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Effect of phosphate quality on foam generation during the phosphoric acid production process

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Abstract: The presence of organics materials in phosphate ores generates foam during the manufacture of phosphoric acid, thus affecting the production performance and the quality of the products. Today, in the phosphate industry defoamers are used to reduce the negative impact of foam phosphoric production. In the present work, we focused on root cause evaluation for foam generation during the phosphoric acid production process, we evaluated the effect of phosphate rock quality in terms of organic carbon (OC) and carbonate content, on foam generation using a laboratory protocol for foaming ability evaluation. The results show that there is a relationship between the volume of the foam generated and the values of those impurities, while the volume of foam generated is higher when the concentration of OC and Carbonate is high. In our work, we confirm that the foaming ability of the phosphate rock can be avoided if the concentration of organic carbon less than 0.1% and less than 3% for carbonate.

Keywords: phosphate rock, foam, organic carbon, carbonate, foamingability test

1. Introduction

It is well known that sedimentary phosphates are the most widely used raw material for the production of phosphoric acid and phosphate products. These types of phosphate minerals are always associated with organic matter (OM), with organic matter, with a concentration varying varies from 1% to 3.5 % (Durand, 1980; Dokhri, 1987; Benmoumen, 1997). The presence of OM generates foams during the wet sulphuric process production of phosphoric acid that increases of sulfuric acid consumption, reduces sulfates to sulfides, and also causes intense equipments corrosion in the installation (El-Jallad, 1977; Mellah et al., 1992; Blazy et al., 1997). However, the formation of foams, when attacking phosphate rock with sulfuric acid, affects the temperature of the reaction, leading to an increase in temperature and viscosity and gives a phosphogypsum hemihydrate form (Becker, 1989; Blazy et al., 1997; Cuney, 2004; Bendada, 2005; Ashraf et al., 2007). Therefore, this results in poor filtration which affects production performance, increases the P₂O₅ losses and decreases the chemical and industrial yield (Blazy et al., 1997; Bendada, 2005; Ashraf et al., 2007). Organic carbon gives a black color to the phosphoric acid produced, affecting the performance of the processes using this quality as raw material. Indeed, the use of black phosphoric acid affects the performance of solvent purification units due to the interaction of the latter with organic matter (Blazy et al., 1997).

Several attempts have been made to overcome these problems and improve the quality of the phosphate and the process of phosphoric acid. Currently, industries use antifoam, the specific consumption of antifoam. The used concentration is generally between 30 g and 70 g/t of P_2O_5 depending on the formulation of the antifoam and the foamability of phosphate rock and phosphoric acid, thus affecting the cost of production (Michael, 1997).

The presence of certain impurities in the phosphate rock (organic or inorganic), tend to stabilize the CO_2 gases, which are released from calcite and dolomite existing in the phosphate rock when reacted with sulfuric acid, and they act as surfactants and make the surface foam more stable and difficult to control, and limiting the ability of gases to escape from the reactor suspension (Partin, 2005, Becker, 1989). One of the main challenges that producers of the phosphoric acid face are the perturbation of operating conditions and increase losses of P_2O_5 due to foam formation in different steps of the process. Defoamers are the worldwide adopted solution to improve phosphoric plant performance (Partin, 2005).

According to several authors, the undesirable effects of organic matter and carbonate on the performance of the phosphoric acid process have been proven (El-Jallad, 1977; Becker, 1989; Mellah et al., 1992; Blazy et al., 1997; Cuney, 2004; Bendada, 2005; Ashraf et al., 2007), but no one has confirmed that there is a relationship between the foaming phenomenon and the content of organic matter and carbonate in the phosphate rock.

In this work, we suggest a new way to face the foam effect on production performance based on the upstream treatment of the phosphate rock as a preventive solution for foaming phenomena. We carried out foaming tests, to follow the evolution of foam as a function of time and contents of organic matter ($\% C_{org}$) and carbonates ($\% CO_2$) in phosphate rock that affects the foamability behavior.

