

Original Research Article

Comparative evaluation of industrial phosphoric acids desulfation capabilities of limes and barium carbonate

Abstract

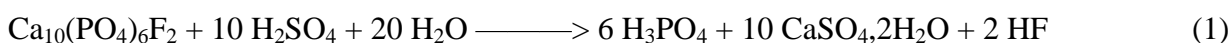
Industrial phosphoric acid is an omnipresent product in the food industry and in the production of fertilisers and detergents. The presence of impurities in the raw material results in a relatively charged acid with various chemical species at the expense of its quality and use. These impurities include sulfate ions that precipitate into phosphoric acid during its manufacture. A desulfation is thus necessary. This study focuses on the reduction of free sulfates in phosphoric acid as impurities. This resulted in the use of three different adjuvants: lime, limestone, and barium carbonate. Three initial sulfate levels mainly contained in phosphoric acid were investigated: 2%, 4% and 6%. After experimentation, the comparison between the resulting yields allows considering barium carbonate as the most effective adjuvant. The desulfation efficiency was 95% in a very short stirring time of 15 min, independently of the initial sulphate content of phosphoric acid. The tests carried out with lime and limestone also lead to very interesting desulfation rates for phosphoric acid with an initial sulfate content of 2 or 4%.

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 origins are found in different countries. 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 the 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 triacid 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 the attack with concentrated sulfuric acid (see Sulfuric acid) at 80°C :



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 sulfate 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 the manufacture of phosphate salts. It is an important intermediate used to prepare the triple superphosphate (TSP) [7], sodium tripolyphosphate $\text{Na}_5\text{P}_3\text{O}_{10}$ and, ammonium phosphates $(\text{NH}_4)_2\text{HPO}_4$. 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 sulfates, 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]. Sulfate ions, in particular, have about 2% weight, and affect undoubtedly the efficiency of the 29% P_2O_5 phosphoric acid concentration unit, due to the solid formation which causes premature clogging of the phosphoric acid concentration unit.

The aim of the present study is to eliminate sulfates impurities by 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 the retainer of the sulfates impurities. These adjuvants are previously crushed and sieved to have a particle size of about $0.16\ \mu\text{m}$. Desulfation tests shall be conducted under agitation at a temperature of 60°C . 200 g

mass of industrial phosphoric acid was used. Different periods of agitated treatment were chosen: 10, 30, 45 and 60 minutes. After treatment, phosphate and sulfate amounts were analyzed by titration and the calculated percentage were:

For phosphoric acid

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

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.

$$\% H_2SO_4 = \frac{(V_{total} - V_{blank}) * 4,9}{E0} \quad (2)$$

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)

3. Results and discussion

3. 1. Desulfation of industrial phosphoric acid 2% H₂SO₄

To verify the quality of the phosphoric acid, P₂O₅ and H₂SO₄ mass titers are determined. The resulting analyses were carried out on samples H₂SO₄ mass title of 2% in phosphoric acid. The analyses were carried out after centrifugation. The results of the analyses are presented in Table 1 and show a sulfate content of 2,87%.

Table 1. Analysis of P₂O₅ and H₂SO₄ contents of the starting phosphoric acid (2%)

	P ₂ O ₅ (%)	%H ₂ SO 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

3. 1. 1. Desulfation of the phosphoric acid 2% 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 1. The lower order of 0.7% is rapidly reached (time = 10 min).

