Original Research Article

Desulfation of industrial phosphoric acid 54% by lime, limestone and barium carbonate

Abstract

Industrial Phosphoric acid is a ubiquitous product in food industry and in the production of fertilizers and detergents. The presence of impurities in the raw material leads to an acid relatively loaded with various chemical species detrimental to its quality and use. Among these impurities are the sulfate ions which precipitate in phosphoric acid during its manufacture. A desulfation is thus necessary. This study deals with the reduction of free sulphates present in phosphoric acid considered as impurities. Therefore, three different adjuvants; quicklime, limestone and barium carbonate were employed. Three initial sulfate levels primarily contained in phosphoric acid were studied: 2%, 4% and 6%. After experimentation, the comparison between the resulting yields allows considering barium carbonate as the most effective adjuvant, it removed yield was 95% in very short stirring times regardless the initial content of sulfate in phosphoric acid. The tests carried out with quicklime and limestone lead also to very interesting desulfation rates for phosphoric acid with initial content of 2 or 4% sulfate.

Keywords: Industrial phosphoric acid, desulfation, lime, limestone, barium carbonate

1. Introduction

Natural phosphate rich in P_2O_5 is a finite, non-renewable natural resource. Geological deposits of different origin are found in different country. Currently, few natural phosphate deposits are mined. Little amounts are being used in the manufacture of animal feed, detergents and chemicals while about 90 percent of its global production is used in fertilizers industry [1, 2]. Herein sulfuric acid and natural phosphate are the raw materials used in the production of phosphoric acid [3]. Phosphoric acid (H_3PO_4) is a triacide capable of yielding three H^+ protons by successively forming three conjugated bases: dihydrogen phosphate (H_2PO^{4-}), hydrogen phosphate (HPO_4^{2-}), and orthophosphate (PO_4^{3-}). Phosphoric acid is essentially obtained from phosphate rock, mainly in two ways. The first is known as the wet process. It consists of the attack of phosphate rock by a strong acid, usually sulphuric acid. The second route is based on a thermal process in which the phosphate rock is reduced to elements that are then oxidized and hydrated to obtain phosphoric acid [4, 5]. Phosphoric acid is generally obtained using the wet process in a natural phosphate reactor ((digester) (mainly calcium fluorophosphate) by attack with concentrated sulfuric acid (see Sulfuric acid) at 80 ° C:

$Ca_{10}(PO_4)_6F_2 + 10\ H_2SO_4 + 20\ H_2O \longrightarrow 6\ H_3PO_4 + 10\ CaSO_4{,}2H_2O + 2\ HF$ (1)

This process has the disadvantage of producing a relatively low concentration of acid (26 to 32% P_2O_5) which requires high energy consumption for its concentration by evaporation of water. The yield based on phosphate is 94-96%, part of the phosphate co-crystallizing with calcium sulphate which contains up to 0.75% P_2O_5 [6]. Phosphoric acid is a chemical compound of great industrial importance as it is involved in many applications like manufacture of phosphate salts. It is an important intermediate used to prepare the triple superphosphate (TSP) [7], sodium tripolyphosphate $Na_5P_3O_{10}$ and ammonium phosphates $(NH_4)_2HPO_4$. Phosphoric acid (H_3PO_4) is broadly applied in many industries: chemical, fertilizers, mineral leaching, water purification, petroleum refining, food and metal production [8–10]. Also manufacturing of phosphoric acid from natural phosphate by sulfuric acid attack inevitably produces impurities such as sulphates, fluorine, organic matter and heavy metals. The analysis of the available literature shows that impurities can be removed in various ways – through extraction [11–16], phospho-gypsum adsorption (co-crystallization) [17–19], crystallization [20], adsorption and biosorption [21, 23], membrane [24] and liquid membrane processes [25,26], and precipitation [27-30]. Sulphate ions, in particular, have about 2% weight, and affect undoubtedly the efficiency of 29% P_2O_5 phosphoric acid concentration unit, due to the solid formation which causes premature clogging of the phosphoric acid concentration unit.

The objective of the present study includes the removal out of sulfate impurities via precipitation using lime, limestone and barium carbonate.

2. Experimental details

2.1. *Sample studied*

The experimental study aims to optimize the desulfation of phosphoric acid with three levels of sulfate content (% mass H_2SO_4). The levels chosen are 2%, 4%, and 6% respectively. These levels are representative of the highest quantities found in industrial phosphoric acid. Three adjuvants; lime, limestone, and barium carbonate were chosen as retainer of the sulfates impurities. These adjuvents are previously crushed and sieved to have a particle size of about 0.16 µm. Desulfation tests shall be conducted under agitation at temperature 60°C. 200 g mass of industrial phosphoric acid were used. After treatment, phosphate and sulfate amounts were analysed by titration and the calculated percentage were:

For phosphoric acid

$$\%P_2O_5 = \frac{CO1 * CO2 * (VP2 - VP1)}{E0} \tag{1}$$

with CO1: factor of the soda solution equal to 1 CO2: constant equal to 3.55;

E0: test portion (1g); VP1: volume of soda consumed up to the pH of the first acidity and VP2: volume of sodium hydroxide consumed up to the pH of the second acidity.

