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TECHNOLOGY****IMPROVEMENTS AND INTENSIFICATION OF INDUSTRIAL CO-
CRYSTALLIZATION PROCESS FOR CADMIUM REMOVAL FROM WET
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ABSTRACT

Cadmium is a natural element present in the environment, including in the soil, in the air and in seawater. The main source of cadmium in the soil is the bedrock, and the most significant man-made cadmium input comes from industrial waste. Cadmium is also naturally present in 95% of global phosphate reserves, which consist of sedimentary rock laid down in seabeds over thousands of years. The purpose of this work consists, first, to establish a baseline knowledge of the status of the cadmium removal technologies from the wet phosphoric acid and, second, to present recent results on the improvement and the intensification of the co-crystallization process for cadmium removal from phosphoric acid, which is the most studied and patented technology in this field. Thus, we have developed new co-crystallization modes (DDS & DDC) that have significantly increased the cadmium removal and the P₂O₅ recovery from wet phosphoric acid, saved the heat energy cost and reduced the process design. The new co-crystallization modes have upgraded the cadmium removal respectively by 34% and 37%, within a high positive impact on the P₂O₅ content in the wet phosphoric acid which has been increased respectively by 0.56 and 1.46 P₂O₅ points.

KEYWORDS: Cadmium; Calcium sulfate; Co-crystallization; Phosphoric acid.**1. INTRODUCTION**

Cadmium is a natural element – a metal like iron or copper – that is naturally present in the environment, including in the soil, in the air and in seawater. The main source of cadmium in the soil is the bedrock, and the most significant man-made cadmium input comes from industrial waste – including from the steel and iron industry – improper waste disposal, vehicle emissions, atmospheric deposition, sewage, manure, and the use of untreated effluents for irrigation and fertilization [1]. Cadmium is also naturally present in 95% of global phosphate reserves, which consist of sedimentary rock that was laid down in seabeds over thousands of years [1]. There is no direct correlation between cadmium levels in the soil and cadmium levels in crops and in human diets. Cadmium uptake by plants is affected primarily by a wide range of factors, including soil acidity, its content of organic matter, clay and chloride, the presence of metal ions such as iron and zinc, an overuse of nitrogen, and crop species and varieties – for instance, differences in cultivars alone can affect cadmium uptake by the plant by up to 10 times. Cadmium levels in food are affected by a wide range of factors such as food processing and diet – for instance, wheat products have less than half the cadmium content of wheat grains and flour, and wheat has ten times more cadmium than eggs [1] [2] [3]. The WHO, FAO [4] and the European Food Safety Authority [5] have found no evidence of adverse health effects attributable to cadmium in any groups in the global populations, including high risk groups, at current exposure levels. The only significant case of cadmium toxicity worldwide occurred in the 1950s in Japan with subsistence farmers who grew rice on soils that were contaminated with industrial wastes [1] and there have been no documented cases, since then, of cadmium affecting public health as there is no scientific correlation between cadmium in fertilizers and health issues [3]. Nonetheless, major countries/states have established cadmium limits in their fertilizers on the basis of comprehensive risk assessments. These countries/states's limits include the following: USA (Washington) 889mg of Cd/kg of P₂O₅, Canada 889mg of Cd/kg of P₂O₅, USA (Oregon) 338mg of Cd/kg of P₂O₅, USA (California) 180mg of Cd/kg of P₂O₅, Japan 148mg of Cd/kg of P₂O₅, Australia 131mg of Cd/kg of P₂O₅, New Zealand 122mg of Cd/kg of P₂O₅, Belgium 90mg of

Cd/kg of P₂O₅, Austria 75mg of Cd/kg of P₂O₅, Denmark 48 of Cd/kg of P₂O₅ and Sweden 44mg of Cd/kg of P₂O₅ [1]. As for the European Union, there are currently no cadmium limits on fertilizers. Cadmium's final content in fertilizers depends both on the type and origin of the phosphate raw material as well as on the phosphoric fertilizers manufacturing processes. The cadmium removal from WPA is a priority for researchers and the industry. In spite of the fact that health risks associated with cadmium are not a cause for concern, various technologies continue to be researched for the removal of cadmium in phosphate rock and in phosphoric acid, including co-crystallization, ionic flotation, precipitation, solvent extraction, ion exchange and membrane separation. Nonetheless, there is still no proven and economically viable decadmiation technology at the industrial scale. Additionally, the management of the removed cadmium remains a big challenge since the corresponding environmental issues for its safe disposal pose a significant constraint. The purpose of this work consists first to establish a baseline knowledge of the status of the cadmium removal technologies from the wet phosphoric acid, and second to present recent studies and researches on the improvement of the co-crystallization. The later has been the most considered and studied technology for the cadmium removal from phosphoric acid. Thus, the present work aims to deepen the study of the thermodynamics and the kinetics of the co-crystallization, and to find novel parameters that have increased the cadmium removal efficiency of the original.

Cd in phosphate rock

Phosphate rock (PR) is naturally occurring mineral assemblages containing high concentration of phosphate minerals, which after processing is used to produce phosphoric acid and fertilizers. It is a natural mineral deposit of phosphorus and calcium, which belongs to the species of the apatite family. PRs resources occur principally as sedimentary marine phosphorites. The largest sedimentary deposits are found in northern Africa, China, the Middle East, and the United States [7]. More than 40 countries all over the world produce PRs which are mainly used for the manufacturing of phosphate fertilizers. The major ones are China, Morocco and United States [7]. In term of cadmium concentration, sedimentary PRs are generally more enriched than the igneous deposits, typically in the range of 3–150 mg Cd per kg of rock [8]. The amounts of Cd vary widely not only among various PRs sources but also even in the same deposit. The composition of phosphate rocks largely depends on its type and origin. Table 1 shows examples of Cd concentration in PRs.

