

PREPARATION OF FEED GRADE DICALCIUM PHOSPHATE FROM COMMERCIAL PHOSPHORIC ACID

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Feed grade dicalcium phosphate was prepared by treatment of uranium barren commercial phosphoric acid with calcium hydroxide, and precipitation of dicalcium phosphate in two stages. The undesired contaminants, such as SO_4^{2-} and F were isolated in first precipitation stage using calcium hydroxide at pH 2.7 – 2.9, where the concentrations of cadmium and other trace elements were reduced by adding a small amount of ammonium sulfide in this stage, then dicalcium phosphate was precipitated by addition of calcium hydroxide in second stage at pH 6 – 7.

X-ray diffraction study showed that the resulting product was mainly a brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$).

Keywords: commercial phosphoric acid, dicalcium phosphate, feed

Introduction

In addition to their value as fertilizer, phosphate compounds are essential as phosphorus supplement for living. These compounds have found large applications in several fields such as medicine, industry and as additive for livestock and poultry feed.

Phosphate rocks contain different levels of harmful contaminants such as fluoride, hazardous trace elements, and radioactive elements, which could be transferred to phosphoric acid produced by wet-process. Such contaminants lead to disuse this acid in food and feed industry [1]. The high cost furnace-process produced phosphoric acid is mostly used for preparation of pure phosphatic compounds for such above mentioned applications. Several manufacturers have started to prepare some phosphatic compounds such as dicalcium phosphate and ammonium phosphate for nourishment purposes starting with wet-process phosphoric acid, after purification or isolation of undesired impurities during the processing procedures.

Dicalcium phosphate CaHPO_4 is produced by treatment of either phosphate ores or phosphoric acid with sulfuric acid or calcium minerals respectively [2]. Care should be considered for undesired impurities in the final products.

Yang applied a procedure by mixing the phosphate rock with sulfuric acid and sodium chloride. CaHPO_4 was precipitated from filtrate after reacting with calcium alkaline [3].

Zao and Duan mentioned that, dicalcium phosphate for nourishment purposes was produced by mixing calcium carbonate with pure phosphoric acid [4]. Kondo *et al* prepared high purity material of calcium phosphate by treatment of commercial phosphoric acid with ammonia at pH range of 2-4, followed by addition of EDTA2Na in the presence of calcium solution CaCl_2 , CaCO_3 and Ca(OH)_2 . The obtained solutions were mixed together and added to a solution consisting of NH_4OH and $(\text{NH}_4)_2\text{HPO}_4$ at pH ~ 7 [5].

Luo *et al* mixed a ratio of (0.5-0.8):1 phosphate rock: sulfuric acid, then the solution was adjusted to a pH value of about 3.2 by adding lime or calcium alkaline, CaHPO_4 was then precipitated from filtrate after reacting with lime or calcium at a pH value of 6.5 [6].

Giulietti and Cekinski precipitated calcium phosphate in two stages. The first one is in the range of pH 2.7-3.4, and the second one is in the range of pH 4-7 either from phosphoric acid medium or from the product of digesting phosphate rock with sulfuric acid using calcium source [7].

Fluoride is the worst impurity found in phosphate rock, which must be eliminated. Its percentage must not exceed one part per hundred parts of phosphorus in the product [8].

Rychnova succeeded in reducing fluoride content to 40-50 %, of its value in phosphate rock solutions by reacting it with silicate and potassium salts or sulfuric acid at the temperature range of 60-80 °C [9]. Abdel-Aal reduced fluorine content to less than 0.17 % from

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commercial - grade phosphoric acid (48 % P_2O_5 , 0.8 % F) by reacting the acid with silica dust, then dicalcium phosphate for animal feed supplement was prepared by addition of sodium hydroxide [10]. Baidoun *et al* reported methods of fluorine reduction in Syrian commercial phosphoric acid, raffinate, by mixing the raffinate with silica gel in three stages and under three different conditions: reduced pressure (0.5-15 torr), high temperature (80-90 °C) and room temperature, the fluorine reduction was about 94-97 %, 98 % and 97 %, respectively [11].

Tian *et al* purified phosphoric acid first by extracting it with tri-octyl amine and di-chloromethane in kerosene leading to reduction in the fluoride level in dicalcium phosphate to less than 0.15 % [12].

This work will focus on the preparation of dicalcium phosphate by reacting uranium barren commercial phosphoric acid with calcium hydroxide at a bench scale level and investigation of parameters, affecting this process and determination of the optimal conditions.