2. Materials and methods

2.1. Materials

In our experiments, we used different grades of Moroccan phosphate rock coming from different sites such as Khouribga, Boucraa, and Youssoufia to have several phosphate qualities in terms of organic carbon and carbonate contents. We simulate in laboratory bench scale the dehydrate wet-process phosphoric acid production using sulphuric acid H_2SO_4 with a concentration of 65%, and 18% of phosphoric acid H_3PO_4 . The acid samples used for this study came from OCP Jorf Lasfar plant. A series of representative phosphate samples have been prepared in the laboratory by crushing

A series of representative phosphate samples were prepared in the laboratory by grinding, homogenization, and quartering to achieve the particle size used on an industrial scale (between $40\mu m$ and $500\mu m$), in particular in the phosphoric acid manufacturing process to have a better reactivity.

The particle size distribution of the sample was determined using Malvern Mastersizer 2000, UK, and the results are shown in Fig. 1. As shown, most of the particle size (95.3%) is between 100 and 500 micrometers and 15% below almost $80\mu m$. The mean volume of the phosphate was approximately $500\mu m$. This particle size distribution is compatible with that used for the production of phosphoric acid,

For the Mineralogical Structure determination, we used XRD measurements type Bruker AXS D-8 diffractometer using Cu-K α radiation in Bragg-Brentano geometry ($q-2q$). The results given in Fig. 2 show that the particles of phosphate rock are predominately composed of the fluorapatite $Ca_{10}(PO_4)_6F_2$ carbonates, which are in two forms dolomite $CaMg(CO_3)_2$ with calcite $CaCO_3$ and quartz SiO_2 .

Thermal analysis methods for solids (DSC, TGA) are complementary of X thermo-diffraction in the characterization and study of the behavior as a function of the temperature of any solid material undergoing modifications of composition (dehydration, decomposition, oxidation, reduction) or/and structure (transition, phase change). Fig. 3 shows the thermogravimetric analysis curve of phosphate rock. According to the curve TGA of the sample, three stages of weight loss were observed. The first weight loss occurs from ambient temperature to $120^\circ C$ whose peak is located towards $80^\circ C$ and can be attributed to the departure of moisture. The second weight Weak exothermic phenomenon which starts around $200^\circ C$ and which is spreading out until $600^\circ C$ probably due to the combustion of the Organic Matter. And the third stages of weight loss were observed between $600^\circ C$ and $900^\circ C$, an endothermic

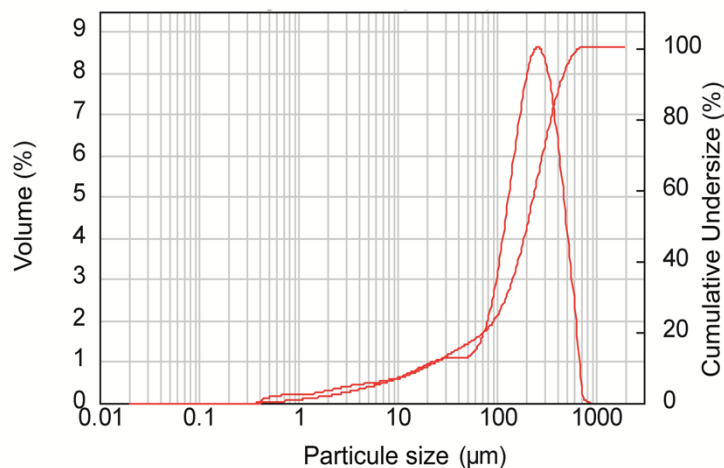


Fig. 1. The size distribution of particles

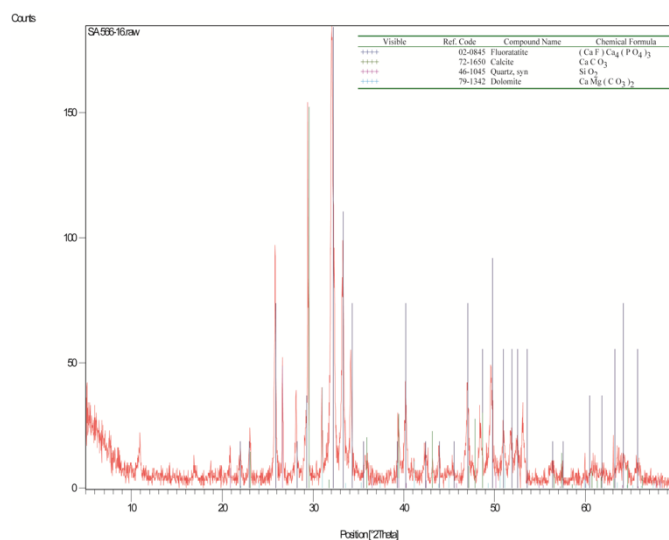
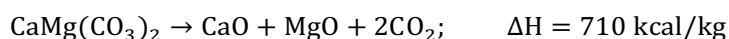