Table 1. Examples of Cd concentration (mg/Kg P₂O₅) in phosphate rocks [6]

| Phosphate rocks | Davister, 1996 | Oosterhuis et al, 2000 |
|---------------------------|----------------|------------------------|
| Igneous rock | | |
| Russia (Kola) | <13 | 0.25 |
| South Africa (Phalaborwa) | <13 | 0.38 |
| Sedimentary rock | | |
| USA (Florida) | 23 | 24 |
| Jordan | >30 | 18 |
| Morocco (Khouribga) | 46 | 55 |
| Syria | 52 | 22 |
| Algeria | 60 | |
| Egypt | 74 | |
| Israel | 100 | 61 |
| Tunisia (Gafsa) | 137 | 173 |
| Togo | 162 | 147 |
| USA (North Carolina) | 166 | 120 |
| Senegal (Taiba) | 203 | 221 |

Technologies of Cd removal

In the last decade several methods for the Cd removal from phosphoric acid and phosphate ore have been developed. Here below, we give a baseline knowledge of the status of Cd removal technologies, with a special focus on the co-crystallization, the most studied way for Cd removal during phosphoric acid manufacturing. The aim is to deepen the understanding and the knowledge about the physico-chemistry of the co-crystallization process, and present recent experiences and improvements of the original co-crystallization process for Cd removal from wet phosphoric acid.

Calcination

The removal of cadmium from phosphate rock by calcination is governed by the known physical properties of cadmium metal and cadmium oxide. Cadmium can be removed from phosphate rock by calcination most effectively at temperatures between approximately 850° and 1150°C under either an inert atmosphere or reductive conditions. The higher end of the temperature range is needed for the most effective cadmium removal. Calcination in the presence of chloride salts allows a temperature as low as 700°C to be used but this results in excessive corrosion [9]. The study of calcocadmated apatites treated at different temperatures (700-900 °C) under H₂S shows the extraction of Cd from apatite structure, essentially in the form of CdS. In the case of the calcination of apatites, the OH⁻ or F⁻ ions are replaced by S²⁻ ions coming from the decomposition of H₂S gas [10]. Significant research has been performed in the area of calcination, and several patents have been granted, for example the CERPHOS process for Cd removal by calcination on two steps, developed in Morocco, decreased the cadmium content, when heated in the range of 750 to 850°C under controlled pressure and atmosphere to reduce and volatilize the cadmium [11]. It appears that the only facility that has been built in the world to remove cadmium was installed (75 mtph) on the Island of Nauru for Nauru Phosphate Corporation and decreased the cadmium content of Nauru PR from about 600 to less than 120 mg/kg P, the exact cost of calcination is not known [12].

Cadmium sulphide precipitation

The earliest methods for the removal of cadmium from wet process phosphoric acid were based on the precipitation of CdS with H₂S or a soluble sulphide salt [13,15]. In some of the patent applications an overpressure was used to obtain low residual cadmium concentrations. Chemische Fabrik Kalk GmbH [13] reported a reduction of the cadmium content of 75 w% H₃PO₄ from 65 ppm to 13 ppm using an overpressure of 5 bar at 20°C. The precipitate was separated by filtration. More recent patent applications report a partial neutralization of the acid before the addition of the sulphide source [16,18]. Boliden AB [17] reported a reduction of the cadmium content of 62 w% H₃PO₄ from 20 mg/l to 2.5 mg/l after neutralization with NaOH to Na/P = 1:10 mol/mol (60°C). Hoechst AG [17] reported the removal of cadmium from Odda acid (30-35% HNO₃, 20-28% H₃PO₄, 7-10% CaO) after neutralization with ammonia until pH = 1. The cadmium content was reduced from 3-6 to 0.2 ppm. The major constraint of this way is that H₂S is a weak acid with low solubility and higher vapor pressure under phosphoric acid media. So, working under higher pressure is required to reduce H₂S emission from phosphoric acid. Another way which is suitable for fertilizer process production and that was recently patented by OCP, consist to increase the pH of the phosphoric acid in order to enhance H₂S solubility and then the uptake of Cd as sulfide form [19].

Cadmium precipitation, adsorption and flotation with organic sulfur containing compounds

Solid diphenyldithiocarbamate salts, Ph₂NCSSM, or their aqueous solutions were used to remove cadmium ions from 65% H₃PO₄. The Cd containing precipitate was separated by filtration [20]. For Cd adsorption, A diorganyl-O,O-ester of dithiophosphoric acid adsorbed on active carbon or silica (20-60% w/w (RO)₂PSSH on adsorbent) was used to remove cadmium ions from a 40% H₃PO₄ solution. The Cd complexing ligand and the adsorbent can also be added separately to the H₃PO₄ solution. Apart from diorganyl-O,O-esters of dithiophosphoric acid, O-esters of dithiophosphonic acid ((RO)RPSSH) and diorganyldithiophosphonic acids (R₂PSSH) were used for the removal of cadmium from Odda-acid. For application at high temperatures (50-80°C) the addition of a large amount of a reductive compound is necessary [21]. About 1 w% Fe powder was used to remove Cd from 72% H₃PO₄ at 70°C. For flotation, After reduction of the phosphoric acid (Fe²⁺/Fe³⁺> 6) a diorganyl-O,O-ester of dithiophosphoric acid was added to the phosphoric acid. The Cd-containing precipitate was removed by flotation [22] [23].

Cadmium removal by liquid-liquid extraction

A 10% w/w solution of a dialkyl-O, O-ester of dithiophosphoric acid (RO)₂PSSH, in kerosene was used to remove cadmium ions from 40-70% w/w H₃PO₄ [24,25]. Re-extraction of the loaded organic phase was performed with 30% w/w HCl or 48% w/w HBr solutions. Apart from diorganyl-O,O-esters of dithiophosphoric acid, ((RO)₂PSSH, O-esters of dithiophosphonic acid, R(RO)PSSH, and diorganyldithiophosphonic acids, R₂PSSH, were used for the extraction of cadmium ions from Odda acid (30-35% HNO₃, 20-28% H₃PO₄, 7-10% CaO). All compounds mentioned above are not stable in the phosphoric acid solution at higher temperatures (> 80°C) and decompose more or less.