Experimental

Materials

The following materials have been used:

1. Orthophosphoric acid from BDH (88 w/w%).
2. Calcium hydroxide $Ca(OH)_2$ (97 %) from Riedel-de Haën.
3. Ammonium sulfide $(NH_4)_2S$ (20 %) from Merck.
4. Syrian purified commercial phosphoric acid from uranium, gypsum and other organic materials, Raffinate which was obtained from the micro-pilot in Homs (24.1 % P_2O_5).
5. Double distilled water.

Instrumentation and equipment

The following apparatus have been used:

1. Fluorometer (GM) from GMBH.
2. Atomic Absorption Spectrometer 2380 from Perkin-Elmer.
3. Compact X-Ray Diffraction system P.W 1840/01/11 from Philips.
4. Anodic stripping Voltammetry 694 VA Stand and 693 VA processor.
5. Gamma-ray Spectrometry with high pure germanium (HPGe) solid state detector, of 25 % relative efficiency and 1.85 keV resolution at 1332 keV gamma peak of ^{60}Co .
6. pH/ion meter (692) from Metrohm combined with fluoride selective electrode and silver/silver chloride reference electrode or combined with pH glass electrode.

7. Micro-balance (No. A-A-160) from Denever Instrument.
8. Gallenkamp oven 300 plus series.
9. Electrical mixer: nuova II from Sybron.
10. Whatman 41 filter paper.

Methods and Measurements

Preparation

Dicalcium phosphate compounds have been prepared by mixing fixed amounts of uranium barren commercial phosphoric acid ($P_2O_5 \sim 24\%$) with appropriate amounts of calcium hydroxide in slurry form with a continuous stirring at fixed temperature (15-30 °C), where a water cooling jacket was used for this purpose. The precipitation was carried out either by one or two stages at various pH values, after that, the precipitates were filtered, dried and analyzed.

Measurements

Chemical analyses of phosphoric acid and products were carried out according to well known methods adopted by association of Florida phosphate chemist [13].

Concentration of P_2O_5 was determined using spectrophotometric method, where the absorbance of molybdovanadophosphate complex was measured at $\lambda = 460\text{nm}$. Sulfate ion (SO_4^{2-}) concentration was determined by the well known gravimetric method by precipitating it in the form of barium sulfate.

Fluoride concentration was measured in the commercial phosphoric acid and solid samples using ion selective electrode method where internal standard addition method was applied to delete the effect of interferences. Density was determined using density flask.

Most of elements (Ca, Zn, Fe, Al, Mg) existed in the phosphoric acid were analyzed by atomic absorption technique. While, lead was identified by X-ray fluorescence technique. Cadmium was determined by polarography, and arsenic was determined by neutron activation analysis. Uranium was determined in phosphoric acid and solid samples using fluorometry.

The percentage of acid insoluble ash of dicalcium phosphate has been determined by taking a known weight of the dried sample and placed in a muffle furnace at high temperature in order to eliminate all organic material. Then, sufficient amount of HCl (5N) was added and the mixture was heated using water bath, filtered and dried at 135 °C for three hours. This process was repeated until a constant weight, then the percentage of acid insoluble ash was calculated.

The mineralogical composition of all prepared compounds was determined using powder X-ray diffraction technique.

Table 1 Specifications of uranium barren commercial phosphoric acid

Major components %				Trace elements $\mu\text{g}\cdot\text{ml}^{-1}$			
P_2O_5	SO_4^{2-}	F^-	Al	Fe	Mg	Zn	Ca
24.1±1.11	4.2±0.4	0.11±0.01	810±13	1350±91	4300±383	251±15	140±5
	Density		U	As	Pb	Cd	-
	1.344±0.05		3.3±0.5	-0.5-1	< 1	2.74±0.11	

Table 2a Characterization of dicalcium phosphate obtained by two stages of precipitation

