Evolution of Soluble Impurities Concentrations in Industrial Phosphoric Acid during the Operations of Desupersaturation

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Abstract

The desupersaturation of industrial phosphoric acid is a unit operation integrated either explicitly or implicitly in the Wet Process for Phosphoric Acid production (WPPA). This operation aims to improve the acid quality by elimination or reduction of impurities, which impair the acid quality and affect the process downstream performance.

Given the importance and impact of the phosphoric acid quality and its treatment on the performance of the whole production chain, we studied the operation of desupersaturation of this acid under various conditions of temperature and residence time. This allows determination, on one hand of the concentration evolution and the nature of various mineral phases of impurities present in the solution acid, and on the other hand the determination of the optimum treatment conditions of the acid to be adopted for improving production units performances. These measures can reduce the negative impacts of impurities in terms of fouling, corrosion, abrasion and produced acid quality.

1. Introduction

Generally, at the industrial scale, the manufacturing of phosphoric acid is made by wet processes (WPPA) [1]. These processes are based on the leaching of inorganic phosphates by acid attack, using concentrated sulfuric acid [2]. This acid attack on phosphate rock, takes place in one or more connected stirred reactors, placed in series with recycling streams as required.

One may summarize all these processes in four main steps: phosphate rock grinding; phosphate ore digestion - reaction and leaching; calcium sulfate separation and in a separate step phosphoric acid concentration [3]. The different process layouts differ mainly by the way how the reactions are carried out, which affect calcium sulfates crystallized forms, and by the desupersaturation unit integration design. Indeed, there are processes where this operation is explicitly integrated and others where it is introduced in an implicit manner. In the case of the first process, there are always special units for this

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unitary operation [2]. While in the second case, the desupersaturation operation takes place simultaneously during the reaction, phosphate rock attack and calcium sulfate crystallization [4, 5].

This desupersaturation operation is of great importance. It allows, on one hand to avoid deterioration of equipment by advanced abrasion; and on the other hand, to eliminate the undesired compounds and impurities from produced acid. These impurities impact negatively the quality of the acid and can lead in the cases where the acid undergoes further treatment, to:

- Deterioration of process equipment (pumps, filters, pipes, …)
- Losses in production time and the availability of units (periodic washing of installations)
- Fouling problems and solid deposits in the downstream production units [6]
- Reduction of storage volumes or residence time
- Degradation of the heat exchange performances.

The optimization of the desupersaturation operation requires a deep knowledge of the optimal conditions for the solubility and mobility of the impurities in the phosphoric acid solutions. Thus, the aim of this study was to determine and simulate the physico-chemical conditions for involved impurities (CaO, MgO, K_2O, Na_2O, SiO_2, Fe_2O_3, Al_2O_3, SO_4 and F) in the fouling phenomena and their evolution as function of temperature in reactors and their concentrations in phosphate rock and concerned reactors.

2. Materials and methods

This study is carried out using 30% P_2O_5 industrial phosphoric acid samples. The different samples are cooled under controlled atmosphere. During the tests, the temperature is then controlled using incubators with a temperature accuracy of ± 0.1 °C in Teflon flasks.

Chemical analyses of aqueous solutions and characterization of deposits (fouling produced) were performed by several techniques in our laboratory:

- P_2O_5 content is determined by gravimetric method in the presence of vanadate and sodium molybdate dehydrates ($Na_2MoO_4.2H_2O$). The measurements were made automatically using an analyzer SKALAR NF T20 476;
- Calcium is determined via titration using ethylene glycol tetra acetic acid (EGTA). The dosage is done in an alkaline media in the presence of magnesium, which makes the most visible change of the indicator;
- The concentration of the sulphur trioxide is determined by turbidimetric technique. The measurement is done using an optical photometer at a wavelength of 460 nm;
- The fluorine content is determined by the potentiometric method. A selective electrode is used under buffered conditions with 0.1% blue bromothymol, 10N sodium hydroxide solution and a fluoride solution at 1g/l, prepared from NaF;
- The chemical characterization of silica is obtained by calorimetric method using a silicomolybdic compound that turns to yellow in acidic medium;
- A spectrophotometer is used to determine potassium, sodium, iron, aluminium and magnesium contents. More precisely, an air-acetylene flame has been used for potassium, sodium and iron with respective wave lengths of: 766.5nm, 589nm and 372nm. As for, aluminium content, an air-nitrous oxide flame at wave length of 309.9 nm has been used. While, magnesium content is determined by an air-acetylene flame at wave length of 285.2nm, after addition of an ionization suppression agent, lanthanum nitrate at 285.2nm;
- The levels of chloride ions are determined using potentiometric titration, with a solution of silver nitrate in nitric-acetone-water medium. The measuring electrode is a silver electrode, while the reference is calomel.