Cadmium removal by ion exchange

For the removal of cadmium by means of ionic exchange, both cation and anion exchangers may be used, while cation exchangers are not selective to other cations (Fe, Mg, Ca) [26]. Ion exchange requires pre-removal of insoluble substances, which otherwise could clog ion exchanger and reduce bed life time; this is frequently omitted aspect of the application of this process. Ion exchanger regeneration generates large volumes of the solution of low metal concentration. The removal of cadmium using anion exchanger requires first its complexing to compounds of structure [CdX_n]²⁻ⁿ where X=Br, Cl, I and n varies from 1 to 4, which exhibit high affinity to anionic resins and thus, they are strongly and quite selectively retained. Achieving the same degree of Cd removal requires much lower amount of Br⁻ or I⁻ than Cl⁻, but it is required to maintain reductive environment. Anion

exchange method for removal of cadmium in form of chloride complex has been tested at the technical scale by Hydro Agri Rotterdam BV in the HDH Extra process [27]. The studies showed no blocking or damaging ion exchange bed, despite using only pre-clarification of acid. HDH Extra process was recommended by Lin and Schorr [28] for consideration as BAT (Best Available Techniques), however only phosphates rock of content up to 50 mg Cd/kg P can be used as raw materials.

Cadmium removal by electrodeposition

Electrodeposition is an elegant method for the removal of Cd, since the element is obtained in a concentrated form without the use of additional chemicals. De Jong and Schmal [29] have performed an investigation on the electrolytical removal of cadmium from concentrated phosphoric acid solutions. The experiments were performed with a rotating disk electrode (2000 rpm) and with parallel flat - plate electrodes (cathode and anode). Graphite or lead were used as the cathode and platinum as the anode. The reference electrode is a saturated calomel electrode (SCE). Cd was reduced at -750 mV SCE with an initial current efficiency of 100%. The current efficiency for cadmium dropped to a value of a few percent after deposition of a layer of cadmium on the cathode. This is caused by the lower hydrogen overvoltage of the cadmium coated electrode compared with a clean graphite or lead electrode. The presence of copper in the phosphoric acid solution caused a tremendous increase of the hydrogen reduction at -500 mV SCE and at the graphite electrode. The lead electrode gave a much smaller hydrogen reduction at potentials more positive than -800 mV SCE.

Cadmium removal by adsorption (ELICAD process)

This process would eliminate cadmium from a continuous flow of phosphoric acid by a selective adsorption of cadmium on an activated material. Once this material is saturated, it can be regenerated five times by a physico-chemical treatment. The process allows also the removal of other trace metals like arsenic, mercury, nickel, copper, zinc, vanadium, chromium and lead and most probably uranium [6]. According to estimates in 2009, the investment costs should be below 1.2 million Euros for an installation treating 1200 tons of phosphoric acid per day and the fertilizer price increase from the use of this technology would be around 12 to 32 Euros/ton P₂O₅ for a 90 % effectiveness [6]. However, these figures need to be refined when data from a pilot plant will be available. This was expected by mid 2010, however no project for constructing a pilot plant found the necessary funding and it is uncertain when this will happen [6].

Cadmium removal by co-crystallization

The co-crystallization process is the most studied and patented technology for the cadmium removal from wet phosphoric acid. The process consists on the co-crystallization of cadmium with anhydrite (CaSO₄) when a concentrated phosphoric acid (50%-54% P₂O₅), including its sludge content, is heated and further treated with calcium phosphate and sulfuric acid. Cadmium shows the highest affinity to anhydrite (CaSO₄) – hundred-times greater than to Dihydrate gypsum [30]. One the major process is the CERPHOS process. It has been patented in 1996 and involved the removal of cadmium in the feed acid by co-crystallization into a precipitate of anhydrite and separation of the latter by settling and/or filtration [31]. A product acid with a cadmium concentration of less than 23 mg kg⁻¹P was consistently produced from a feed acid with a cadmium concentration of 170 mg kg⁻¹P (Davister, 1996) [27]. However, Van Kauwenbergh [12] has pointed out that in evaluating the costs some caution should be used in applying the value of the cadmium-containing rejects as a way of reducing the costs per ton of phosphorus for the co-crystallization process. He emphasizes the very variable and decreasing value of cadmium metal between 1995 and 1999, and the cost of disposing of reject material as a hazardous waste. The disadvantage of this method is a production of significant amounts of phosphogypsum with considerable P₂O₅ losses. This will impact significantly both investment and operating cost at the industrial scale. So, this has yet to be taken to the semi-industrial pilot plant scale to estimate the effective cost of co-crystallization process.

2. MATERIALS AND METHODS

Experimental

Thermodynamics of the cadmium removal by co-crystallization

Uptake of Cd²⁺ in calcium sulfate proceeds by isomorphous substitution of Ca²⁺ ions [32/33]. The degree of uptake is given by the partition coefficient D that takes into account the competition of Cd²⁺ and Ca²⁺ for the same lattice site. D is defined as:

$$\frac{[Cd^{2+}]/[Ca^{2+}](\text{solution})}{[Cd^{2+}]/[Ca^{2+}](\text{Crystal})} \quad (i)$$