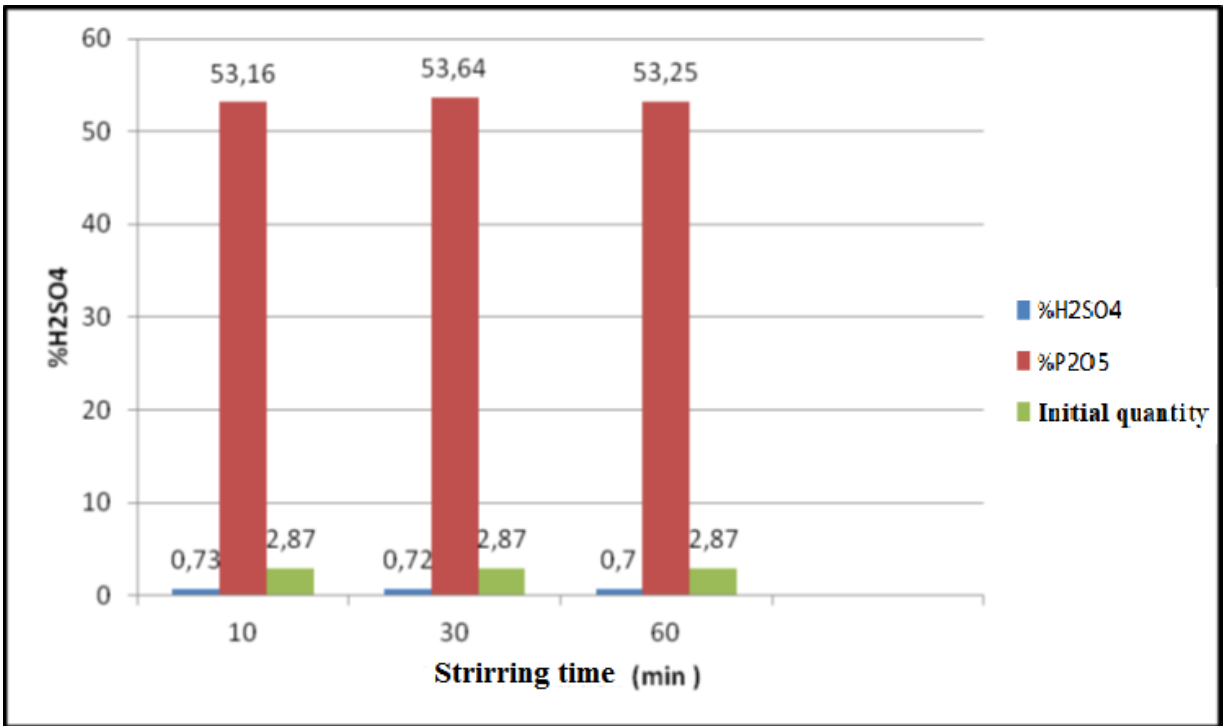


Figure 1. desulfation results of the phosphoric acid (2%) by limes.

3. 1. 2. Desulfation of the phosphoric acid (2%) by limestone

The results of limestone desulfation analyses are presented in Figure 2. These sulfate levels of 7% are largely satisfactory by the application of industrial phosphoric acid.

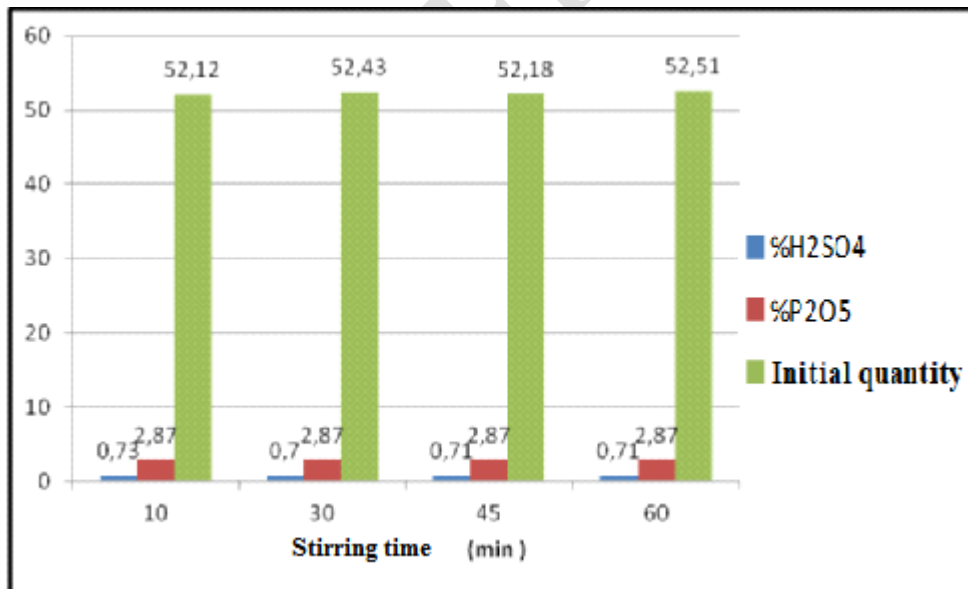


Figure 2. Desulfation result of the phosphoric acid (2%) by limestone.

