall at a height of 5 mm from the bottom of the reactor. The fluid velocity of the calcium solution is 0.024–0.041 m s⁻¹.

The calcium reagent and fluoride solutions were injected into the fluidized bed reactor using peristaltic pumps (Watson Marlow 323 and 313S).

The experimental facility is completed with several regulation valves and flow meters.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Operation time (h)</th>
<th>(C_{F, \text{in reactor}}) (mg L⁻¹)</th>
<th>((\text{Ca/F})_{\text{in}}) (-)</th>
<th>(C_{F, \text{bottom reactor}}) (mg L⁻¹)</th>
<th>(F_{F, \text{in reactor}}) (mL min⁻¹)</th>
<th>(F_{Ca, \text{in reactor}}) (mL min⁻¹)</th>
<th>Seed material</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-1</td>
<td>90</td>
<td>250</td>
<td>1.1</td>
<td>150</td>
<td>103</td>
<td>69</td>
<td>SiO₂ (150–300 μm)</td>
</tr>
<tr>
<td>C-2</td>
<td>110</td>
<td>250</td>
<td>1.1</td>
<td>150</td>
<td>103</td>
<td>69</td>
<td>CaCO₃ (150–300 μm)</td>
</tr>
<tr>
<td>C-3a</td>
<td>120</td>
<td>250</td>
<td>1.1</td>
<td>150</td>
<td>60</td>
<td>40</td>
<td>CaCO₃ (100–160 μm)</td>
</tr>
<tr>
<td>C-3b</td>
<td>110</td>
<td>250</td>
<td>1.1</td>
<td>150</td>
<td>105</td>
<td>70</td>
<td>Pellets from Exp. No. C-3a</td>
</tr>
</tbody>
</table>
2.2. Materials

The synthetic fluoride wastewater used as feed stream was obtained by diluting a concentrated hydrofluoric acid. 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 (Saha, 1993; Yang and Smith, 1990). In addition, the Ca(OH)\(_2\) particles are likely to dissolve along the bed length, distributing the supersaturation more evenly throughout the bed (Seckler et al., 1996c).

The particle size of the seed materials is shown in Table 2. Silica sand (Exp. No. C-1), granular calcite (Exp. Nos. C-2 and C-3a), and pellets of calcium fluoride from the experiment C-3a (Exp. No. C-3b) have been introduced as seed materials.

2.3. Fluoride removal

Synthetic fluoride wastewater was introduced in the FBR at room temperature following the experimental design shown in Table 2. Samples were taken from the effluent of the reactor at different times. Turbidity and pH measurements were conducted with a turbidity meter (TURBIQUANT 3000IR, Merck) and a pH meter (CRISON GLP 22), respectively.

The inlet and outlet concentrations were measured. Dissolved fluoride was analysed by a specific fluoride ion electrode (CRISON 120/S7) provided with a reference electrode (CRISON 5240).

Suspended solids in the outlet stream were filtered with a 0.45\(\mu\)m filter, and a mass balance was applied to the solid in order to estimate the fluoride amount of fluoride released as fines.

The evaluation of the crystallization process in the fluidized bed reactor is based on the calculation of three variables: the reactor dimensionless conversion \(X\), fines fraction \(X_F\) and reactor efficiency \(X_R\) as a function of time for several seed materials: (a) silica sand (Exp. No. C-1); (b) granular calcite (Exp. No. C-2); (c) granular calcite (Exp. No. C-3a) and pellets of calcium fluoride from experiment C-3a (Exp. No. C-3b).
(X_F, Eq. (5)), and the reactor efficiency (X_R, Eq. (6)).

\[
X = X_F + X_R = \frac{w_{F,\text{bottom reactor}} - w_{F,\text{out reactor}}}{w_{F,\text{bottom reactor}}}, \tag{4}
\]

\[
X_F = \frac{w_{F,\text{fines}}}{w_{F,\text{bottom reactor}}}, \tag{5}
\]

\[
X_R = \frac{w_{F,\text{grains}}}{w_{F,\text{bottom reactor}}}, \tag{6}
\]

where \(w_{F,\text{bottom reactor}}\) is the fluoride molar flow rate (mol min\(^{-1}\)) at the bottom of the reactor, \(w_{F,\text{out reactor}}\) is the fluoride molar flow rate in the filtered samples at the outlet of the reactor, \(w_{F,\text{fines}}\) is the fluoride molar flow rate as small particles at the outlet of the reactor, and \(w_{F,\text{grains}}\) is the fluoride molar flow rate removed and recovered as calcium fluoride from the reactor. The set-up of the reactor and streams is described in Fig. 1.

## 2.4. Analysis of calcium fluoride pellets

The fluoride-coated grains were removed from the bottom of the reactor at different times and air dried for further characterization.