The precipitates, obtained after each stage of cooling acid samples, are characterized by scanning electron microscope (SEM).

3. Experimental methods

In order to determine experimentally, the evolution of the impurities contents as function of the temperature, hot samples of phosphoric acid are taken, at the outlet of the reactor. The samples are rapidly filtered in order to separate the calcium sulfate (as at industrial scale). The phosphoric acid solutions thus sampled (at 80°C) are kept in incubators where they are gradually cooled under controlled atmosphere.

Three cooling intervals were carefully selected. During the first interval, the samples are gradually cooled from 80°C to 60°C for a period of 20 days in order to reach the "thermodynamic equilibrium" and precipitate most of the oversaturated solid compounds.

In the second interval, the cooling process is established from the temperature 60°C to 40°C. In the third and final interval, the samples are cooled again from 40°C to 25°C.

The selection of these intervals is based on the fact that 80°C is the average temperature in which the produced acid leaves the reactor. However, temperature interval [60°C - 40°C] is the range in which, the acid leaves the purification and clarification unit, while the last temperature 25°C is the finished product one which is an average ambient temperature. The acid reaches this temperature when it is stored for relatively long period of time.

At the end of each interval aqueous phase was analyzed and precipitated phases were identified and characterized.

4. Results and discussions

4.1. Evolution of P_2O_5 content

The monitoring of P_2O_5 content evolution in the acid phase (Fig. 1) shows an increase when the temperature of the solution decreases. It evolves, from 26.75% P_2O_5 to 27.13% P_2O_5. This increase of 0.38% P_2O_5 took place especially at the temperature ranging from 80°C to 60°C. Indeed, in this stage, the P_2O_5 concentration increased by 0.276% P_2O_5 (approximately 72.63% of the total increase). For the other temperature ranges [60°C to 40°C] and [40°C to 25°C], the P_2O_5 increases in the liquid phase are, respectively, 0.039% and 0.062% P_2O_5, approximately, 12.26% and 16.31% of the overall increase in all the cooling process.

SEM analysis of the solid precipitated shows that the phosphorus content in the precipitate obtained after the first stage of cooling is very low. In addition, the majority of phosphorus is in the form of aqueous chemical species, which may explain the increase of P_2O_5 in the liquid phase.

4.2. Calcium / Sulfates (CaO /SO₄)

The results of the cooling tests show that the calcium content in the liquid phase decreases with temperature. Indeed, at the beginning, the calcium has a content of 0.6%, while towards the end of the trials; the calcium content decreases to 0.32% (Fig. 2). This reduction in the calcium content is very intense in the interval [80°C-60°C] where calcium decreased by 0.26%, or 80.77% of the overall decrease in cumulative recorded on three intervals cooling.

SEM analysis and the results of material balance calculations for calcium, show that the rate of calcium precipitate is as follows:

- 38% in the first cooling interval (from 80 °C to 60 °C),
- 5% trapped by the solid phase during cooling of the sample from 60 °C to 40 °C,
- 8% during the cooling interval from 40°C to 25°C.

The results show also that the content of SO_4 (sulfate), has a similar behavior to the evolution of CaO (Fig. 3). The material balance calculation of SO_4 shows that the trapping rate of SO_4 by the solid phase in the first cooling interval is 13.66%, while at the second and third interval it is respectively 4.85 and 7.16%.

4.3. Fluoride

The results indicate low decrease of fluorine content in the liquid phase following the desupersaturation of the phosphoric acid. Indeed, at the beginning, this content was 1.93% in solution, and dropped to 1.87% at the last cooling temperature (25 °C). An overall decrease of the fluorine content is only of 0.06% (Fig. 4).