A constant D-value implies that the resulting Cd²⁺ concentration in the crystals can be influenced by either the Cd²⁺ or the Ca²⁺ concentration in the solution. Thermodynamically, an expression has been derived for D:

$$D = \frac{\gamma(\text{Ca}^{2+})_s}{\gamma(\text{Cd}^{2+})_s} * \frac{\gamma(\text{Cd}^{2+})_l}{\gamma(\text{Ca}^{2+})_l} * \frac{K_{sp}(\text{CaSO}_4)}{K_{sp}(\text{CdSO}_4)} * e^{(-\epsilon_{el}/RT)} * e^{(-\Delta\mu(\text{CdSO}_4 \rightarrow \text{CaSO}_4)/RT)} \quad (\text{ii})$$

D comprises the activity coefficients γ of Cd^{2+} and Ca^{2+} in the solution (i) and in the solid phase (s), the thermodynamical solubility products of calcium and cadmium sulfate, the energy of elastic lattice deformation ϵ_{el} and the free energy required to make a CdSO_4 lattice isomorphous with the corresponding CaSO_4 lattice. The activity coefficients represent in fact the deviation from ideality, which can also be expressed as an excess free energy ($\Delta G = -RT \ln \gamma$). Changes in energy affecting the activity coefficients can thus also be written as an exponent. For pure calcium sulfate $\gamma(\text{Ca}^{2+})_s$ equals 1, while $\gamma(\text{Cd}^{2+})_s$ is related to the bonding energy of Cd^{2+} in the calcium sulfate lattice. If all parameters in (ii) were known, D could be calculated. Mostly, however, the values of these parameters are not available, which hampers the use of equation (ii) for prediction of the D-value. It is hard to make an a priori prediction of the D-value on basis of (ii), but under certain conditions the effect of some parameters can become visible. For instance, at constant temperature and pressure the exponential terms as well as the solubility product remain constant. If in addition the uptake does not exceed a value of about 1%, the activity coefficients in the solid are also unaltered. In that case the D-value only depends on the activity coefficients in the solution and thus solely on the solution composition. Although an a priori prediction of D is as said not possible, the observed D-values may be understood by comparing the physical and chemical properties of Cd^{2+} and Ca^{2+} . Therefore in table. 2, some characteristics of these two ions are listed. The radii of Cd^{2+} and Ca^{2+} are almost equal, enabling replacement of Ca^{2+} by Cd^{2+} without introducing much lattice strain. It is therefore expected that the ϵ_{el} term in equation (ii) is small.

Table 2. Comparative properties of Ca^{2+} and Cd^{2+}

| Properties | Ca^{2+} | Cd^{2+} | Unit | Ref. |
|---------------------------------|------------------|------------------|--------|------|
| Radius (8-coordination) | 112 | 107 | pm | [35] |
| Hydration enthalpy | -1602 | -1833 | KJ/mol | [36] |
| Hydration enthalpy sulfate salt | 18 | 52 | KJ/mol | [37] |
| Pitzer constant sulfate salt | | | | |
| $\beta^{(0)}$ | 0.20 | 0.2053 | | |
| $\beta^{(1)}$ | 2.65 | 2.62 | | |
| $\beta^{(2)}$ | -55.7 | -48.07 | | |
| Solubility of sulfate salt | 2.10^{-2} | 6 | Mol/Kg | [38] |

Kinetics of the cadmium removal by co-crystallization

The incorporation of an impurity takes place at the surface. Uptake is therefore mostly influenced by surface processes as growth [33]. The first is that the growth rate is so high that any Cd^{2+} or Ca^{2+} near the crystal surface has an equal chance to become incorporated with equal diffusion coefficients for these two ions, The resulting D value is equal to 1. For Cd^{2+} in gypsum where D is smaller than 1 this means an increase with respect to the equilibrium situation, due to entrapment at the surface. The second situation is equilibrium without growth, but with an exchange of ions between the solid state and the solution. Since this will only occur at a very large time scale, equilibrium partition coefficients can only be obtained by extrapolation to growth rate zero. In practice, D will lie between the thermodynamical value and the value determined by the diffusion rates. The kinetical aspects have long been recognized. In many studies, efforts are made to explain the trapping of impurities as a function of growth rate. For a proper explanation the reactions occurring during growth of the crystals and uptake should be considered for each case separately. By comparing the respective reaction rates of, in this case, Cd^{2+} and Ca^{2+} some prediction of the kinetical behaviour of uptake may be done. The reactions that can be considered are bulk diffusion, adsorption desorption, surface diffusion, transport along a step, bonding at the kink site, or direct attachment from the solution. Since during these reactions dehydration occurs, the reaction rates are somehow related to well-known processes as ligand exchange, dehydration and diffusion.

Materials & experiments

A typical co-crystallization process for cadmium removal from phosphoric acid consists on cadmium incorporation during hemihydrate/anhydrite co-crystallization. The degree of incorporation depends on the

supersaturation, which is affected by the sulfuric acid excess [33/34], the free sulfuric acid content and the phosphoric acid concentration as a driving forces for co-crystallization. For that, the concentrated phosphoric acid (50%-54% P₂O₅), is heated at 75°C under specific conditions in terms of free sulfate and solid content, and further treated with phosphate rock to adjust the final free sulfate content. The free sulfuric acid content points out the amount of sulfate ions in excess of the calcium ions, and is given as weight percentage of free H₂SO₄ in solution. This percentage can thus be either positive for excess sulfate ions or negative for excess calcium ions. To improve the original co-crystallization process for cadmium removal from industrial phosphoric acid, several semi batch lab scale experiments were done. All semi-batch experiments were conducted typically to the process as shown in Fig.2 below, using small reactors of one-liter capacity, filter and raw materials:

- Phosphoric acid industrial grade (52 wt % to 54 wt % P₂O₅).
- Sulfuric acid H₂SO₄ (96 wt %).
- Phosphate rock (31 wt % P₂O₅).
- Phosphogypsum slurry (35 wt % solids).