For sulfuric acid.

$$\%\ H_2SO_4 = \frac{(Vtotal - Vblanc) * 4,9}{E0} \tag{2}$$

Vtotal: volume of barium chloride solution added until the color changes from purple to blue

Vblank (ml): volume of barium chloride solution, added during the blank test

E0: sample taken (2g)

Results and discussion

2. 2. Desulfation of industrial phosphoric acid 4% H_2SO_4

To verify the quality of the phosphoric acid, P_2O_5 and H_2SO_4 mass titers are determined. The resulting analyses, carried out on samples H_2SO_4 mass title of 4% in phosphoric acid of are grouped in Tables 1 and 2. The measured P_2O_5 mass titer is within the acceptable range of concentrations (46% to 54%).

Table 1. ***P_2O_5 content of the starting acid***

	Trial 1	**Trial 2**	**Trial 3**	**Trial 4**
E0 (g)	1,085	1 ,055	1,015	1,032
% P_2O_5	49 ,25	49,24	49,51	49,49
Average value	49,38 %			

Table 2. ***H_2SO_4 Content in the starting acid***

	Trial 1	**Trial 2**	**Trial 3**	**Trial 4**
E0(g)	2 ,196	2,174	2 ,089	2,058
V $BaCl_2$ added (ml)	2,8	2 ,7	2,6	2,6
%H_2SO_4	4,19	4,01	3,94	4
Average content		4,04%		

2.2. *Desulfation of phosphoric acid 4% by lime*

Desulfation was done by adding quicklime (CaO) in a stirred beaker maintained at a temperature 60°C. Different stirring times were used to follow the desulfation of phosphoric acid (4% H_2SO_4) by lime. For each duration, three tests were carried out. Finally, P_2O_5 and sulphate analyses are performed on the liquid phase separated by centrifugation. The obtained results of desulfation by lime are presented in Table 3.

It has been found that for stirring times greater than 10 min there are no remarkable effects on the final sulfate content. Indeed, a stirring time of 10 min is ample to achieve the desulfation of phosphoric acid (4% in H_2SO_4) by lime. The sulfate content has decrased from an initial value of 4.04% to a final value of 1.67%.

Table 3. ***Desulfation of the phosphoric acid by lime***

	MA ph (g)	**mCaO (g)**	**% P_2O_5**	**% H_2SO_4**	**R (%)**
Desulfation of the phosphoric acid by lime for 10 min					
Trial 1	200,000	4,620	52 ,09	1,7	57,92
Trial 2	200 ,430	4,620	51,73	1,7	52,97
Trial 3	200,061	4,625	52,09	1,7	57,92
Average value			51,97	1,7	56,27
Desulfation of the phosphoric acid by lime for 30 min					
Trial 1	200,080	4,622	54 ,49	1,69	58,17
Trial 2	200 ,155	4,620	53,21	1,67	58,66
Trial 3	200,023	4,625	54,38	1,66	58,91
Average value			54,02	1,67	58,58
Desulfation of the phosphoric acid by lime for 60 min					
Trial 1	200,038	4,620	54 ,38	1,65	59,16
Trial 2	200 ,040	4,627	53,23	1,62	59,90
Trial 3	200,043	4,626	54,12	1,62	59 ,90
Average value			54,02	1,63	59,65

2.3. *4% Acid desulfation by limestone*

Desulfation is done by adding fine limestone into a stirred beaker heated at 60°C. The reaction equation is the following:

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2$$

The results of phosphoric acid desulfation (4% H_2SO_4) by limestone obtained for different stirring times are grouped in Table 4. It is noted that after a stirring time of 30 min, the sulfate content becomes practically constant. In the case of desulfation by limestone, a kept time of 30 min corresponds to an optimal desulfation. That is a final sulfate level of 2.13 %. Desulfation acid has a P_2O_5 content of 52%.

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Table 4. ***desulfation of phosphoric acid by Limestone***

	$M_{A\ ph}$ (g)	**m_{CaCO3} (g)**	**% P_2O_5**	**% H_2SO_4**	**Y (%)**
Limestone desulfation of phosphoric acid for 10 min					
Trial 1	200,038	8,343	52 ,33	2,31	42,82
Trial 2	200 ,040	8,341	52,66	2,11	42,65
Trial 3	200,043	8,341	52,46	2,29	43,32
Average value			52,48	2,28	42,93
Limestone *desulfation* of phosphoric acid for 30 min					
Trial 1	200,050	8,340	52 ,15	2,11	47,77
Trial 2	200 ,000	8,340	52,95	2,16	46,53
Trial 3	200,091	8,341	51,93	2,13	47,28
Average value			52,34	2,13	47,19
Limestone *desulfation* of phosphoric acid for 45 min					
Trial 1	200,102	8,340	52 ,33	2,15	46,78
Trial 2	200 ,470	8,340	51,56	2,14	47,03
Trial 3	200,000	8,340	52,24	2,17	46 ,29
Average value			52,04	2,15	46,70
Limestone *desulfation* of phosphoric acid for 60 min					
Trial 1	200,070	8,341	51 ,67	2,14	47,03
Trial 2	200 ,470	8,340	51,01	2,14	47,03
Trial 3	200,000	8,340	52,34	2,17	46,29
Average value			51,67	2,15	46,78

2.4. *Desulfation of the acid by barium carbonate*

The desulfation reaction by barium carbonate is given by the following equation:

$$BaCO_3 + H_2SO_4 \longrightarrow H_2O + BaSO_4 + CO_2$$

The results of phosphoric acid desulfation (4 % H_2SO_4) by barium carbonate after centrifugation for a stirring time of 10 minutes, 30 minutes and 60 minutes are grouped in Table 5.