3. 1. 3. Desulfation of the phosphoric acid (2%) by barium carbonate

The mass of barium carbonate theoretically required to the desulfation of the phosphoric acid with a sulfate content of 2.87 % is 11.56 g. Indeed, this adjuvant allows an intense desulfation of the acid during the separation of the solid and liquid phases (Figure 3). The total desulfation remains difficult to achieve.

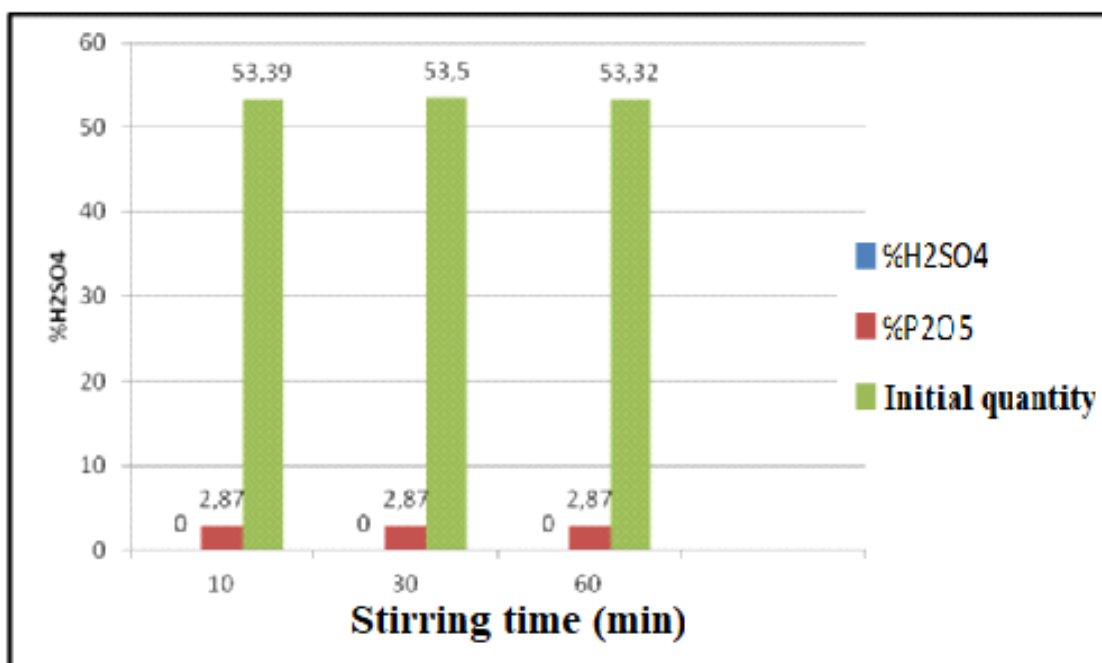


Figure 3. desulfation result of the phosphoric acid (2%) by barium carbonate.

3. 1. 4. Comparison of different additives

Barium carbonate desulfation produces a technical-grade phosphoric acid regardless of its initial sulfate content (Fig. 4). 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 a very long kept time. 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.