The material balance calculation shows that 4.057% of fluorine initially contained in the liquid phase was precipitated as a mineral phase during the cooling process. The significant part of this migration to the mineral phase precipitated is recorded during the first cooling interval.
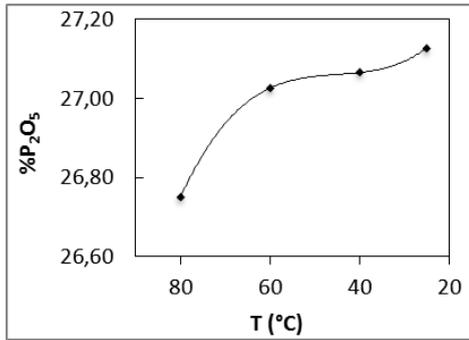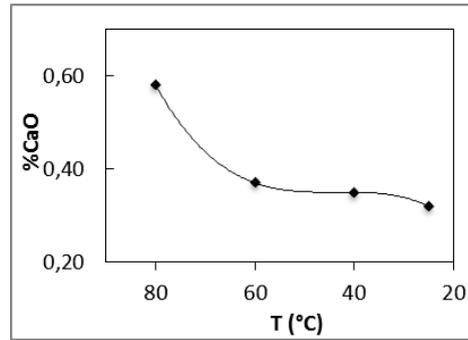
Fig. 1. Evolution of %P_2O_5 as function of temperature
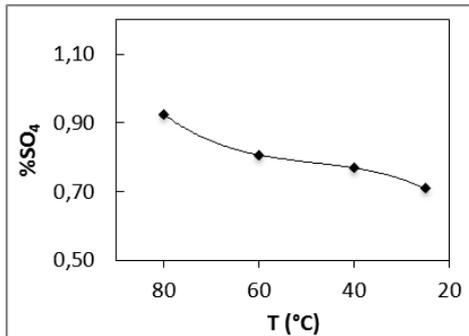

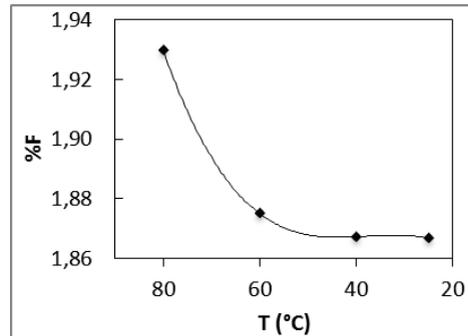Fig. 2. Evolution of %CaO as function of temperature

Fig. 3. Evolution of %SO_4 as function of temperature

Fig. 4. Evolution of %F(fluoride) as function of temperature

4.4. Silica

Through the experimental process of cooling, the silica content in the liquid phase has dropped from 0.840% to 0.717% SiO_2. This drop is relatively intense in both cooling intervals [80°C-60°C] and [40°C-25°C]. It is respectively in the range of 0.112% SiO_2 and 0.01% SiO_2. Otherwise, 91% and 6.5% of the total decrease of the silica had held respectively in these two levels of cooling (Fig. 5).

The material balance calculation of the silica shows that within the interval [80°C - 60°C], 16% of the silica initially contained in the liquid phase, prior to cooling tests, is trapped by precipitated solids.

4.5. Sodium

The monitoring of the sodium content (expressed as % Na_2O) in the liquid phase shows that the cooling of the industrial phosphoric acid, leads to an important removal of this impurity from the liquid phase. Figure 6 shows that this content has decreased, in fact, from 0.22% to 0.188% Na_2O. This drop is observed in particular, at the interval of cooling [80°C - 60°C].