Tableau 5. ***Desulfation of phosphoric acid with baryum carbonate***

	$M_{A\ ph}$ (g)	**m_{BaCO3} (g)**	**% P_2O_5**	**% $H_{2S}O_4$**	**Y (%)**
Desulfation of phosphoric acid for 10 min					
Trial 1	200,000	16,270	49 ,82	0,48	88,12
Trial 2	200 ,053	16,271	49,65	0,45	88,86
Trial 3	200,001	16,274	49,66	0,45	88,86
Average value			49,71	0,46	88,61
Desulfation of phosphoric acid for 30 min					
Trial 1	200,008	16,272	52 ,90	0,47	88,36
Trial 2	200 ,055	16,269	52,86	0,43	89,36
Trial 3	200,020	16,270	52,91	0,45	88,86
Average value			52,89	0,45	88,86
Desulfation of phosphoric acid for 60 min					
Trial 1	200,091	16,271	51 ,41	0,24	94,06
Trial 2	200 ,045	16,275	51,32	0,23	94,31
Trial 3	200,034	16,270	51,65	0,25	93 ,81
Average value			**51,46**	**0,24**	**94,06**

The results obtained show a reduction in the sulfate level ***(desulfation)*** yield of the order of 95%. However, these results are to be verified because the separation of the precipitate formed by centrifugation was not complete given the size of the solid particles formed. This is why gravimetric analysis is used in this case. The latter is performed on samples of the liquid phase obtained for different stirring times. Table 6 shows the average values obtained in each case.

Table 6. ***Results of gravimetric analysis of barium carbonate desulfation***

Stirring time (min)	**10**	**30**	**60**
H_2SO_4 content (%)	0,25	0,19	0,16

2.5. *Comparison of different additives*

Gravimetric analyses show a much higher rate of desulfation, in the case of barium carbonate; than with the other two adjuvants. Lime ensures a sulfate level of less than 1.7%, a value widely sufficient for several applications of industrial phosphoric acid. Limestone provides relatively less effective desulfation,but has the advantage of having the lowest cost. The results obtained for various adjuvants during desulfation of phosphoric acid 4% are shown in Figure 1.

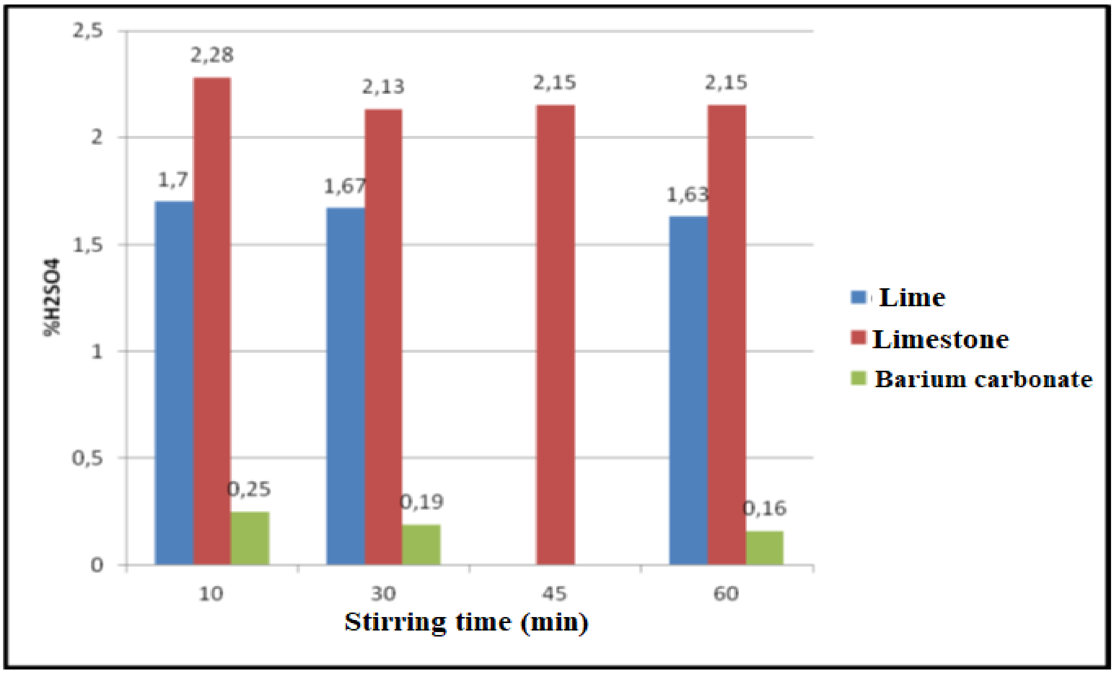

Figure 1. Effect of different additives on acid (4%) desulfation.