The experiments were based on a phosphate rock sample containing already a very low 10 ppm cadmium content, which is well below the average for sedimentary rock that typically ranges from 23 to 203 mg Cd/kg P₂O₅ (see Table 1). Basically, for each experiment, the operating conditions such as temperature, free sulfate and solid contents during co-crystallization steps, and final free sulfate content at the free sulfate removal step, were carefully studied and chosen to reach a high kinetics of Dihydrate/Hemihydrate/Anhydrite co-crystallization. Finally, solids were separated by press filtration to recover the phosphoric acid with reduced cadmium concentration. The chemical analysis of the P₂O₅ content was carried out by UV/VIS Spectrometry, and the cadmium content by Inductively Coupled Plasma Spectrometry (ICP), the free sulfate was determined by titration with standard barium chloride solution. The calcium sulfate crystallization form was characterized by X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM).

Methodology for the original co-crystallization process (OCC)

There are many patents concerning the cadmium removal (decadmiation) from phosphoric acid by co-crystallization. For this experimental and improvement work we have referred to the process block diagram given in Fig.1 below.

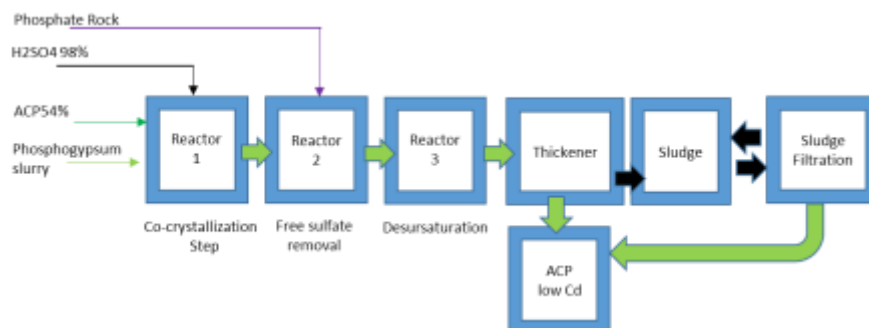


Fig.1. Original co-crystallization process for cadmium removal from phosphoric acid

The process concerns the cadmium removal from concentrated phosphoric acid (54 wt % P₂O₅) and involves several steps:

- The co-crystallization step: phosphogypsum slurry and concentrated sulfuric acid (98 wt%) were added to the phosphoric acid to reach respectively 6 wt% of free sulfate and 6% wt of solid. The working temperature is 70°C.
- The free sulfate removal step (desulfation): the free sulfate is removed by precipitation using fine phosphate rock within particle size distribution less than 160 μm. The working temperature is about 90°C.



With x equaling 0.5 or 2 depending on working conditions (temperature and P₂O₅ content).

- The desaturation step: after the free sulfate removal step, the treated phosphoric is given an additional residence time for desaturation in order to complete kinetics of reactions and having therefore very lower free sulfate content.

- The solid removal: at the end of the process, the treated phosphoric acid is clarified to separate solids from the phosphoric acid with reduced cadmium concentration. The sludge is filtered by press filter to increase the P_2O_5 recovery and dispose the calcium sulfate solid.

Methodology for the improved of the OCC process

Besides the original process philosophy (Fig.1), we have investigated two new improvements of the OCC process to explore how both P_2O_5 recovery and cadmium removal could be enhanced. For the first improvement, we have particularly developed DDS mode (Separated Decadmiation Desulfation) in which the decadmiation and the desulfation steps are separately conducted, each one has had its specific process parameters ($T^\circ C$, P_2O_5 , residence time, sulfate and solid contents).

The second improvement developed consists on the DDC mode (Combined Decadmiation Desulfation) in which the decadmiation and the desulfation steps are conjointly conducted during the de desulfation step. The major improvement related to the DDS and the DDC modes in comparison to the OCC process, is that the phosphogypsum solid which is calcium sulfate Dihydrate, is not brought as phosphogypsum slurry. The point is typically to avoid the dilution of the CPA out by the addition of phosphogypsum slurry containing about 75 wt% of WPA at 29 wt% P_2O_5 . This will consequently increase the kinetics of the co-crystallization, save the heat energy cost and reduce process design by eliminating the phosphogypsum stream (tank, agitator, pumps and piping).

3. Results and discussions

OCC process Test

The driving force for the cadmium removal by co-crystallization is the recrystallization of calcium sulfate Dihydrate or Hemihydrate to Anhydrite. This is why in the OCC process (Fig.1 above), phosphogypsum slurry (calcium sulfate Dihydrate) and concentrated sulfuric acid (98 wt%) were added to the ACP 54% (CPA Feed). In that case, the CPA Feed's free sulfate and solid contents were increased to reach 6 wt% each. The working temperature is about $70^\circ C$. After the co-crystallization, the free sulfate is removed by precipitation at $90^\circ C$ using fine phosphate rock within particle size distribution less than $160 \mu m$ (desulfation step).

Table 3 gives the chemical composition of the CPA Feed used for the experiments. Referring to the X-Ray Diffraction analysis in Fig.3, the CPA Feed's sludge is mainly composed of Anhydrite ($CaSO_4$) with small quantities of Hemihydrate ($CaSO_4 \cdot 1/2H_2O$) and Sodium fluosilicate (Na_2SiF_6). Fig. 2 and 4 show X-Ray Diffraction and Scanning Electron Micrographs of phosphogypsum ($CaSO_4 \cdot 2H_2O$). In the final stage of the process, the CPA is given an additional residence time for desaturation in order to complete kinetics of reactions and having therefore very lower free sulfate content. Solid is then removed by clarification from the CPA out. The sludge is filtered by press filter to increase the P_2O_5 recovery.