The material balance of sodium shows that, in the first cooling interval 12% of sodium has precipitated as solid complex and 4% in the third interval. However, during the second period, the rate of to the sodium trapping by the solid phase does not exceed 1% of Na_2O initially contained in the liquid phase.
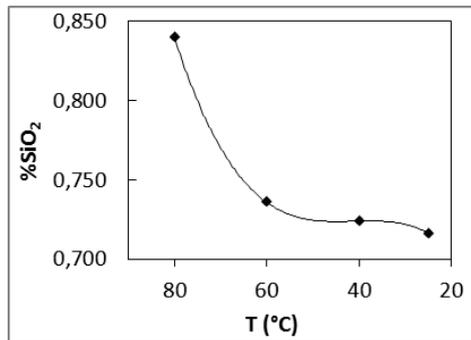
Fig. 5. Evolution of %SiO_2 as function of temperature
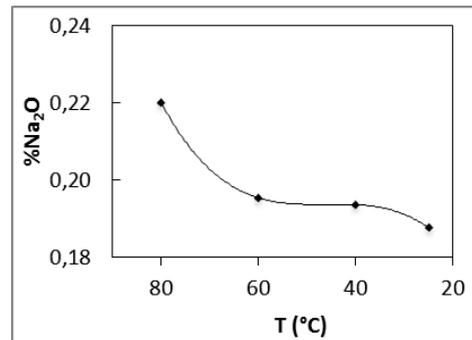
Fig. 6. Evolution of %Na_2O as function of temperature

4.6. Potassium

The monitoring of the K_2O content in the liquid phase shows that it decreases with cooling acid samples. The total decrease is about 0.03% K_2O. During the interval [80°C-60°C], the content decreases by about 0.01% K_2O. However, it remains practically constant over the range 60°C -40°C, and then fall sharply during cooling of the sample from 40°C to 25°C (Fig. 7).

The mass balance calculation for potassium after each cooling stage shows that the precipitation and the risk of fouling by potassium may occur during the first and third cooling stage. Indeed, during these two intervals, the transfer rates of potassium are respectively 2.77% and 6.83% of the amount of potassium initially present in the liquid phase.

4.7. Magnesium

The monitoring of the evolution of Mg content (expressed as % MgO) in the aqueous phase and results of analysis of solid precipitates by electron microprobe show that magnesium remains preferentially in the liquid phase. Indeed, this change of the MgO content registers a very small variation in the liquid phase (Fig. 8).

4.8. Aluminum

The cooling tests of phosphoric acid show a great decrease in aluminum concentration in the liquid phase (Fig. 9) and its precipitation as crystalline solid phase, especially Chukhrovite ($Ca_4SO_4AlSiF_6.12H_2O$). This mineral phase is present in all chain of phosphoric acid production [2].

The material balance, reflecting the distribution of aluminum between the liquid and solid phases, show that about 88% of initial aluminum content in the liquid phase is precipitated as solid phase during the first cooling interval. Therefore, we can conclude that the risk of fouling by aluminum can take place as soon as the acid attack leaves the reactor and begins to cool, either by natural convection under the effect of vacuum applied for filtering the phosphoric slurry or in the concentration step.

4.9. Iron

During the three cooling steps of the acid 30% P_2O_5, sampled from the reactor, the iron content (expressed as % Fe_2O_3) in the liquid phase evolves very weakly and recorded an increase of 0.27 % Fe_2O_3 to 0.2725% Fe_2O_3 (see figure 10). Such evolution may reflect the high solubility of iron in phosphoric acid solution. The great majority of the iron remains in the liquid phase in the form of aqueous chemical species [7, 8].
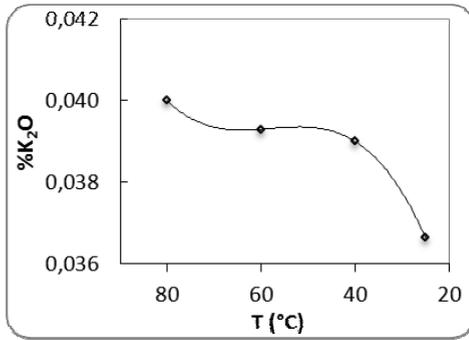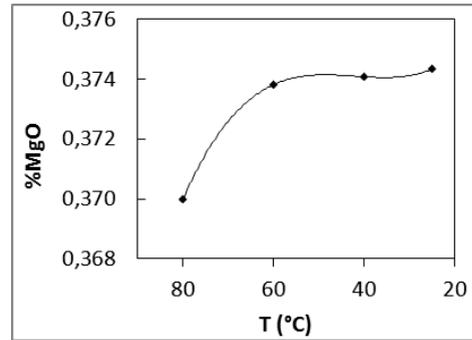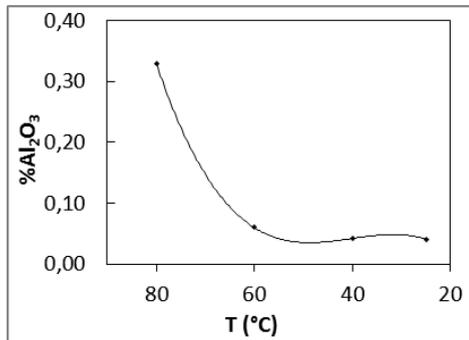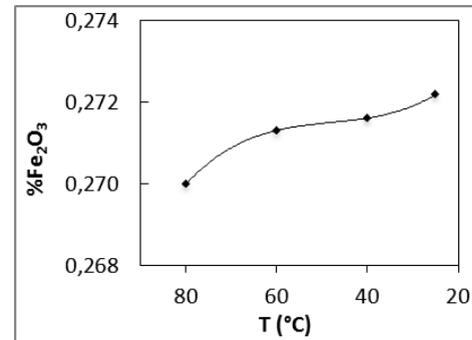
Fig. 7. Evolution of %K_2O as function of temperature