3. Phosphoric acid 6% H_2SO_4

The results of the characterization analyses for 6% H_2SO_4 are presented in Table 7, confirming the contents retained and will then be used to determine the contents of the various adjuvants.

Table 7. ***Phosphoric acid (6%) characterization***

	P_2O_5 (%)	H_2SO_4 (%)
Trial 1	49,06	5,76
Trial 2	49,01	5 ,55
Trial 3	49,06	6,24
Average value	49,04	5,85

3.1. *Desulfation by Lime*

The mass of lime is theoretically required to desulphurize phosphoric acid with a sulfate content of 5.58% is m_{CaO} =6.69 g. The sulfate contents measured after centrifugation are shown in Figure 2. Phosphoric acid desulfation (6%) by lime ensures a sulfate level of 2.66% after one hour. This value exceeds the values required by customers.

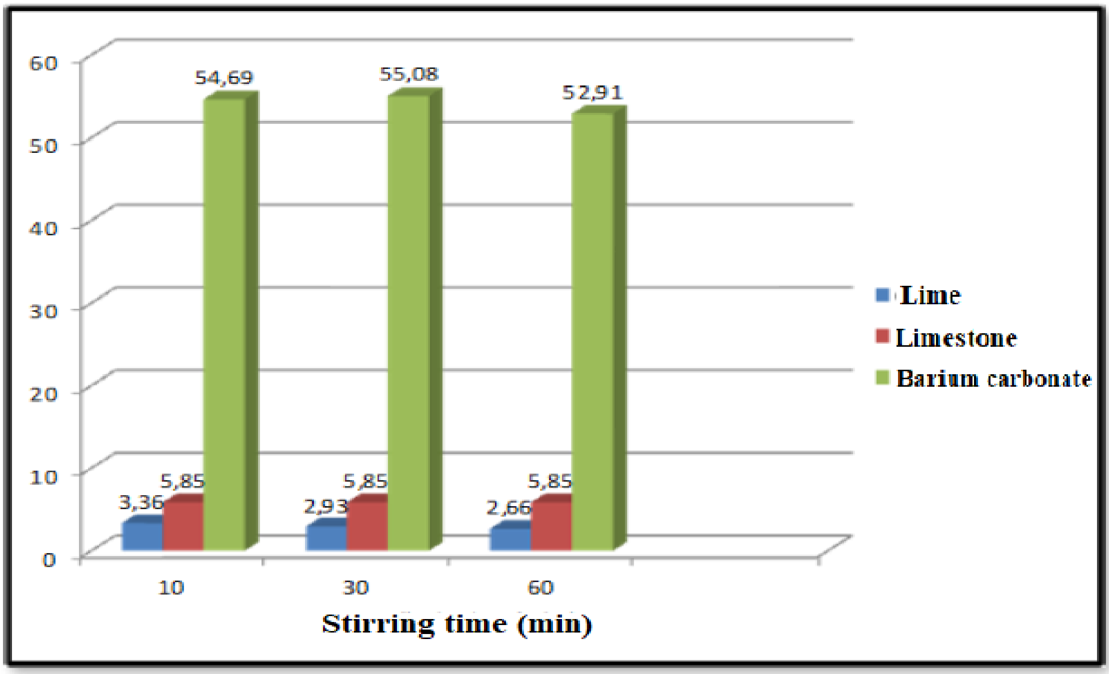

Figure 2. desulfation of the phosphoric Acid (6%) by lime.

3.2. *Desulfation by limestone*

The theoreticall mass of limestone needed to desulfation of phosphoric acid with a sulfate content of 5.85% is m_{CaCO_3} =11, 94 g, the limestone mass then becomes m_{CaCO_3} =12, 06 g. The analysis of the liquid phase separated by centrifugation gives the following results presented at Figure 3. The phosphoric acid desulfation (5.85% H_2SO_4) by limestone ensures a sulfate content of 2.62% after 30 min of agitation.