Fig. 2. RX diffractogram of crude phosphate

phenomenon which can be due to the decomposition of carbonates (calcite $CaCO_3$ and the dolomite $CaMg(CO_3)_2$) according to the following reactions:



The elemental composition of phosphate samples was determined by ICP-AES, Total Organic Carbon (TOC) was determined by the Shimadzu TOC-L Series and CO_2 was analyzed by the chemical bernard calorimeter, which measures the volume of CO_2 released by the action of hydrochloric acid (HCl) on the calcium carbonate ($CaCO_3$) of a phosphate sample. This chemical analysis is grouped in Table. 1 and 2. In Table 1, we presented the main elements found in rock phosphate, taken from the literature, in different forms and at different levels and which can be removed by heat treatment.

Table 1. Chemical compositions of the main elements of phosphate ore

| Elements | | P_2O_5 | CO_2 | SO_3 | SiO_2 | CaO | MgO | Fe_2O_3 | Al_2O_3 | Na_2O | K_2O | C_{org} |
|----------|-----------|----------|--------|--------|---------|-------|-------|-----------|-----------|---------|--------|-----------|
| Weight | Khouribga | 29.46 | 6.3 | 1.6 | 3.1 | 50.2 | 0.7 | 0.2 | 0.4 | 0.8 | 0.1 | 0,22 |
| % | Yousoufia | 30.65 | 8.72 | 1.44 | 9.7 | 51.75 | 0.32 | 0.07 | 1.32 | 1.97 | 0.05 | 1.5 |
| | Boucraa | 30.08 | 2.7 | 1.01 | 8 | 48 | 0.4 | 0.48 | 0.65 | 0.49 | 0.09 | 0.12 |

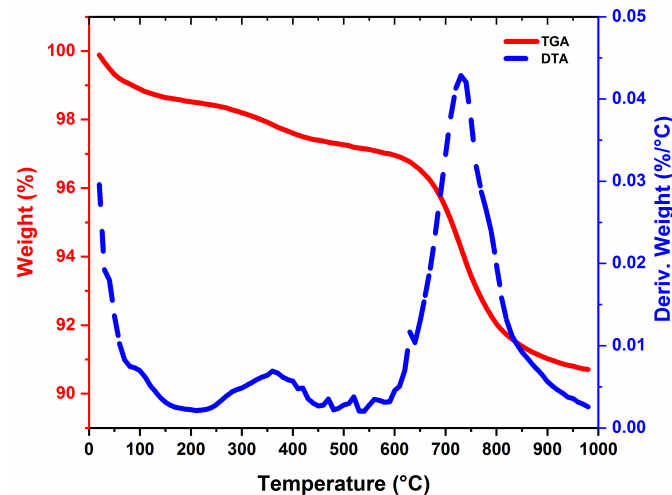


Fig. 3. TGA of crude phosphate

2.2. Method

2.2.1. Foaming test

During the simulation in bench lab-scale of the dehydrate wet sulfuric acid production process foams were generated and overflow with time. The foaming test was based on the simulation, under industrial hydrodynamic conditions, of the foamability of a resulting reaction slurry using different phosphate rock qualities. The test gave, as a result, a volume of foam generated (foamability) and time resistance or stability of the foam using The Ross-Miles test device (Fig. 4, A) and the method of Bikerman (Fig. 4B) (Salager and Choplin, 2008). According to these two methods we were able to create a valid method to evaluate the degree of foam generation for phosphate rock, the following method is described below:

To perform the foaming test, we introduced phosphate in a test tube containing a magnetized bar, we put sulphuric acid and phosphoric acid at once, and then immediately start the stopwatch. We then noted the height of the foam until it was fixed. The foaming test was carried out at the lab-scale device to simulate the foamability of different phosphate grades. The carbonaceous materials in the acidic reaction medium transformed into CO_2 . The latter released forms first miscellaneous then transformed into the stable foam with a decomposed organic matter from phosphate rock and the calcium sulfate particle (Fig. 4C).