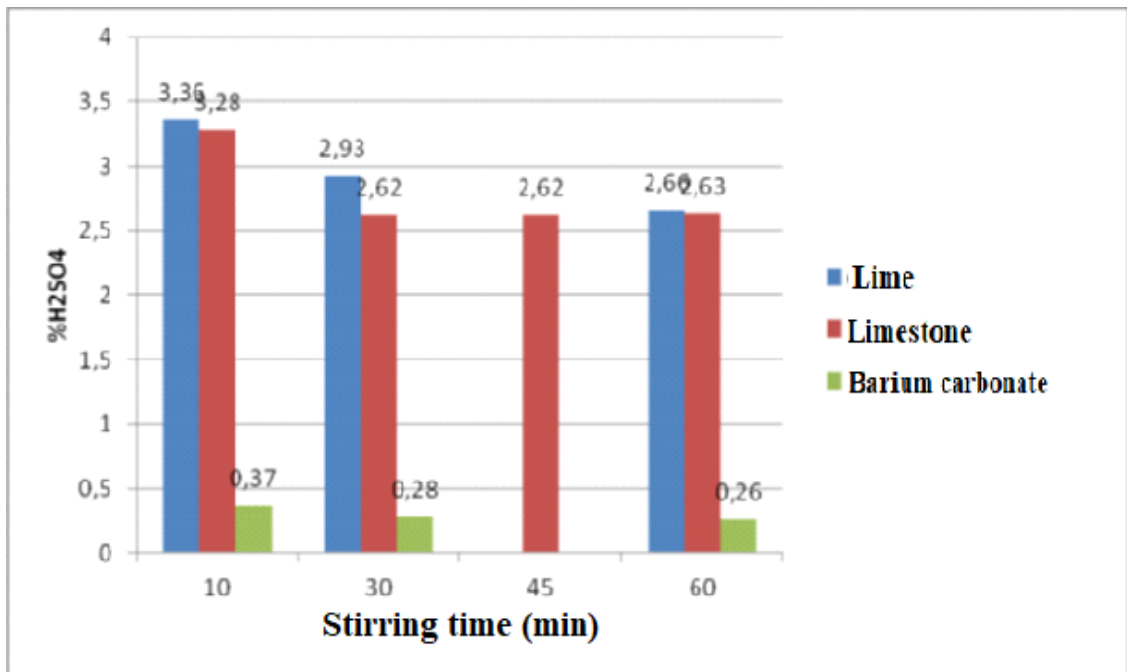


Figure 4. The effect of different adjvants on the phosphoric acid (2%) desulfation.

3. 2. Desulfation of industrial phosphoric acid 4% H₂SO₄

To verify the quality of the phosphoric acid, P₂O₅ and H₂SO₄ mass titers were determined. The resulting analyses are grouped in Tables 2 and 3. The measured P₂O₅ mass titer is within the acceptable range of concentrations (46-54%).

Table 2. Analysis of P₂O₅ content of the starting phosphoric acid

	Trial 1	Trial 2	Trial 3	Trial 4
E0 (g)	1,085	1,055	1,015	1,032
% P ₂ O ₅	49,25	49,24	49,51	49,49
Average value	49,38 %			

Table 3. Analysis of H₂SO₄ content in the starting phosphoric 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 ₂ SO ₄	4,19	4,01	3,94	4
Average content	4,04%			

3. 2. 1. Desulfation of phosphoric acid 4% by lime

Desulfation was done by adding lime (CaO) in a stirred beaker maintained at a temperature of 60°C. Different stirring times were used to follow the desulfation of phosphoric acid (4% H₂SO₄) by lime. For each time, three tests were carried out. Finally, P₂O₅ and sulfate analyses were performed on the liquid phase separated by centrifugation. The obtained results of desulfation by lime are presented in Table 4.

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 H₂SO₄) by lime. The sulfate content has decreased from an initial value of 4.04% to a final one of 1.67%.

Table 4. Analysis results of the desulfation of the phosphoric acid (4%) by lime

<i>Desulfation of the phosphoric acid by lime for 10 min</i>					
	MA ph (g)	mCaO (g)	% P₂O₅	% H₂SO₄	R (%)
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
<i>Desulfation of the phosphoric acid by lime for 30 min</i>					
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
<i>Desulfation of the phosphoric acid by lime for 60 min</i>					
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

3. 2. 2. Desulfation of phosphoric acid 4% by limestone

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



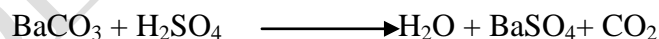
The results of phosphoric acid desulfation (4% H₂SO₄) by limestone obtained for different stirring times are grouped in Table 5. It is noted that after a stirring time of 30 min, the sulfate content becomes practically constant. In the case of desulfation by limestone, a kept time of 30 min corresponds to an optimal desulfation. That is a final sulfate level of 2.13 %. Desulfation acid has a P₂O₅ content of 52%.