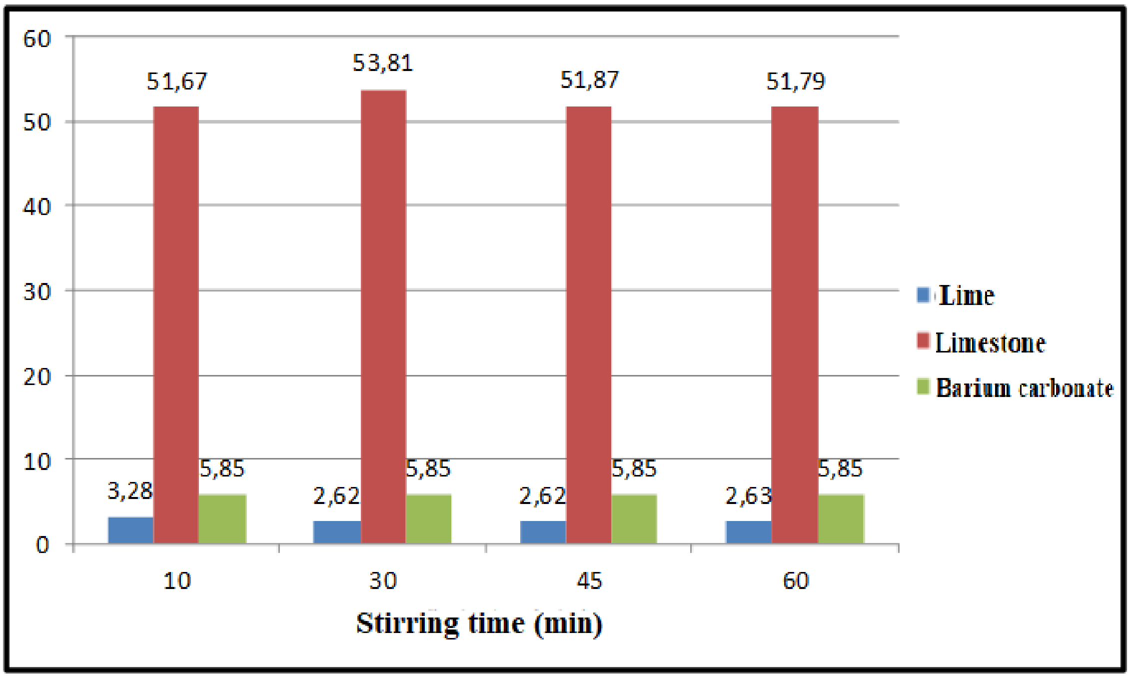

Figure 3. Desulfation of the acid (6%) by limestone.

4.3. Desulfation of the phosphoric acid by barium carbonate

The mass of barium carbonate theoretically required to desulfation phosphoric acid with a sulfate content of 5.85% is 23.56g. Barium carbonate is still the most effective desulfation adjuvant, which may be explained by the fact that the barium sulfate ($BaSO_4$) formed is very soluble (s = 3,10-3 g.L^{-1}). These results are shown in Figure 4.

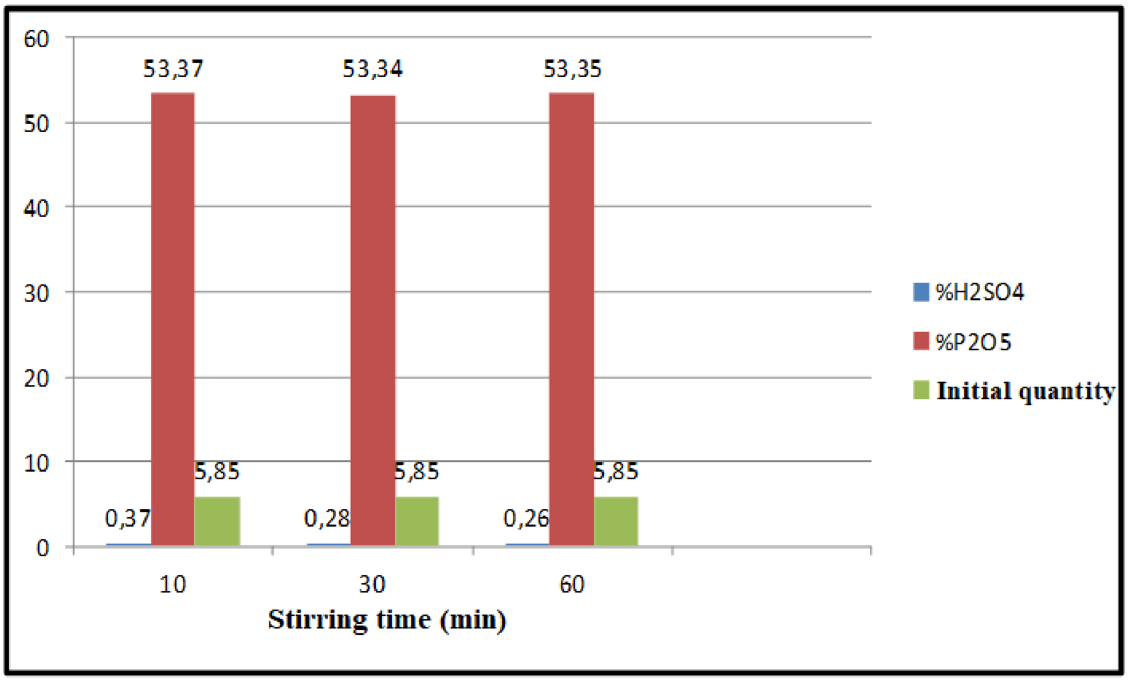

Figure 4. desulfation of the acid (6%) by barium carbonate.

3.3. *Comparison of the different adjuvants*

The obtained results for the various adjuvants during desulfation of phosphoric acid 6% are shown in Figure 5. Sulfate levels obtained following the desulfation by lime and limestone are greater than 2%, these values are not satisfactory. An improvement of this desulfation rate by the use of an excess of adjuvants or by the second step of desulfation is thus necessary.

