

CLEAN PROCESS FOR THE PRODUCTION OF DEFLUORINATED DICALCIUM PHOSPHATE USING PHOSPHATE ROCK

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ABSTRACT

A new process for the production of defluorinated dicalcium phosphate using phosphate rock was developed. This new process has the main characteristic of being clean, without the production of any liquid waste. The process has essentially three main steps: phosphate rock digestion, defluorination and neutralization. In the first step a phosphate rock slurry is batch digested with concentrated sulfuric acid in the presence of some additives that retain the fluorine in the solution, as well as enable the adequate growth of the calcium sulfate crystals and maximize the phosphate dissolution. At the end of the digestion the slurry is filtrated and the mother liquor is sent to the next step. The second step of the process is a fluorine salt precipitate sedimentation carried out by the addition of a potassium or sodium salt. The clear solution containing mainly a weak phosphoric acid is then neutralized, in the third step, in order to produce the final dicalcium phosphate product. After filtration the dicalcium phosphate is dried and the mother liquor is recycled to the first step of the process, the phosphate rock digestion. All the liquids of the process are recycled and no wastes are produced. This new process is economically interesting because it uses a very cheap raw material, the phosphate rock, instead of the conventional defluorinated phosphoric acid.

INTRODUCTION

Phosphorus is an essential nutrient for living systems. Its main source in the nature is the so called apatite, a phosphate mineral, found in most cases in igneous or sedimentary deposits of fluorapatite, also called natural phosphate. In order to be used as fertilizer or mineral supplement for animals the mineral fluorapatite must be in a soluble form. There are basically two solubilization processes: thermal, that destroy the crystalline structure using heat, and the wet process, that uses the chemical energy to make this destruction. After the solubilization, other soluble phosphorus compounds are produced, mainly calcium and ammonium phosphates. For animal feed use, the most popular product is dicalcium phosphate (DCP) in dihydrate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) or anhydrous (CaHPO_4) form.

DCP is generally obtained by the neutralization reaction between defluorinated phosphoric acid and a calcium source, normally calcium carbonate or calcium hydroxide. The defluorinated phosphoric acid is more expensive than the normal wet phosphoric acid; it is used at 48-54% P_2O_5 , less than 0.2% F and is produced in large units of more than 100 thousands tpy of P_2O_5 [1]. Small units are not economically feasible due to the high costs of evaporation to concentrate the acid. So, the defluorinated phosphoric acid is an expensive raw material and it is available only near large phosphoric acid producers. On the other hand, phosphate rock is a relatively cheap and available raw material. In the international markets, the price relation between the P_2O_5 from the phosphoric acid @ 48-54% P_2O_5 and phosphate rock @ 32-36% P_2O_5 , varies from 2.5 to 5.0.

For defluorinated phosphoric acid, obtained by the thermal process or by solvent extraction, this relation can reach the value of 10.0. On the other hand, for the DCP, the relation between P_2O_5 content and defluorinated phosphoric acid P_2O_5 content is only 1.3.

The economic interest to produce DCP directly from phosphate rock lies in this price relation. It is possible to obtain relations between the market price of P_2O_5 in DCP to the cost of P_2O_5 of phosphate rock with values near 3.0. This is very attractive from the economic point of view.

PROCESS DESCRIPTION

The proposed process uses phosphate rock and produces phosphoric acid with the objective of producing DCP, without the need for concentrating phosphoric acid, which is normally a complex and energetically expensive step. This makes it possible to produce phosphoric acid in small scale, with nominal capacities of less than 20 thousand tpy of P_2O_5 and even in batch processing.

Figure 1 shows the proposed process diagram. Phosphate rock is fed in the digestion reactor with the recycle water that comes from the gas washing column and with some additives that promote good crystal growth of gypsum, $CaSO_4 \cdot 2H_2O$, and aids the fluorine removal. Concentrated sulfuric acid is slowly added to the digestion reactor. The heat released by the reaction elevates the reaction temperature, thus favoring the phosphate rock attack. The gases liberated by the reaction are absorbed in a washing column that utilizes the water that comes from the DCP filter. The washed gases are discharged to atmosphere. The main reaction occurring in the digestion reactor is:



After completion of the reaction the slurry is discharged to a filter where the gypsum and insoluble impurities are separated from the phosphoric acid solution. After the filtration, the cake is washed with fresh water to remove the retained phosphoric acid. The amount of water used must be nearly the same as the water retained by the cake. In this way the total water balance is conserved. The gypsum produced has about 30% humidity, a small amount of unreacted phosphate rock and can be used in this form in agriculture, as soil conditioner[2].