Fig. 8.Evolution of %MgO as function oftemperature.

Fig. 9. Evolution of %Al_2O_3as function oftemperature

Fig. 10. Evolution of %Fe_2O_3 as function of temperature

5. Results synthesis and main outlooks

In these experimental tests, we found that the evolutions in the concentrations of soluble impurities, due to desupersaturation stepwise cooling, lead to the formation of mineral phases causing fouling problems in various manufacturing facilities of phosphoric acid.Table 1 summarizes the main results obtained by XRD analysis of solid precipitates and balance calculation for sharing impurity between the liquid phase and the solid precipitates.

Table 1.Precipitated solids from the acid samples and result of material balance calculation

compound	80°C – 60°C		60°C – 40°C		40°C – 25°C	
	Impurity Transfer rate at precipitated solid	Mineral phases formed	Impurity Transfer rate at precipitated solid	Mineralphases formed	Impurity Transfer rate at precipitated solid	Mineral phases formed
P_2O_5	0.00% ± 0.28%		0.00% ±0.28%		0.00% ±0.28%	
CaO	36.86% ±0.36%		5.55%±0.36%		8.78%±0.36%	
SO_4	13.61%±0.03%		4.86%±0.03%		7.99%±0.03%	
F	4.08%±0.05%	- Gypsum ($CaSO_4,2H_2O$) - Chukhruvite ($Ca_4SO_4AlSiF_6OH,12H_2O$)	0.32%±0.05%	Gypsum ($CaSO_4,2H_2O$)	0.26%±0.05%	- Gypsum ($CaSO_4,2H_2O$) - Quartz (SiO_2) - Chukhruvite ($Ca_4SO_4AlSiF_6,12H_2O$)
SiO_2	14.26%±0.1%		0.45%±0.1%		1.46%±0.1%	
Na_2O	12.06%±0.03%		1.06%±0.03%		3.31%±0.03%	
K_2O	2.67%±0.01%		0.32%±0.01%		6.82%±0.01%	
MgO	0.00% ± 0,09 %		0.10%±0.09%		0.17%±0.09%	
Al_2O_3	86.70%±0.08%		2.36%±0.08%		2.57%±0.08%	
Fe_2O_3	0.54%±0.05%		0.04%±0.05%		0.03%±0.05%	

The analysis of these results shows that the impurities that have great potential to generate fouling and solid deposits in these facilities of phosphoric acid production, are mainly: SO_4, CaO, F, SiO_2, Al_2O_3 and Na_2O.
These impurities are precipitated in the solid phases:

- Gypsum and Chukhruvite, during the first interval of cooling
- Gypsum, during the second interval ;
- Gypsum, Chukhruvite and quartz, during the third interval

The control of these fouling problems and the improvement of the key steps of such processes need also to develop thermokinetic models, computer codes and the development of interactive databases which integrate all the major impurities matrix of inorganic phosphates.