The grains were analysed to determine the morphology using scanning electron microscopy (SEM-JSM 5800LV, Jeol). The composition of calcium fluoride grains was analysed after distillation by a potentiometric method using a fluoride sensitive electrode (CRISON 120/S7) according to the standard method (ISO 5439:1978), and by means of thermogravimetry (TGA 7, Perkin Elmer). The white crystals obtained in the process were analysed with an X-Ray Diffraction Analyzer (XRD-PW 1279, Philips) in order to establish a qualitative composition of the product.

Particle size of the grains was determined by Laser-Ray Diffraction (Mastersizer S, Malvern Instruments).

Finally, surface area and porosity of the products were measured using a Surface Area Analyzer BET Gas Adsorption (ASAP 2000, Micromeritics).

## 3. Results and discussion

### 3.1. Removal of fluoride

Fig. 2 shows the dimensionless conversion \((X)\), the fines fraction \((X_F)\) and the reactor efficiency \((X_R)\) from the removal of fluoride in the crystallization process using silica sand and granular calcite as seed materials according to the experimental conditions of Table 2. From Fig. 2a–c, which show experimental results from Exp. No. C-1, Exp. No. C-2, and Exp. No. C-3 (a-b), respectively, it is possible to establish the behaviour of the crystallization process at a laboratory scale.

The fluoride conversion is around 92% as it can be observed in Table 3. The seed material shows a negligible influence on the total fluoride conversion, which depends only on the fluoride concentration in the reactor and the calcium fluoride solubility at a given pH and a calcium overdose (Aldaco et al., 2005a).

From Table 3 it is possible to check that the increase of the particle size of the seed material in the reactor decreases the efficiency of the process, raising the suspended solids and the turbidity of the effluent, which is related to the fines

### Table 3 – Removal of fluoride by crystallization in a fluidized bed reactor

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Reactor parameter</th>
<th>Effluent parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(X)</td>
<td>(X_F)</td>
</tr>
<tr>
<td>C-1</td>
<td>0.92</td>
<td>0.23</td>
</tr>
<tr>
<td>C-2</td>
<td>0.92</td>
<td>0.22</td>
</tr>
<tr>
<td>C-3a</td>
<td>0.91</td>
<td>0.16</td>
</tr>
<tr>
<td>C-3b</td>
<td>0.92</td>
<td>0.19</td>
</tr>
</tbody>
</table>

Fig. 3 – Photographs of seed material (a) and (b) CaF\(_2\) Pellets (Exp. No. C-3b).
generation by primary nucleation. Efficiencies between 69% and 75% have been obtained in the crystallization process under the experimental conditions of this laboratory scale work.

The particle size of the seed material contributes to a slight decrease in the fluoride recovery since it determines the available surface area for nucleated precipitation. The use of granular calcite with particle size between 100 and 160 µm allows to achieve efficiencies near 75%, while when granular calcite with particle size in the range of 150 to 300 µm is used the efficiency decreases around 5% respect to the previous case.

The supersaturation and the abrasion in the fluidized bed could be main reason of the limited efficiency of the process. Referred to the supersaturation, the fluoride recovery capacity in a FBR is rather limited because the unwanted primary nucleation is not easy to avoid. Multiple dosages can be useful because the reaction between $\text{F}^{-}$ and $\text{Ca}^{2+}$ ions is very fast, and the reaction takes place mainly at the bottom of the reactor (van den Broeck et al., 2003). On the other hand, abrasion of the grains in the fluidized bed is presented as an important drawback to obtain high efficiencies of the process (Chen and Yu, 2000; Seckler et al., 1996a; Wilms et al., 1992). The high flow rate, which allows the fluidization, increases the turbulence that induced the grains erosion. In these conditions, the fines generation increases in the reactor and the efficiency of the process is reduced. The formation of fines by abrasion in the reactor is difficult to avoid; a proper selection of the hydrodynamical conditions may reduce abrasion.

4. Product characterization

4.1. Product morphology

Fig. 3 shows photographs of the product from the crystallization process (3b) when granular calcite (3a) is used as seed material. As it can be seen in Fig. 3, the obtained products are homogeneous white spherical particles (pellets).

Fig. 4 – SEM views: (a) silica sand, $d_p = 150–300$ µm; (b) pellets from the crystallization process using silica sand as seed material (Exp. No. C-1); (c) pellets from the crystallization process using granular calcite as seed material (Exp. No. C-3b).
In addition, the use of SEM allows the morphological characterization of the pellets as shown in Fig. 4, where silica sand (4a), pellets from the crystallization process using silica sand as seed material (4b), and pellets from the crystallization process using granular calcite as seed material (4c) are presented. The pellets from silica sand as seed material consists of spherical particles formed by a compact mineral layer with a smooth surface, which is broken as a result of the superficial stress after drying. Pellets from granular calcite as seed material present a quite irregular surface, caused by the diffusion of carbonate out of the particles according to the reaction:

$$\text{CaCO}_3(s) + 2F^- \rightarrow \text{CaF}_2(s) + \text{CO}_3^{2-}. \quad (7)$$

The molecular volume of CaF$_2$ in fluorite is 33% smaller than that of CaCO$_3$ in calcite, so that replacement leaves 33% additional porosity in fluorite, which facilitates the diffusion of F$^-$ ions into and of CO$_3^{2-}$ ions out of the particles (Sato et al., 1995; Yang et al., 1999).