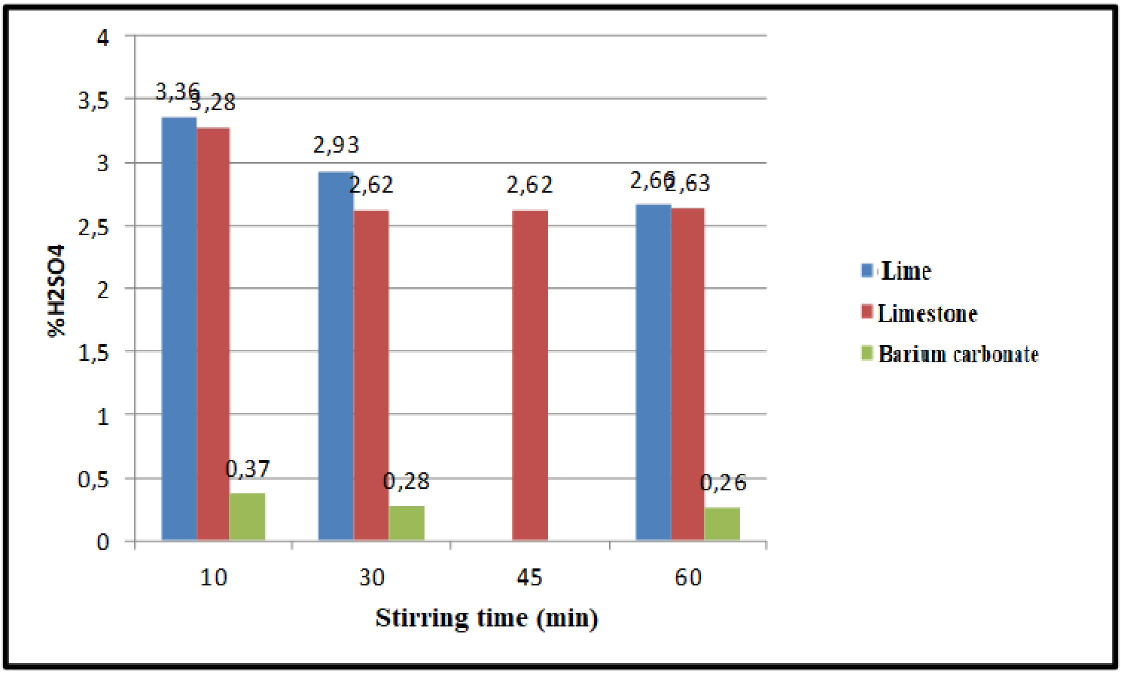

Figure 5. Effect of different additives on acid (6%) desulfation.

4. Phosphoric acid desulfation 2% H_2SO_4

The analyses are carried out after centrifugation. The of H_2SO_4 mass titer of 2% of the concentrated phosphoric acid. The results of the analyses (Table 8) show a sulfate content of 2.87%.

Table 8. ***Phosphoric acid characterization (2%)***

	P_2O_5 (%)	%H_2SO_4
Trial 1	53,29	2 ,87
Trial 2	53,29	2 ,87
Trial 3	53,29	2 ,87
Trial 4	53,29	2 ,87
Average value	53,29	2 ,87

4.1. Desulfation *of the phosphoric acid by Lime*

The mass of lime required for the desulfation of 200 g phosphoric acid is m_{CaO}= 3.28 g. The sulfate contents measured after centrifugation is shown in Figure 6. The lower order of 0.7% is rapidly reached (time = 10 min).