Table 5. Analysis results of the desulfation of the phosphoric acid 4% by Limestone

	$M_{A\text{ph}}$ (g)	m_{CaCO_3} (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 <i>desulfation</i> 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 <i>desulfation</i> 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 <i>desulfation</i> 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

3. 2. 3. Desulfation of the phosphoric acid 4 % by barium carbonate

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



The results of phosphoric acid desulfation by barium carbonate after centrifugation for a stirring time of 10 minutes, 30 minutes, and 60 minutes are grouped in Table 6.

Tableau 6. Analysis results of the desulfation of the phosphoric acid 4 % with barium carbonate

	$M_{A\text{ ph}} \text{ (g)}$	$m_{\text{BaCO}_3} \text{ (g)}$	$\% \text{ P}_2\text{O}_5$	$\% \text{ H}_2\text{SO}_4$	$Y \text{ (\%)}$
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) with a yield (Y) of the order of 95%. However, these results are to be verified because the separation of the precipitate formed by centrifugation was not complete regardless 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 7 shows the average values obtained in each case.

Table 7. Results of gravimetric analysis of the desulfation of phosphoric acid 4 % with barium carbonate

Stirring time (min)	10	30	60
H₂SO₄ content (%)	0,25	0,19	0,16

3. 2. 4. Comparaison between the different additives

Gravimetric analyses show a much higher desulfation rate, in the case of barium carbonate than that with the other two adjuvants. Lime ensures a sulfate level of less than 1.7%, a value widely sufficient level 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 the desulfation of phosphoric acid 4% are shown in Figure 5.

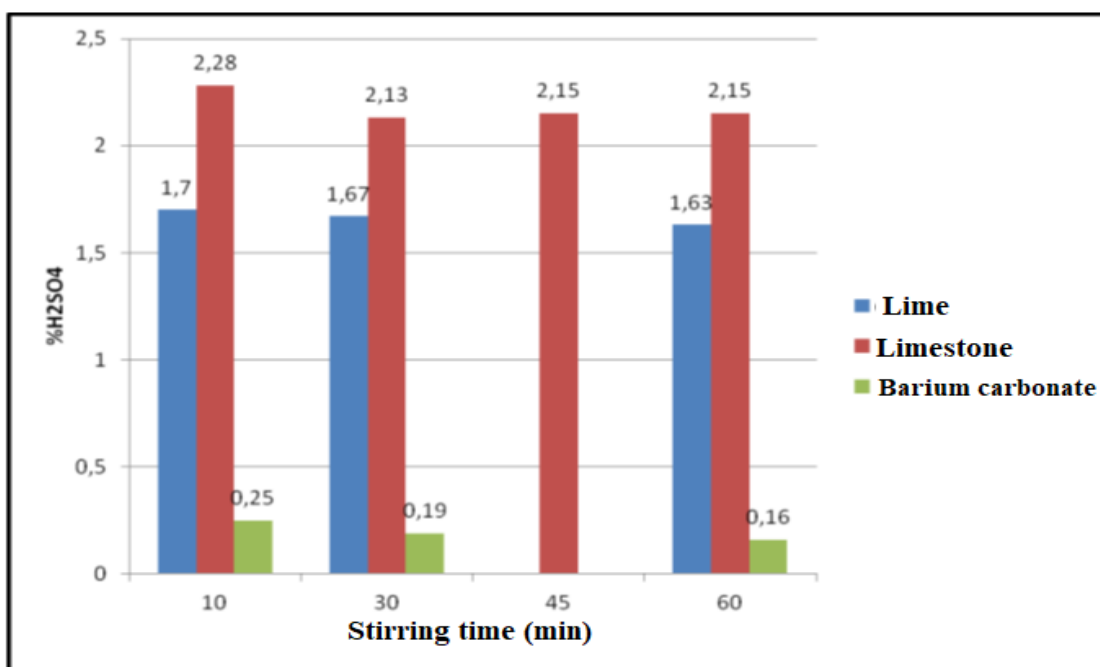


Figure 5. Effect of different additives on desulfation of phosphoric acid (4%).

3. 3. Desulfation of industrial phosphoric acid 6% H₂SO₄

The results of the different analyses for the phosphoric acid (6%) are presented in Table 8, confirming the contents retained and will then be used to determine the contents of the various adjutants.