Sample code*	Ca(OH) ₂ added (g)	pH of precipitation	Precipitate weight (g)	Product precipitate composition				
				Zn ($\mu\text{g}\cdot\text{g}^{-1}$)	F ⁻ (%)	SO_4^{2-} (%)	P (%)	Ca (%)
C ₁	11.47	1.0	14.82	184±4	0.06±0.01	36.6±0.5	10.1±0.2	16.5±0.3
L ₁	25.53	7.20	66.13	268±6	0.19±0.02	< 3	17.3±0.4	24.1± 0.5
C ₂	13.69	1.50	16.71	189±4	0.07±0.01	30.6±0.4	10.9±0.2	16.5±0.3
L ₂	23.31	7.40	68.58	282±6	0.19±0.02	< 3	17.3±0.4	22.5±0.5
C ₃	15.91	2.0	17.35	216±5	0.13±0.01	27.3±0.4	11.7±0.2	17.3±0.4
L ₃	21.09	7.45	64.96	314±7	0.16±0.02	< 3	17.5±0.4	23.8±0.5
C ₄	17.5	2.50	19.67	233±17	0.09±0.01	30.3±0.4	11.9±0.2	17.8±0.7
L ₄	17.5	7.0	61.54	380±27	0.16±0.02	< 3	17.5±0.4	18.9±0.8
C ₅	17.39	2.65	25.26	259±18	0.10±0.01	25.8±0.3	13.6±0.3	24.8±1.0
L ₅	19.61	7.25	55.86	408±29	0.16±0.02	< 3	18.4±0.4	19.8±0.8
C ₆	19.04	2.85	27.73	341±24	0.22±0.02	17.8±0.2	12.1±0.2	14.0±0.6
L ₆	16.22	7.0	51.69	431±30	0.10±0.01	< 3	18.0±0.4	22.0±0.9
C ₇	16.65	3.10	31.72	401±28	0.24±0.02	16.6±0.2	13.4±0.3	28.7±0.6
L ₇	20.35	7.1	50.0	348±25	0.10±0.01	< 3	16.7±0.3	29.5±0.6

*C, L: refer to the first and second precipitation stage respectively

Results and Discussion

In this work, the optimal conditions for the precipitation of dicalcium phosphate from uranium barren commercial phosphoric acid with calcium hydroxide were determined.

Calcium phosphate compounds have been precipitated either by one or two stages at various pH values.

Table 1 shows the characteristics of uranium barren Syrian phosphoric acid, which was used in this work. The major impurities in this acid were the fluoride (~0.11 %) and sulfate (~4 %), which should be reduced in the final product because they are considered as harmful impurities. One stage precipitation of dicalcium phosphate at pH value of about 6, will lead to complete transfer of these ions to the products producing levels of about 0.19 % of fluoride and 7 % of sulfate. The two levels are high and should be reduced.

In order to determine the pH value at which the precipitation process can remove most of the impurities without a major loss in the P_2O_5 content, several precipitation processes were carried out at fixed pH values ranged between 0.2 – 7.2.

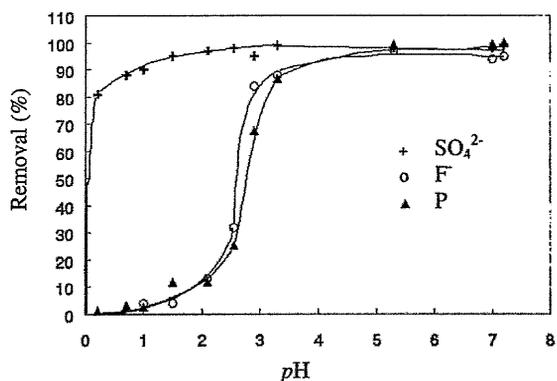


Fig.1 Removal of major impurities at different pH value

Fig.1 shows that about 90 % of SO_4^{2-} ions are precipitated at pH value of about 1, where this percentage increased with increasing pH value to reach complete precipitation at pH ~2.5.

Fluoride also showed high precipitation rate at pH values between 2.5-3, where about third of its amount is precipitated at pH value of 2.6. At this value of pH,

Table 2b Recovery of fluoride, sulfate and phosphorus in precipitate

Sample code	Recovery of fluoride (%)	Recovery of sulfate (%)	Recovery of phosphorus (%)
C1	6±2	96±6	11±1
L1	95±10	-	85±5
C2	9±2	90±5	13±1
L2	98±11	-	88±5
C3	17±3	94±5	15±1
L3	81±9	-	84±5
C4	13±3	105±6	17±1
L4	74±8	-	80±5
C5	18±3	100±6	25±2
L5	67±7	-	76±5
C6	48±8	100±5	25±1
L6	39±6	-	69±4
C7	58±7	94±6	32±2
L7	40±5	-	62±4

about 20 % of phosphorus content is precipitated where it almost showed similar behaviour to that of fluoride.