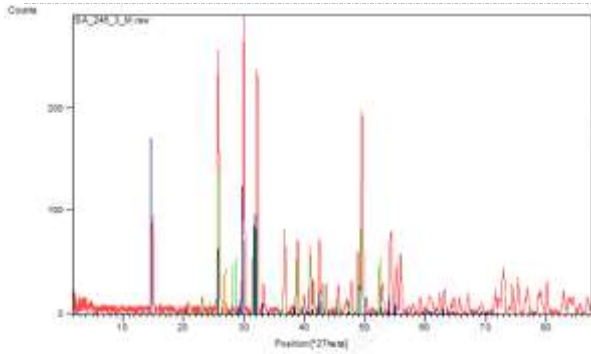
Table 4 gives the process parameters and results according to the OCC process tests. The results show a low Cd removal of about 31.6% (based on $mgCd/kgP_2O_5$ ratio) within a significant negative impact on the P_2O_5 content in the CPA Out which has been decreased by 1.34 P_2O_5 points due to the dilution by the added phosphogypsum slurry. As mentioned in Fig. 5 and 6, the CPA Out's sludge still containing a high quantity of phosphogypsum (calcium sulfate Dihydrate) which involves an inefficient recrystallization Dihydrate-Anhydrite during the OCC process, and therefore a low cadmium uptake by Co-Crystallization. The presence of Anhydrite is mainly due to the CPA Feed.



Fig.2. Scanning Electron Micrographs of phosphogypsum

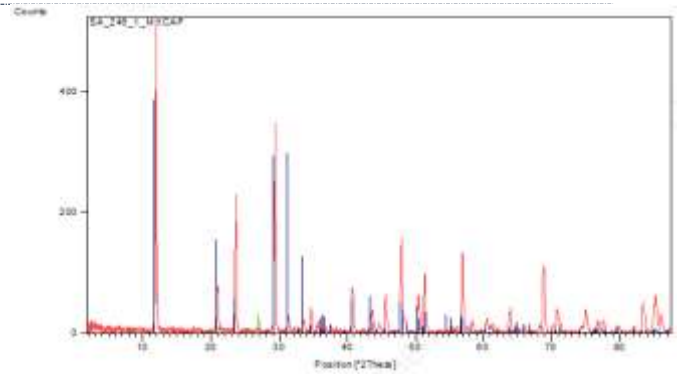
Table 3. Chemical analysis of CPA Feed

| Element | Wt % in WPA |
|--------------------------------|-------------|
| P_2O_5 | 52,34 |
| CaO | 0.37 |
| SO ₃ | 1.94 |
| SiO ₂ | 0.43 |
| MgO | 0.21 |
| Fe ₂ O ₃ | 0.29 |
| Al ₂ O ₃ | 0.66 |
| Na ₂ O ₃ | 0.10 |
| F | 0.79 |
| K ₂ O | 0.05 |
| C org | 0.01 |
| Cd | 0.0012 |



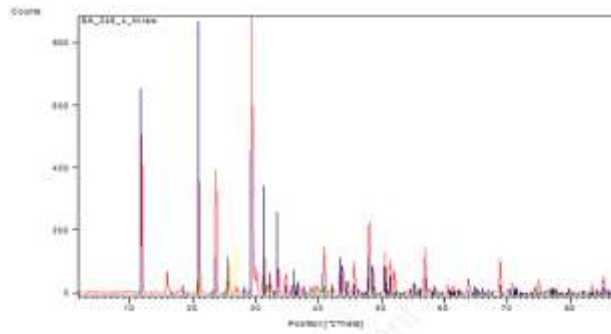
| Visible | Ref. Code | Compound Name | Chemical Formula |
|---------|-----------|-------------------------|----------------------|
| +++ | 03-0368 | Anhydrite | Ca (S O4) |
| +++ | 83-0438 | Calcium Sulfate Hydrate | Ca (S O4) (H2 O) 0.5 |
| +++ | 83-2468 | Quartz, syn | Si O2 |

Fig.3. X Ray Diffraction of CPA Feed's sludge



| Visible | Ref. Code | Compound Name | Chemical Formula |
|---------|-----------|---------------|--------------------|
| +++ | 70-0983 | Gypsum | Ca (S O4) (H2 O) 2 |
| +++ | 83-2468 | Quartz, syn | Si O2 |

Fig.4. X Ray Diffraction of phosphogypsum.



| Visible | Ref. Code | Compound Name | Chemical Formula |
|---------|-----------|---------------|--------------------|
| +++ | 72-0596 | Gypsum | Ca (S O4) (H2 O) 2 |
| +++ | 74-2421 | Anhydrite | Ca (S O4) |
| +++ | 83-2468 | Quartz, syn | Si O2 |

Fig.5. X Ray Diffraction of CPA Out's sludge (OCC process).

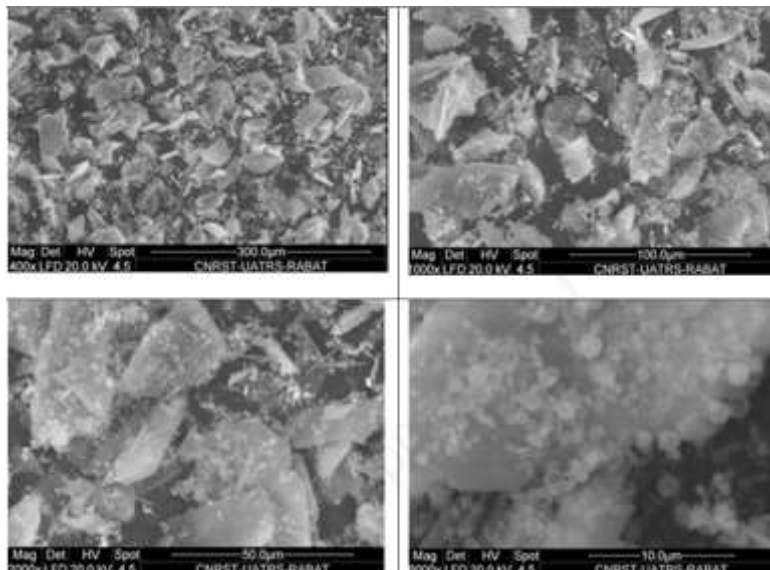


Fig.6. Scanning Electron Micrographs of CPA Out's sludge (OCC process)