Table 8. Analysis of P₂O₅ and H₂SO₄ contents of the starting phosphoric acid (6%)

	P ₂ O ₅ (%)	H ₂ SO 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. 3. 1. Desulfation of phosphoric acid 6 % by Lime

The mass of lime is theoretically required for the desulfation of the 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 6. The phosphoric acid (6%) desulfation by lime ensures a sulfate level of 2.66% after one hour. This value exceeds the values required by customers.

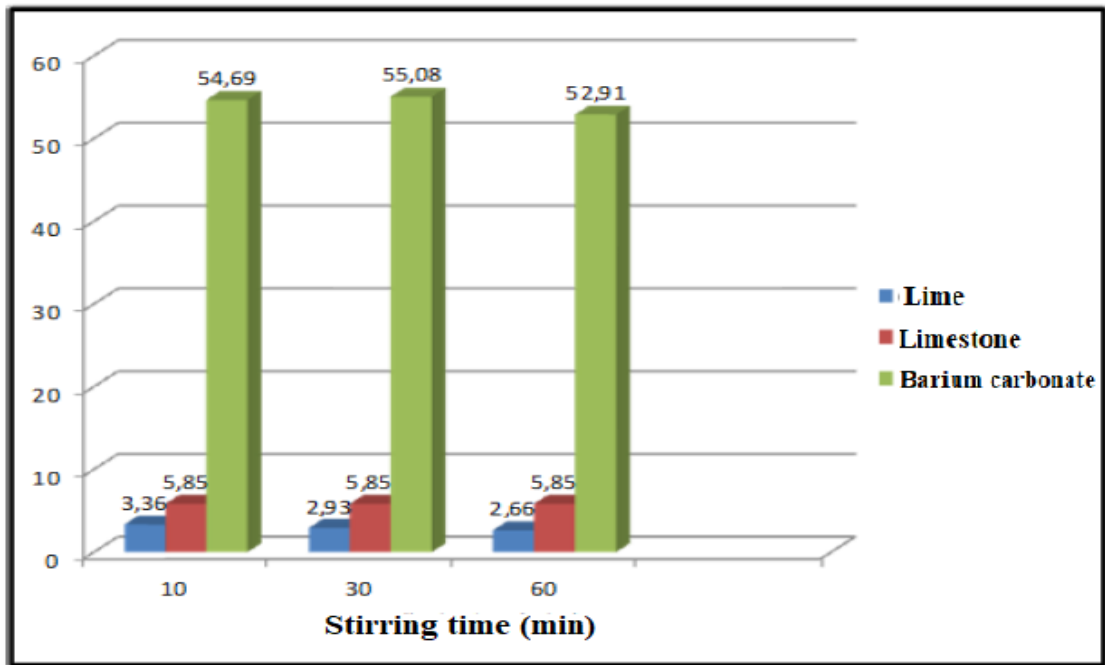


Figure 6. Desulfation of the phosphoric acid (6%) by lime.

3. 3. 2. Desulfation of phosphoric acid 6 % by limestone

The theoretical mass of limestone needed for the desulfation of phosphoric acid with a sulfate content of 5.85% is $m_{CaCO_3} = 11.94$ g. Thus, the limestone mass becomes $m_{CaCO_3} = 12.06$ g. The analysis of the liquid phase separated by centrifugation gives the following results presented in Figure 7. The phosphoric acid desulfation (5.85% H_2SO_4) by limestone ensures a sulfate content of 2.62% after 30 min of agitation.