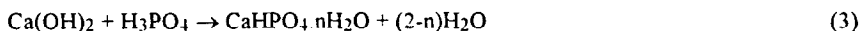
The next step of the process, is the defluorination of the diluted phosphoric acid produced. This is made by the addition of an inorganic salt, such as sodium chloride in a settling chamber. After decantation the clear and defluorinated phosphoric acid solution is removed by slowly siphoning, in order to prevent the removal of fluossilicate salt. The main reaction involved in the defluorination step is, for the NaCl case:



If the amount of silica in the phosphate rock is not enough to complete the fluorine removal, a supplement of active silica must be added in the reaction step. The precipitated fluossilicate salt can be removed from the decanter, washed and dried to be used as a fluorine supplement in water treatment systems, or as a fluorine source in the pharmaceutical industry.

The defluorinated phosphoric acid solution is then sent to the neutralization step, where the DCP is produced. The clear acid solution must be free of sulfate ion. This can be done by correcting the pH in the digestion reaction step. The sulfate free acid solution is then neutralized with a calcium source, such as calcium hydroxide or calcium carbonate. This step is controlled by the pH value of the solution. Temperature defines the form of the precipitated DCP crystals. For

temperatures above 90°C, anhydrous DCP will preferentially be formed. During the neutralization, the main reaction occurring in the system is, for the Ca(OH)₂ case:



with n=2 for the dihydrate form or n=0 for the anhydrous form.

To obtain a DCP product with a good crystallinity and with well-formed crystals it is necessary to control the supersaturation during the neutralization. This can be done by slow addition of the calcium source. In this way the formation of insoluble phosphates can also be avoided. After reaction completion, about 2 hours, the slurry is sent to a filter for separation of the DCP and the mother liquor. The DCP must be washed with fresh water in the same amount as the contained humidity (about 40%), in order to keep control of the total water balance. The mother liquor receives the DCP washing water and is sent to the washing gas column, closing the cycle. In this way, no effluents are produced.

The DCP produced is then dried in a convective way and sent to the storage system. The DCP can be produced at different concentrations, which gives good flexibility to the process.

EXPERIMENTAL

Several experiments were conducted for all process steps. The experiments were done in a 1 liter closed flask with control of the temperature by means of a thermostated bath. The flask has also a gas washing system that eliminates the fluorine in the effluent gas and prevents the water from evaporating, in order to keep the global water balance. This system is also used for the other process steps, i. e., fluorine removal and diluted phosphoric acid neutralization. For all the solid-liquid separations vacuum Büchner filter is used.

Three kinds of phosphate rock raw materials were used: Morocco (sedimentary), Catalão (igneous) and Patos de Minas (sedimentary). The chemical analyses of these phosphate rocks are presented in Table 1. In all experiments the phosphate rocks were ground to -200 mesh. The sulfuric acid used was of commercial grade. Calcium hydroxide, as well calcium carbonate, was of technical grade. Normally these present good quality and a low impurity content.

In all cases only the batch way of processing was used, taking in account however the mother liquor recycle aspect. In this way all experiments were conducted recycling five times the mother liquor to the digestion reactor.

The parameters studied for each process step is described below. For the phosphate rock digestion reaction step, the parameters studied were as follows:

- digestion reaction time: 2, 4 and 6 hours.
- digestion reaction temperature: 50 and 75°C.
- speed rotation of the reactor impeller: 90 and 300 rpm.
- free sulfate level in the reactor: 1, 2 and 5%.
- surface active agent in the reactor: 0 and 0.5%.
- addition of active silica: 0 and 50% of the stoichiometric needs.
- addition of gypsum crystal growth conditioner: 0 and 1%.
- final pH: 0.2 to 1.5.
- time of sulfuric acid addition: 20 to 70% of the total reaction time.

For the defluorination step, the parameters studied were as follows:

- sedimentation time: 6, 12 and 24 hours.
- addition of fluosilicate salt seeds: 0, 0.1 and 2%