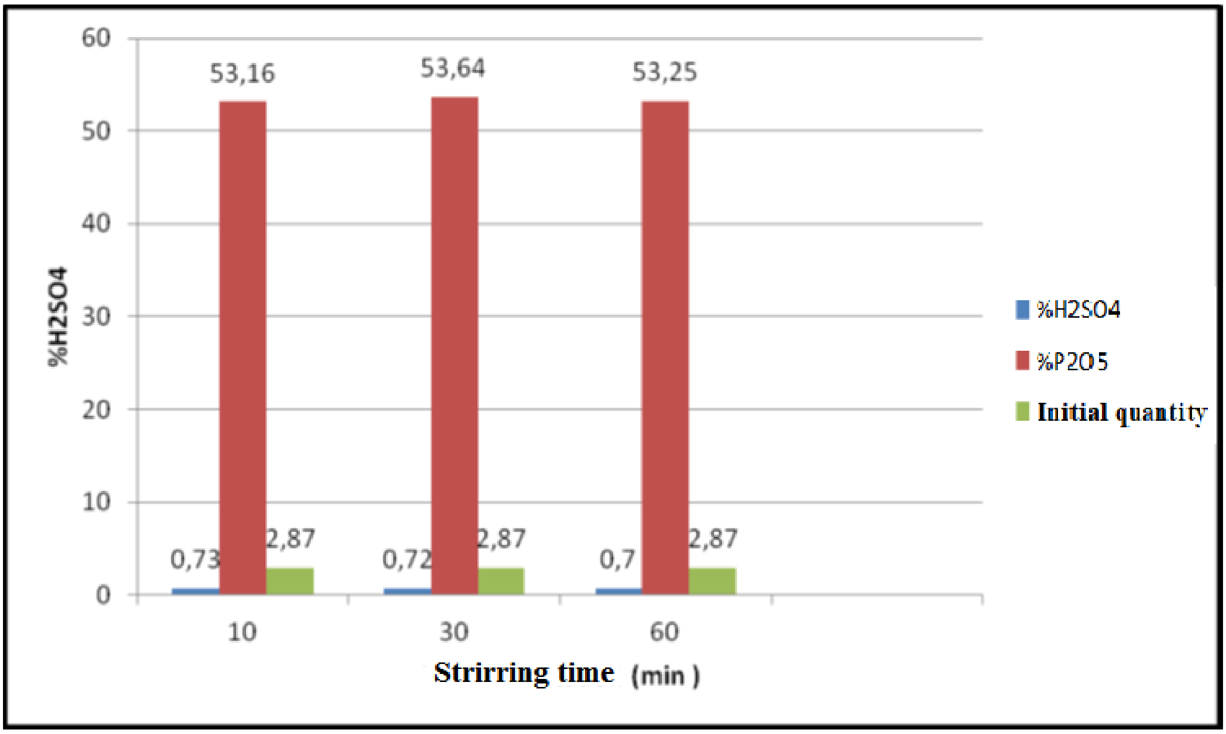

Figure 6. desulfation of phosphoric acid (2%) by limes.

4.2. *Desulfation of the phosphoric acid by limestone*

The results of limestone desulfation analyses are presented in Figure 7. These sulfate levels of 7% are largely satisfactory by the application of industrial phosphoric acid.

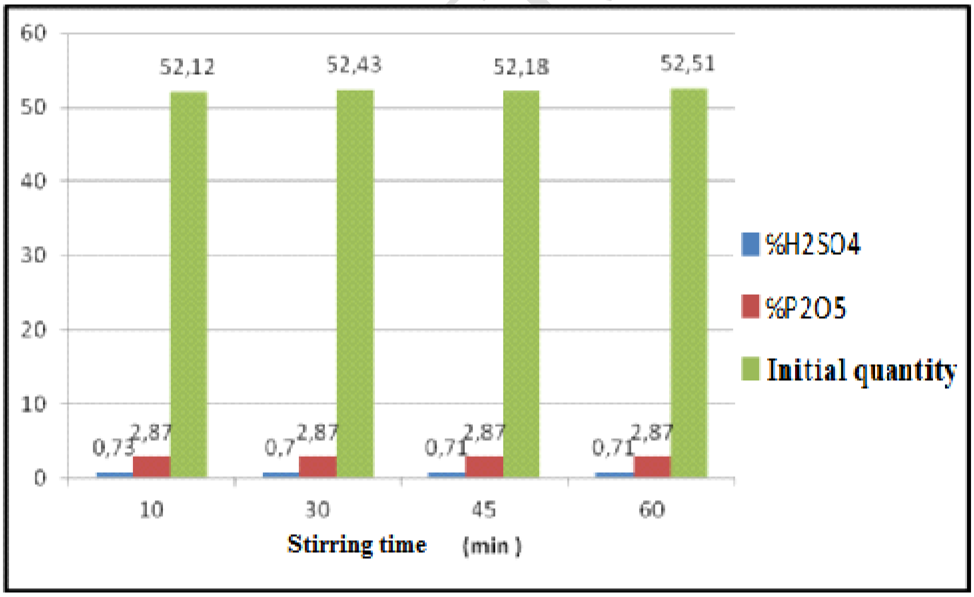

Figure 7. Phosphoric Acid (2%) desulfation by limestone.

4.3. *Desulfation by barium carbonate*

The mass of barium carbonate is theoretically required to de-sulfate phosphoric acid with a sulfate content of 2.87 % and 11.56 g (Fig 8). Indeed, this adjuvant allows an intense and total desulfation of the acid during the separation of the solid and liquid phase remains difficult to achieve.