Table 4. Results of CPA decadmiation through the OCC process

| Specific consumption | Step | Wt% P ₂ O ₅ | T°C | Wt% SO ₄ ²⁻ | Wt% Solid | Cd (ppm) | Cd (mg/KgP ₂ O ₅) |
|--|--------------------|-----------------------------------|-----|-----------------------------------|-----------|-------------------|--|
| Sulfuric Acid 93.78g/Kg P ₂ O ₅ | CPA Feed | 52.34 | 55 | 4.00 | 0.4 | 12 | 22.93 |
| | Co-crystallization | 50.00 | 70 | 6.00 | 6.0 | 11 | 22.00 |
| Phosphogypsum 492g/Kg P ₂ O ₅ | Desulfation | 50.43 | 90 | 1.00 | 13 | 9 | 17.85 |
| | CPA Out | 51.00 | 60 | 0.67 | 0.5 | 8 | 15.69 |
| Phosphate Rock 157g/Kg P ₂ O ₅ | | | | | | Cd removal | 31.6% |

DDS co-crystallization mode Test

In order to improve the cadmium removal and P₂O₅ recovery of the OCC process, we have developed the DDS mode. The point is that the decadmiation and the desulfation steps still separately conducted as in the OCC process, with the same process parameters (T°C, P₂O₅, residence time, sulfate and solid contents). The key difference compared to the OCC process is the elimination of the phosphogypsum stream, which brings calcium sulfate Dihydrate solid, and consider only the CFA Feed’s solid content (1.6 wt%) for cadmium removal by co-crystallization. This improvement aims to avoid the dilution of the CPA caused by the addition of the phosphogypsum slurry containing about 75 wt% of phosphoric acid with 29 wt% P₂O₅, and also to maintain a high P₂O₅ content during the co-crystallization so as to improve the deshydration of the calcium sulfate Dihydrate and then the kinetics of co-crystallization. Table 5 gives the process parameters and the obtained results according to the DDS mode.

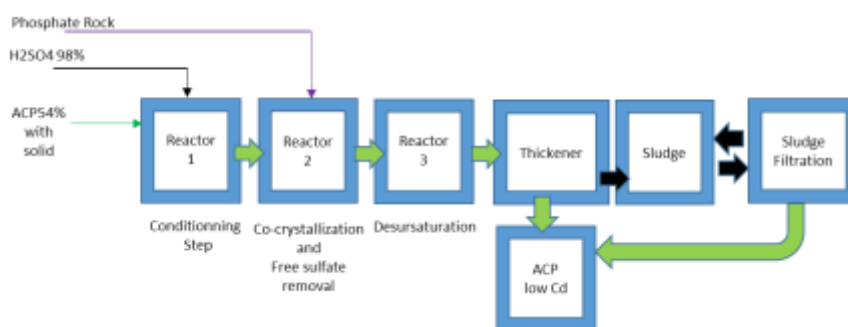


Fig.7. DDS mode for cadmium removal from phosphoric acid

Table 5. Results of CPA decadmiation through the DDS mode

| Specific consumption | Step | Wt% P ₂ O ₅ | T°C | Wt% SO ₄ ²⁻ | Wt% Solid | Cd (ppm) | Cd (mg/KgP ₂ O ₅) |
|---|--------------------|-----------------------------------|-----|-----------------------------------|-----------|-------------------|--|
| Sulfuric Acid 103g/Kg P ₂ O ₅ | CPA Feed | 52.34 | 55 | 4.10 | 1.6 | 12 | 22.93 |
| | Co-crystallization | 52.00 | 74 | 6.10 | 2.6 | 10 | 19.23 |
| Phosphate Rock 187g/Kg P ₂ O ₅ | Desulfation | 52.50 | 90 | 1.00 | 8.0 | 8 | 15.24 |
| | CPA Out | 52.90 | 60 | 0.70 | 0.5 | 8 | 13.23 |
| | | | | | | Cd removal | 42.3% |

As prospected, the results point out the good effect of the DDS mode for improving the performance of cadmium removal and P₂O₅ recovery relatively to the OCC process. In fact, the DDS mode allows a cadmium removal of about 42.3% (based on mgCd/kgP₂O₅ ratio), which constitutes an increase of cadmium removal of about 34% compared to the OCC process, within a positive impact on the P₂O₅ content in the CPA Out which has been increased by 0.56 P₂O₅ point. Thus means that the elimination of the phosphogypsum slurry stream and

considering only the CPA Feed's solid content (1.6 wt%) has limited the dilution of the CPA Feed, and induced a high P₂O₅ content during the Co-Crystallization step. Accordingly, there were good conditions for calcium sulfate dehydration, and consequently a sufficient kinetics for Hemihydrate-Anhydrite recrystallization. As a result, the removal by co-crystallization has been significantly enhanced.

DDC co-crystallization mode Test

Depending on the phosphate ore origin, especially the impurities content, sometimes the calcium sulfate precipitated during phosphoric acid concentration would mainly be Anhydrite instead of Hemihydrate. As regards our case, we have found that the CPA Feed's solid (1.6 wt%) is mainly Anhydrite (see Fig.3 above) with a small quantity of Hemihydrate. For that reason, we have thought that using CPA Feed free solid (0.4 wt%) could be a good choice for increasing the CPA Feed's P₂O₅ content. As a result, the dehydration of calcium sulfate Hemihydrate during the desulfation step will be enhanced and then the cadmium removal by co-crystallization. To confirm that, we have investigated the DDC co-crystallization mode (Combined Decadmiation Desulfation) shown in Fig.8, in which the decadmiation and the desulfation steps are conjointly conducted during the desulfation step (Reactor 2 in Fig.8). In fact, the DDC mode will benefit fundamentally from the Hemihydrate-Anhydrite co-crystallization during desulfation step at the condition of the high P₂O₅ content of the CPA, which ensures good kinetics for the cadmium removal by co-crystallization and consequently improve the efficiency of the cadmium uptake from the CPA.