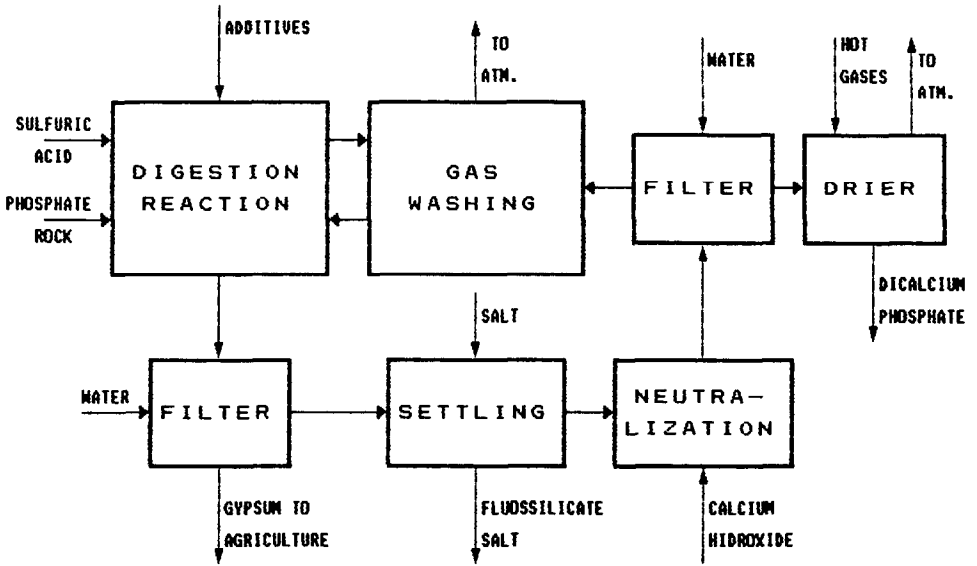


Fig.1: Schematic diagram for DCP proposed process

Table 1. Phosphate rocks chemical analysis

% CONTENT	PHOSPHATE ROCK		
	MOROCCO	CATALÃO	PATOS DE MINAS
P_2O_5	32.1	36.2	30.7
CaO	53.4	50.5	41.9
Fe_2O_3	0.68	2.75	1.38
Al_2O_3	0.52	2.57	2.72
F	3.60	2.22	2.16
SiO_2	1.85	3.87	18.1
TiO_2	0.01	0.17	0.42
MnO	0.03	0.28	0.09
SrO	0.06	1.06	0.25
K_2O	0.10	0.20	0.62
Na_2O	0.85	0.28	0.44
MgO	0.94	0.09	0.35
L.I.	5.60	1.13	3.70

- sedimentation pH: 0.2 to 1.5.
- defluorination salts: NaCl, Na(SO₄)₂, KCl, K₂SO₄, NaNO₃, KNO₃, CaCl₂, NaHCO₃, MgCl₂, NaCl, KCl.
- salt:F molar ratio: 0.8 to 2 of the stoichiometric.
- addition of extra active silica: 0 and 5%.

Finally, for the neutralization step, the parameters studied were the follows:

- neutralization time: 0.5, 1, 2 and 3 hours.
- neutralization temperature: 40, 60 and 95°C.
- calcium excess: 0, 5 and 20% of the final stoichiometric value.
- initial pH: 0.2 to 1.5
- final pH: 2.8 to 6.0
- time of calcium source addition: 10 and 70% of the total neutralization time.

In order to adequately evaluate the effects of changing the above described parameters, the following variables, for each step, were measured.

For the phosphate rock digestion reaction step:

- filterability of the gypsum cake.
- P₂O₅ conversion.
- fluorine removal.
- gypsum crystal size distribution.
- sulfate and calcium in the dried cake.
- X ray diffraction of the dried cake.

For the defluorination step:

- fluorine removal.
- X ray diffraction of the precipitate.

For the neutralization step:

- filterability of the cake (DCP product).
- P₂O₅ conversion.
- calcium, total and soluble (in neutral ammonium citrate solution) phosphorus, sulfate and fluorine analysis.
- X ray diffraction of the final dried product.

In this way, almost all process variables were evaluated and the results are discussed below.

RESULTS AND DISCUSSION

In the phosphate rock digestion step it is possible to state that the conversion, expressed as the ratio of P₂O₅ in the leaving gypsum to the P₂O₅ fed, is not affected by the rotation speed, in the range studied. For the three phosphates the best results for the P₂O₅ conversion are:

- digestion reaction time: 4 hours.
- digestion reaction temperature: 50°C.
- free sulfate level in the reactor: 2%.
- surface active agent in the reactor: 0.5%.
- addition of active silica: 50% of the stoichiometric.
- addition of gypsum crystals growth conditioner: 1%.

- final pH: 1.1.
- time of sulfuric acid addition: 60% of the total reaction time.

In order to obtain good gypsum crystals and consequently good cake filterability it is necessary to create adequate crystal growth conditions. High reaction temperatures cause a high number of nuclei and tend to give bad cake filterability in spite of increase of the P_2O_5 conversion. Long reaction times tend to give big crystals, but reduce the production rate. The range of gypsum crystal size for almost all experiments was from 30 to 80 microns as the mean diameter.