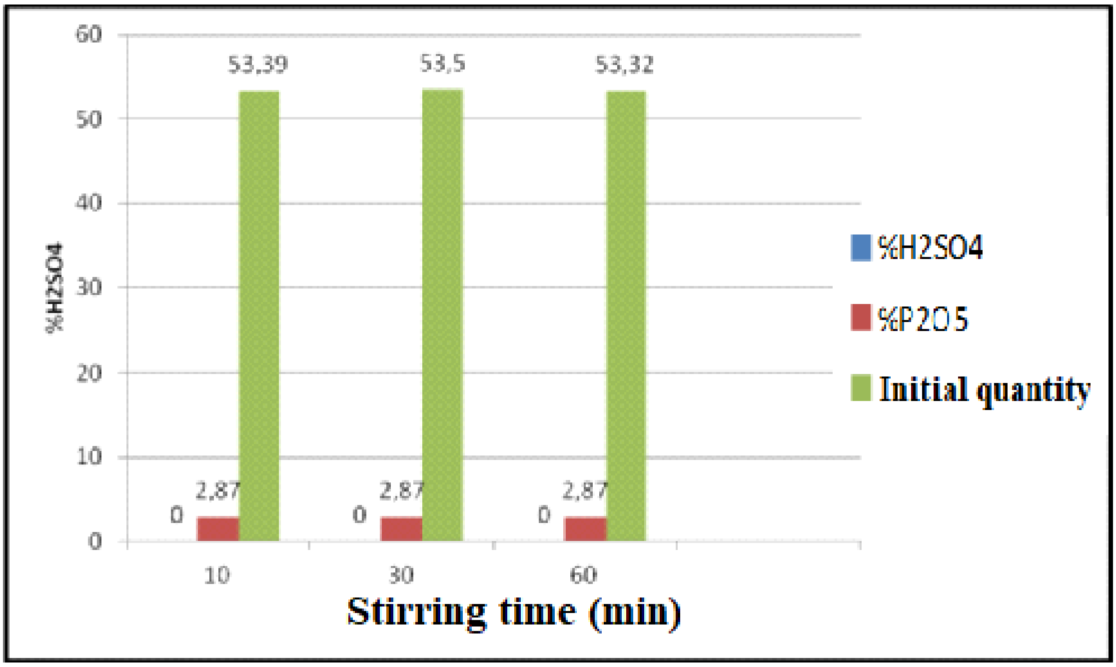

Figure 8. desulfation of the acid (2%) by barium carbonate.

4.4. *Comparison of different additives*

Barium carbonate desulfation produces a technical-grade phosphoric acid regardless of its initial sulfate content (Fig 9). The problem with this adjuvant lies in the separation phase which now remains incomplete, following the fineness of the barium sulfate particles formed the complete separation of the solid phase by centrifugation on an industrial scale, is very difficult and requires very long kept times.

Limestone and lime ensure a very high desulfation rate and allow meeting the requirements of customers. The choice between two additives will be based on their price.

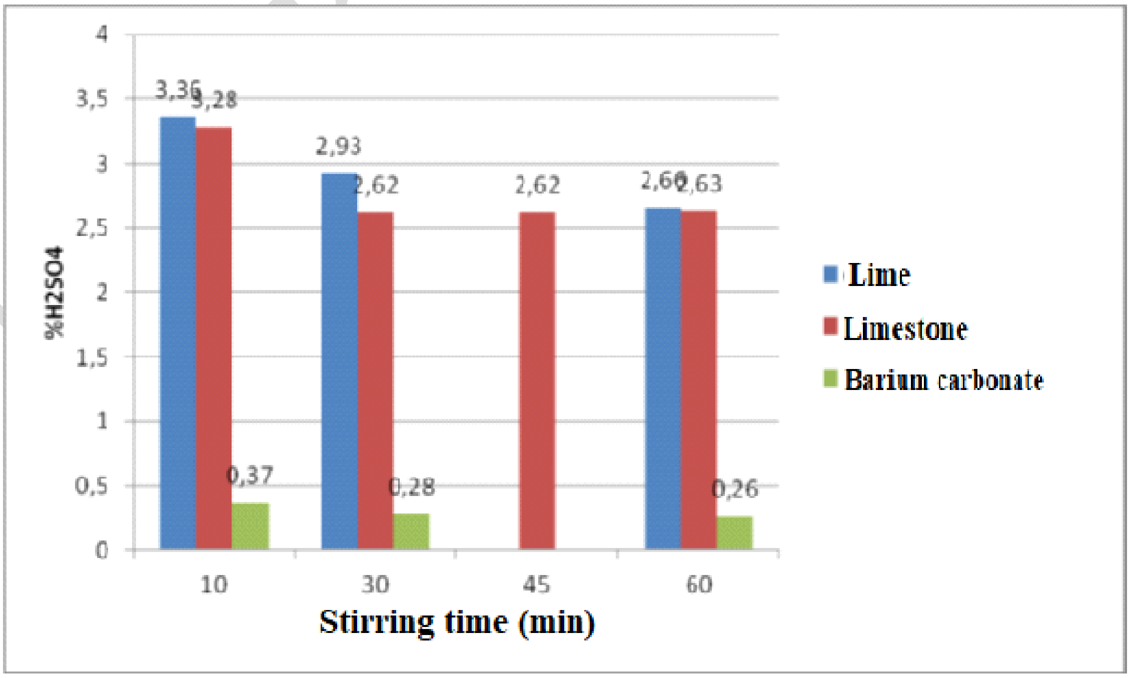

Figure 9. The effect of different adjuvants on acid desulfation (2%).

Conclusion

Phosphoric acid desulfation has been carried out using three different additives; Quicklime, limestone, and barium carbonate. The added quantities depend on the free sulphate content of the industrial acids. Three primary sulfate contents were studied: 2%, 4%, and 6%. After that the analyses are carried out on the liquid phase separated by centrifugation. The comparison of the obtained results allow to consider barium carbonate as the most effective adjuvant, it enables very low sulfate levels to be achieved for very short stirring times, regardless of the initial sulfate content in phosphoric acid. Moreover, due to the fineness of the formed barium sulfate particles, the complete separation of the solid phase by centrifugation on an industrial scale; is very difficult and requires very long kept times.

The tests carried out with quicklime and limestone lead to very interesting acid desulfation with initial sulfate content of 2 or 4%. In the case of a sulfate level of 6%, the experiments showed a sulfate content in desulphurised acid greater than 2%.

Limestone and lime have very similar desulphurised capacity thus the limestone presented the advantage of having the lowest price. Therefore it is considered as the most suitable adjuvant.

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