Table 6 gives the process parameters and results according to the DDC mode. As mentioned in the table, the results highlight and confirm the expectations, the cadmium removal was upgraded to about 43.2% (based on mgCd/kgP₂O₅ ratio) which represents an increase of cadmium removal of about 34% compared to the OCC process, within a significant positive impact on the P₂O₅ content in the CPA Out which has been increased by 1.46 P₂O₅ points.

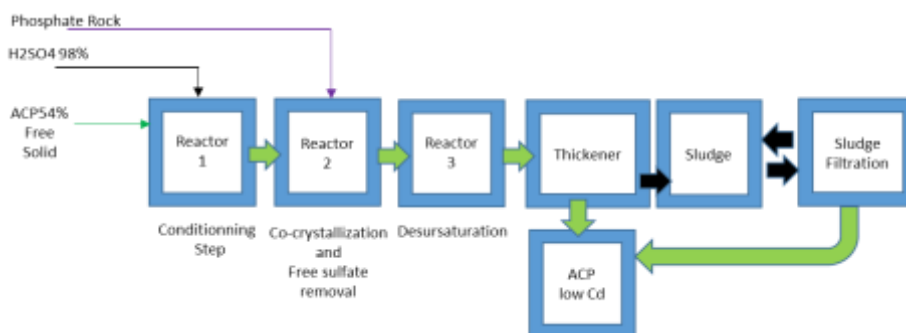


Fig.8. DDC mode for cadmium removal from phosphoric acid

Table 6. Results of CPA decadmiation through the DDC mode

| Specific consumption | Step | Wt% P ₂ O ₅ | T°C | Wt% SO ₄ ²⁻ | Wt% Solid | Cd (ppm) | Cd (mg/KgP ₂ O ₅) |
|---|--------------------|-----------------------------------|-----|-----------------------------------|-----------|-------------------|--|
| Sulfuric Acid 95g/Kg P ₂ O ₅ | CPA Feed | 52.34 | 55 | 4.00 | 0.4 | 12 | 22.93 |
| | Co-crystallization | 52.20 | 70 | 6.00 | 1.0 | 9 | 17.24 |
| Phosphate Rock 202g/Kg P ₂ O ₅ | Desulfation | 53.00 | 90 | 1.00 | 6.0 | 7 | 13.21 |
| | CPA out | 53.80 | 60 | 0.50 | 0.5 | 7 | 13.01 |
| | | | | | | Cd removal | 43.2% |

4. CONCLUSION

In this experimental study, we have developed new solutions for the intensification of the industrial and original co-crystallization process, the most studied and patented technology for the cadmium removal from phosphoric acid. Basically, we have found out new Co-Crystallization modes (DDS & DDC) that have significantly increased the cadmium removal and the P₂O₅ recovery from wet phosphoric acid, saved the heat energy cost and reduced the process design by eliminating the phosphogypsum stream (tank, agitator, pumps and piping). In fact, the driving force for the cadmium removal by co-crystallization is the recrystallization of calcium sulfate Dihydrate

or Hemihydrate to Anhydrite. Accordingly, suitable conditions are required for a high calcium sulfate deshydration, and consequently a faster kinetics for recrystallization and cadmium Co-Crystallization.

Referring to the OCC process (Original Co-Crystallization), the DDS mode (Separated Decadmiation Desulfation) has allowed an increase of cadmium removal of about 34% within a positive impact on the P₂O₅ content in the CPA Out which has been increased by 0.56 P₂O₅ point. The key improvement was the elimination of the phosphogypsum slurry stream and considering only the CPA Feed's solid content (1.6 wt%), and thus has limited the dilution of the CPA Feed, and induced a high P₂O₅ content during the Co-Crystallization step. Accordingly, there were good conditions for calcium sulfate dehydration, and consequently a sufficient kinetics for Hemihydrate-Anhydrite recrystallization.

Concerning the DDC mode (Combined Decadmiation Desulfation), additionally to the phosphogypsum slurry elimination, we have increased the CPA Feed's P₂O₅ content by using CPA Feed free solid (0.4 wt%). Therefore, the Hemihydrate-Anhydrite co-crystallization during desulfation step was carried out at the condition of the high P₂O₅ content of the CPA, and thus has occurred faster kinetics for the cadmium removal by co-crystallization and consequently improved the efficiency of the cadmium uptake from the CPA. As a result, compared to the OCC process, the cadmium removal was upgraded by 37% within a considerable high positive impact on the P₂O₅ content in the CPA Out which has been increased by 1.46 P₂O₅ points. Table 7 below gives a sum up of the co-crystallization processes investigated in this present work.

Table 7. Sum up of Cd removal from CPA: Original co-crystallization process Vs Improved modes (DDS&DDC)

| Process | OCC | DDS | DDC |
|---|------------------|------------------|------------------|
| P ₂ O ₅ in CPA Feed | 52.34 wt% | 52.34 wt% | 52.34 wt% |
| Cd in CPA Feed (ppm) | 12 ppm | 12 ppm | 12 ppm |
| (mg Cd/KgP ₂ O ₅) | 22.93 | 22.93 | 22.93 |
| Cd in CPA out (ppm) | 8 ppm | 7 ppm | 7 ppm |
| (mg Cd/KgP ₂ O ₅) | 15.69 | 13.23 | 13.01 |
| Cd removal | 31.6 % | 42.3% | 43,3% |
| P ₂ O ₅ CPA out | 51.00 wt% | 52.90 wt% | 53.80 wt% |

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