The diffusion of carbonate out of the particles increases the porosity of the pellets as it can be seen in Fig. 5. Table 4 shows the specific surface and pore size of the pellets. The results allow to confirm the increase of the pellets porosity due to the additional granular calcite reaction with fluoride, increasing the fluoride content in the pellets.

### 4.2. Product growth

Fig. 6 shows the particle size of the pellets from the FBR as a function of time. The particle size of the pellets from silica sand increases from 250 to 850 µm within 90 h (Exp. No. C-1), while the particle size of the pellets from granular calcite increases from 225 to 950 µm within 110 h (Exp. No. C-2). The linear growth rate ($G$):

$$G = \frac{dL}{dt}, \quad (8)$$

where $L$ is the particle size (m) and $t$ is the residence time (s). The average linear growth rate is $1.70 \times 10^{-9} \text{m s}^{-1}$. Therefore, the composition of seed materials shows a minor influence on the pellet growth.

The maximum pellet growth is limited by two factors: (i) the fluidization of the pellets, in order to prevent pellets cementation, and (ii) the reactor height, because the pellet growth increases the bed height and therefore, it is necessary to control the bed expansion in order to avoid the pellets out

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**Fig. 5 – SEM views: surface of pellets from the crystallization process using (a) silica sand and (b) granular calcite as seed material.**

**Fig. 6 – Particle size of pellets of calcium fluoride as a function of time.**

**Table 4 – Specific surface, pore size, particle size and composition of pellets from the crystallization process**

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Specific surface (m$^2$ gr$^{-1}$)</th>
<th>Pore size, 4 V/A BET (Å)</th>
<th>Particle size D[4,3] (µm)</th>
<th>Composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ca(OH)$_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CaCO$_3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>SiO$_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CaF$_2$</td>
</tr>
<tr>
<td>C-1</td>
<td>38.2</td>
<td>82.7</td>
<td>854.1</td>
<td>1.10 1.30 10.30 85.10</td>
</tr>
<tr>
<td>C-2</td>
<td>—</td>
<td>—</td>
<td>970.6</td>
<td>0.87 4.91 — 89.47</td>
</tr>
<tr>
<td>C-3a</td>
<td>—</td>
<td>—</td>
<td>462.9</td>
<td>0.56 7.45 — 87.97</td>
</tr>
<tr>
<td>C-3b</td>
<td>21.7</td>
<td>140.6</td>
<td>769.2</td>
<td>0.45 1.20 — 97.7</td>
</tr>
</tbody>
</table>
at the top of the reactor. Under these considerations, maximum fluoride content in the product could be achieved for high residence times as well as for fine seed material. In order to reach maximum pellets growth, it has been carried out an experiment with the experimental conditions shown in Table 2 (Exp. No. C-3b) using the pellets of calcium fluoride from the experiment C-3a as seed material. A particle size of 769 μm was obtained after a 230 h continuous operation as it can be seen in Table 4.

4.3. Product composition

(i) Qualitative analysis: Fig. 7 shows X-ray diffraction diagrams of the standard calcium fluoride (CaF$_2$ > 99%, Merck) and the obtained pellets from the crystallization process under the operation conditions shown in Table 2. It can be seen that the data of the standard calcium fluoride are very close to that of the synthetic calcium fluoride, indicating that the products from the crystallization process are mainly calcium fluoride.

(ii) Quantitative analysis: Fig. 8 shows pellet composition as a function of growth. It can be seen in Fig. 8, the pellet composition is a function of growth.
Table 4 shows the composition of the final pellets obtained in the crystallization process when silica sand and granular calcite are used as seed material. The use of silica sand as seed material involves an amount of SiO$_2$, which remains in the synthetic calcium fluoride.

Granular calcite as seed material (Exp. No. C-3b) allows to obtain pellets of more than 97% of CaF$_2$ after a 230 h continuous operation and negligible presence of SiO$_2$.

5. Conclusions

Fluoride wastewater by means of CaF$_2$ crystallization on seed material in a FBR has been studied to obtain synthetic calcium fluoride to be reused in the hydrofluoric acid manufacture.

The use of silica sand as seed material allows to obtain synthetic calcium fluoride containing small amounts of silica, and therefore, it is acceptable for ceramic and metallic industry.

The use of granular calcite as seed material allows to obtain pellets with a calcium fluoride content higher than 97% and negligible silica content. The synthetic calcium fluoride may be reused as raw material in the HF manufacture.

The crystallization process in a FBR applied to the removal of fluoride from wastewaters may be considered as a best available technology (BAT) according to the Council Directive 96/61/EC on Integrated Pollution Prevention and Control (IPPC). This technology contributes to an environmental friendly production, because it allows to reduce the waste production as well as the recovery of materials.

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