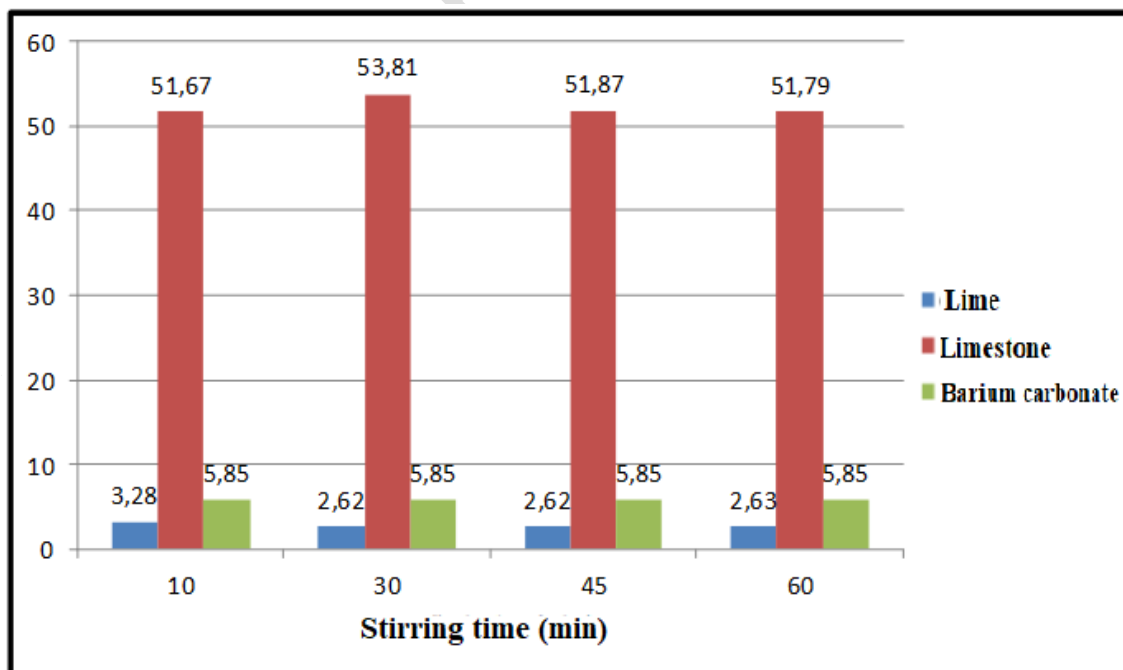


Figure 7. Desulfation of the phosphoric acid (6%) by limestone.

3. 3. 3. Desulfation of phosphoric acid 6 % by barium carbonate

The mass of barium carbonate theoretically required for the desulfation of the phosphoric acid having 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 slightly soluble ($s = 3.10^{-3} \text{ g.L}^{-1}$). These results are shown in Figure 8.