In the phosphate rock reaction step, the fluorine removal was from 40 to 60% for all phosphate rocks studied, in the best operational conditions described above.

For the conditions studied, the cake was formed essentially of calcium sulfate dihydrate with small amounts of calcium sulfate hemihydrate, besides unreacted phosphate rock, silica and fluosilicate salts. The P_2O_5 conversion in the phosphate rock digestion step was always between 85 to 96%.

In the fluorine removal step, it is possible to state that the higher the sedimentation time the more efficient the fluorine removal. Best results were obtained when the sedimentation was seeded with fluosilicate salt crystals.

The fluorine removal tends to be higher at elevated pH. Increasing the salt : F molar ratio the fluorine removal also increases but not significantly. Addition of extra active silica does not affect the yield of fluorine removal. Best results were observed when potassium salts were used. The analysis of the precipitate by X ray diffraction always shows the presence of the corresponding fluosilicate salt and a small amount of gypsum. The fluorine removal in this step varied from 60 to 85%, which represents globally, 70 to 95% removal.

In the neutralization step good results were observed for all phosphate rocks studied. The best operational conditions observed for the neutralization were as follows:

- neutralization time: 1 hour.
- neutralization temperature: 95°C.
- calcium excess: 5% of the final stoichiometric value.
- initial pH: 1.2
- final pH: 3.5
- time of calcium source addition: 50% of the total neutralization time.

In terms of P_2O_5 conversion, it is possible to say that best results were observed at high temperatures and long neutralization times. For higher temperatures the P_2O_5 content increases due to the formation of anhydrous DCP, instead the dihydrate DCP. The filterability of the final DCP cake product is better when the neutralization is conducted at low temperatures because then the number of nuclei formed is lower and the crystal size higher. High final pH values result in higher amounts of "insoluble" phosphates, like hydroxiapatite or fluorapatite, which results in low quality of the final DCP product. When a sulfate salt is used in the defluorination step, a small amount of calcium sulfate is present at the final product.

The X ray diffraction analysis always shows the presence of anhydrous DCP for temperatures below 70°C. The amount of P_2O_5 precipitated at the neutralization step was always above 90%. In this way, the global P_2O_5 conversion is in the order of 90%.

The final F:P mass ratio was above 100 for the better operational conditions, which agree with most of standards for feed grade phosphates.

CONCLUSIONS

A new, clean process for the production of DCP is presented, which uses phosphate rock as raw material. Three different rocks were studied and the process shows good results with all of them.

Figure 2 shows the schematic flow diagram of a DCP production batch unit. For a nominal capacity of 10 thousand tpy of DCP product an investment of about 500 thousand US\$ dollars can be expected. For a typical unit like that, a pay-out time of 8 months can be attained for a stable production market.

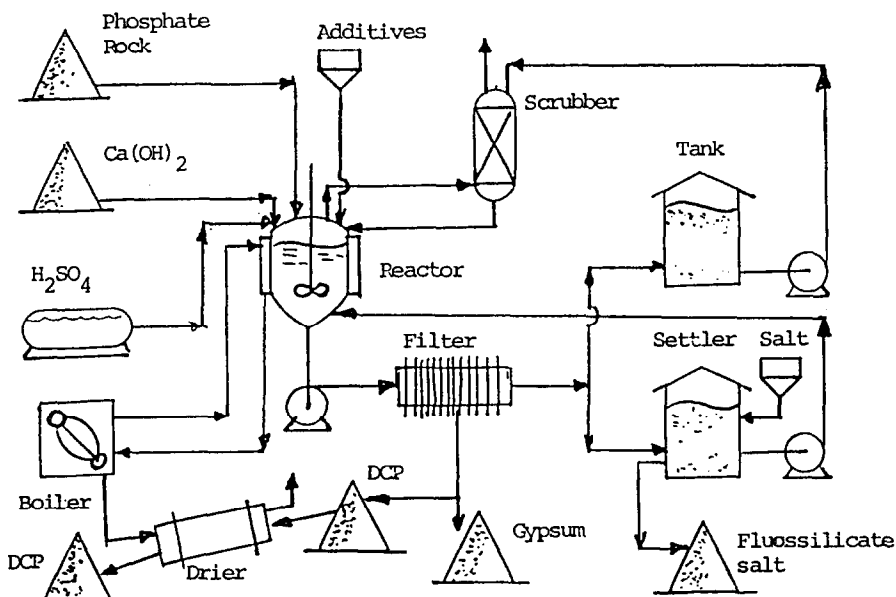


Fig2: Flow diagram for a DCP production batch unit.

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