6. Conclusion

In this work, it was shown that the desupersaturation step, which take place via the cooling process, mainly during the cooling interval [80°C-60°C], is crucial for controlling and managing the fouling problem. Indeed, at this level of purification, the majority of soluble species (impurities) in the industrial phosphoric acid precipitates as solid phase. These can give rise to solid deposits in the whole production chain (reactors, filters, pipe, storage tanks ...). However, potassium has a behavior that differs from other species. The results of the monitoring of its concentration in the liquid phase show that the K_2O tends to migrate into the acid liquid phase in the third step of cooling [40°C - 25°C].

The results of this careful diagnosis of solid deposits and the determination of the repartition of impurities between the liquid phase and the solid phases newly formed, requires extensive thermodynamic studies that incorporate all the laws of chemical equilibriums in solution and the theory of highly concentrated electrolytes and brines [6, 9], for a better understanding of the mechanisms governing such complex thermodynamic equilibrium possibly with some kinetic constraints. The prediction of these mineral complex phases begins with the simplest case in which the laboratory has resulted in very satisfactory results through modeling [10-12]. However, the reliability of a thermodynamic model is appreciated by the capability to reproduce the experimental observations and industrial realities.

Moreover, the results obtained in this work are very interesting for thermodynamic complex systems rich in industrial phosphoric acid. They can indeed be used for upgrading (by checking, validating, etc.) some computer codes and thermodynamic simulation software by enriching their databases and success cases.

References

[1] S. Van Der Sluis; A clean technology of phosphoric acid process. Delft University Press. TRdiss 1550 – Juin 1987.
[2] P. Becker; Phosphate and phosphoric Acid.Second Edition. Marcel DEEKER, Inc. New York and Basel 1983.
[3] A.V. Slack; Phosphoric Acid, Fertiliser Science and Technology Series,V(1), Marcel Dekker, New York, 1968.
[4] M. Miyamoto. Performance and operation of a new Nissan phosphoric acid process plant. The Hague the Netherlands, IFA, 13-16 September 1976
[5] K. V. Gobbitt E de. Design and Operating Data from the World's Biggest and Newest Hemihydrate Phosphoric Acid Plant.IFA Technical Conference. New Orleans, Louisiana, USA. 1-4 October 2000.
[6] M Azaroual; C. Kervevan; A. Lassin; L.André; M. Amalhay; L. Khamar; M. EL Guendouzi, Thermo-kinetic and Physico-Chemical Modeling of Processes Generating Scaling Problems in Phosphoric Acid and Fertilizers Production Industries. Procedia Eng. 2012, 46, 68-75.
[7] A. W.Frazier; Y. K. Kim. Redistribution of impurities in commercial wet-process acid. Fertilizer Research 1989, 21, 45-60.
[8] A. W. Frazier ; J.P.Smith; J. R. Lehr.Precipitated Impurities in Fertilizers Prepared from Wet-Process Phosphoric Acid. J. Agr. Food Chem. 1966, 14, 522-529.
[9] M. EL Guendouzi; A. Errougui; Solubility in the ternary aqueous systems containing M, Cl$^-$, NO$_3^-$ and SO$_4^{2-}$ with M = NH$_4^+$, Li$^+$, or Mg^{2+} at T = 298.15 K. J. Chem. Eng. Data. 2009, 54, 376-381.
[10]A. Rifai, M. El Guendouzi, M. Amalhay, M. Azaroual. Thermodynamic properties of aqueous fluorosilicate acid H_2SiF_6(aq) at 298.15 Kand 333.15 K. Proceedings COVAPHOSIII, 2009, 5, 125-129.
[11]M. Aboufaris El Alaoui, M. El Guendouzi, M. Amalhay, M. Azaroual Thermodynamic properties of the aqueous binary and ternary systems of phosphates $MgHPO_4-H_2O$ and $H_3PO_4-MgHPO_4-H_2O$ at 298.15 K. Proceedings COVAPHOS III,2009,5, 142-146.
[12]A. Benbiyi, J. Faridi, M. El Guendouzi, M. Amalhay, M. Azaroual Thermodynamic properties of the aqueous binary and ternary systems of phosphates $CaHPO_4-H_2O$ and $H_3PO_4-CaHPO_4-H_2O$ at 298.15 K . Proceedings COVAPHOSIII,2009, 5, 130-134.