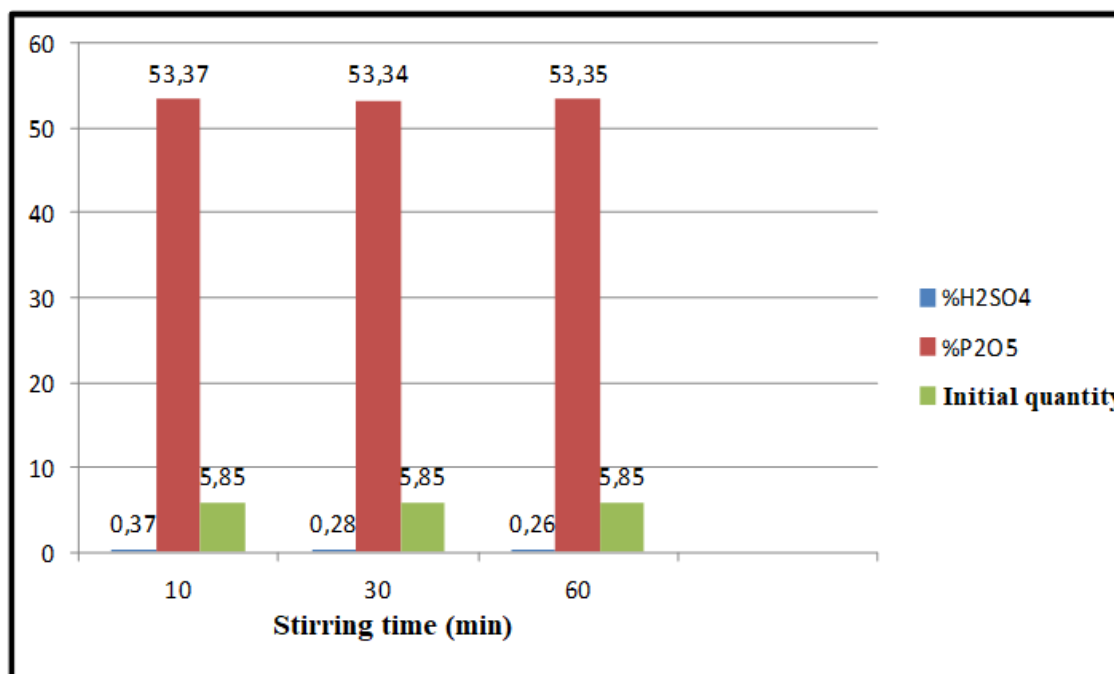


Figure 8. Desulfation of the phosphoric acid (6%) by barium carbonate.

3. 3. 4. Comparison of the different adjuvants

The obtained results for the various adjuvants during desulfation of the phosphoric acid 6% are shown in Figure 9. Sulfate levels obtained after 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.

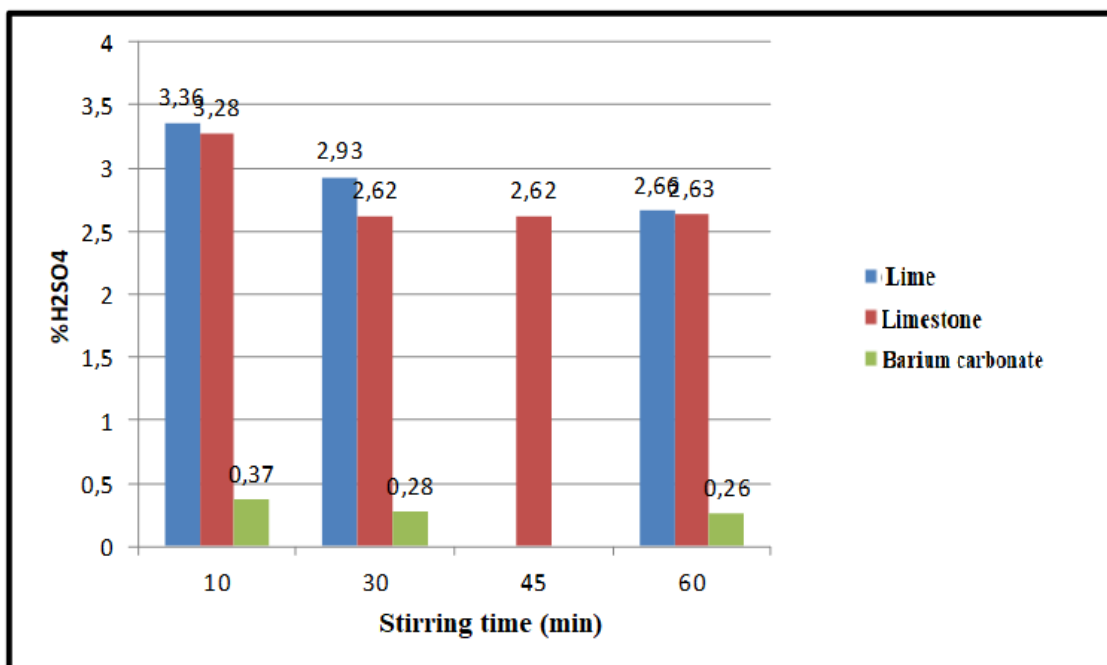


Figure 9. Effect of different additives on phosphoric acid (6%) desulfation.

4. Conclusion

The desulfation of phosphoric acid was performed using three different additives: lime, limestone, and barium carbonate. The quantities added are dependent upon the free sulfate content of the industrial phosphoric acids. Three main sulfate concentrations were investigated: 2%, 4% and 6%. The tests are then carried out on the centrifugally separated liquid phase. A comparison of the results obtained enables barium carbonate to be regarded as the most effective adjuvant. It enables very low sulfate levels to be reached for short stirring times; the yield was 95% during 15 min, independently 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 phosphate is very difficult and requires a too long stirring time.

The tests carried out with lime and limestone led to a very interesting acidic 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 treated phosphoric acid greater than 2%. Limestone and lime have very similar desulfation capacity though the limestone presented the advantage of having the lowest price.

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