These results reveal the possibility of elimination of all sulfate impurities and about 35 % of fluoride impurities with calcium phosphate precipitated at pH value of about 2.6-2.7. This precipitation also removes about 20 % of phosphorus.

Re-precipitation of phosphorus remained in the solution (~80 %) at high pH value ~7, could produce more pure dicalcium phosphate.

Tables 2a and 2b show the results obtained when 100 ml of Syrian phosphoric acid was treated with calcium hydroxide in two stages. The pH value of precipitation was controlled by the amount of Ca(OH)₂ added.

The precipitation rate at first stage was slow with increasing pH value up to a pH value of 2.5. All precipitation processes carried out in this pH range had removed all sulfate impurities with less than 13 % of the fluoride impurities and less than 17 % of phosphorus content. Re-precipitation of the remained solution at pH of about 7 led to produce dicalcium phosphate with high content of fluoride (~0.16 %), which is higher than the allowed limit (Table 3). Therefore the pH of first precipitation medium was slightly increased up to about 2.85. At this stage the removal of fluoride had increased up to about 50 % with some increase in the amount of precipitate where the percentage of removed phosphorus increased to about 25 %. Re-precipitation of the remained solution had led to about 52 g of dicalcium phosphate with composition of 22 % calcium, 18 %, phosphorus, and 0.1 % fluoride. This composition is in accordance with Syrian standard limits for feed grade dicalcium phosphate (Ca>21 %, P>16 %, F≤0.1 %). Therefore the resulting precipitate in the second stage can be used as feed additive dicalcium phosphate.

Furthermore, trace elemental analysis of the resulting dicalcium phosphate prepared in accordance

Table 3 Specifications of feed grade dicalcium phosphate

Contents	Concentration limit*	Obtained value
Ca %	>21.0	22.0
P %	>16.0	18.0
F %	≤ 0.1	0.10
Pb µg.g ⁻¹	< 30	<1
As µg.g ⁻¹	< 10	<1
Cd µg.g ⁻¹	-	<1
Zn µg.g ⁻¹	-	<200
U µg.g ⁻¹	-	<2
Acid insoluble ash %	< 1.0	0.40
Moisture %	< 7.0	2.70

*These limits are according to Syrian standard certificate N° 580, 1988

with above mentioned method showed very low levels of harmful elements such as Pb, As and Cd (Table 3). The highest level of trace elements was found for Zn (~400 µg.g⁻¹). Although this element is not classified as harmful one, but its level could be reduced to less than a half of this value by addition of 5 ml of 1 % ammonium sulfide, (NH₄)₂S solution to the mixture before first stage of precipitation. In this case most of the trace elements like Pb, As and Cd were precipitated in first stage at pH ~2.85 and the final product obtained from the second stage was almost free from trace elements.

Uranium level in the final product was found to be about 4 µg.g⁻¹ without treatment with ammonium sulfide in first stage of precipitation. Addition of ammonium sulfide in first stage of precipitation reduced the level of uranium in the final precipitate to less than 2 µg.g⁻¹. This figure is also reduced in the feed at least by factor of 10 since dicalcium phosphate is added to the feed mixture with percentage of about 10 %. This amount of uranium in the feed is equivalent to about 5 Bq.kg⁻¹ radioactivity where the total radioactivity limit allowed in the feed is about 500 Bq.kg⁻¹.

X-ray diffraction analysis of the resulting dicalcium phosphate showed that more than 95% of it was in the form of brushite (CaHPO₄·2H₂O), while about 5 % of it was as monetite (CaHPO₄).

Water and acid insoluble ash of the resulting dicalcium phosphate was about 2.7 % and 0.4 % respectively and these two values are much less than Syrian standard limits 7 % and 1 % respectively.

Conclusion

Feed grade dicalcium phosphate could be prepared from uranium barren Syrian phosphoric acid without pre-purification from impurities. Most of undesired impurities could be isolated by precipitation of calcium phosphate at low pH medium (pH ~2.85). This process led to precipitation of sulfate, ~50 % of fluoride and some other trace elements impurities. Addition of sulfide ions at this stage led also to isolation of several trace elements like Pb, As, Cd and U.

Re-precipitation of the resulting solution at $pH \sim 7$ led to pure feed grade dicalcium phosphate with recovery of about 70 % of phosphorus. The precipitate obtained in the first stage, which contains about 25 % of total phosphorus, could be used as fertilizer since the percentage of P_2O_5 is about 25 %.

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