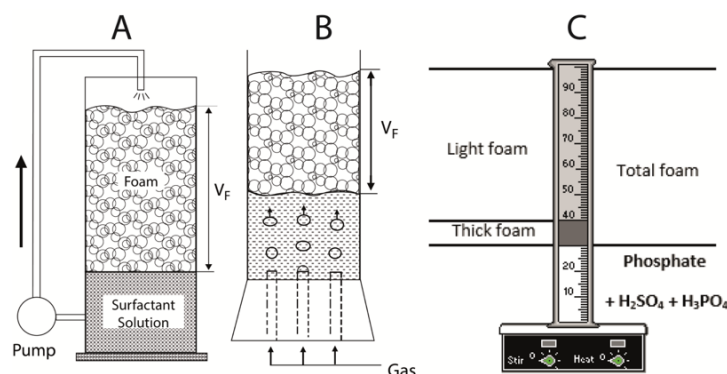


Fig. 4. Typical behavior of foam

3. Results and discussion

During our tests, we were interested in studying the foamability during the manufacture of phosphoric acid by evaluating, the effect of variation in CO_2 content and Organic Matter on the formation of foams and their persistence within time (Table 2 and 3).

Table 2. Chemical compositions average of the main elements in Khouribga, Boucraa, Youssoufia phosphate

| | % P ₂ O ₅ | % C _{org} | % CO ₂ |
|----------------------|---------------------------------|--------------------|-------------------|
| Khouribga Phosphate | 29.94 | 0.18 | 6.52 |
| Youssoufia Phosphate | 30.88 | 1.92 | 8.06 |
| Boucraa Phosphate | 30.10 | 0.1 | 2.24 |

In order to have various phosphate rock qualities in term of carbonate and organic matter content, we prepared a mixture from these 3 phosphate sources that give the qualities mentioned in Table 3:

- B quality is a mixture between 50% Youssoufia phosphate and 50% Khouribga,
- E quality is composed of 50% of Khouribga phosphate and 50% of Boucraa,
- D quality is a mixture of 50% Khouribga phosphate and 50% of the mixture E,
- G quality is composed of 50% of the mixture D with 50% of the Khouribga phosphate,
- F quality is treated by leaching using solvent of Khouribga phosphate

Table 3. Contents of C_{org} and CO₂ in different qualities of phosphate

| | Quality of phosphate | % C _{org} | % CO ₂ |
|---|----------------------|--------------------|-------------------|
| A | Youssoufia | 1.92 | 8.06 |
| B | 50% A+ 50 % C | 1.05 | 7.29 |
| C | Khouribga | 0.18 | 6.52 |
| D | 50% E + 50% C | 0.16 | 5.45 |
| E | 50% H + 50% C | 0.14 | 4.38 |
| F | C treated | 0.13 | 3.3 |
| G | 50% D + 50% H | 0.12 | 3.31 |
| H | Boucraa | 0.1 | 2.24 |

The foaming tests carried out on the different qualities of phosphate led to the results shown in Fig. 5:

From the images, we noticed that:

- For phosphates A and B, we noticed that the foam is not stable, it consists of a large bubble that breaks quickly to form a foam in the form of a stage. On the other hand, we observed that for the phosphates C, D, E, F, and G, the foam consists of small stable and compact bubbles which break mechanically after a few minutes of their appearance, and finally the H phosphate which led to a mixture without foam.

From the curves of the same figure we can see that:

- On the one hand, when the phosphate is rich in OM and carbonate, precisely at the contents greater than 1% for %C_{org} and exceeds 6% for %CO₂ (as in the case of Figs. 5. A and 5B), the foam is generated in large quantities (greater than 6 cm in the case of our test), and this characterized by large bubbles that are unbreakable and stabilized by C_{org}.
- On the other hand, when the phosphate is characterized by low contents of OM and carbonates such as 0.1<%C_{org}<1, and 3<%CO₂<6 (Figs. 5E, 4F, and 5G); the foam phenomena is weak (less than 3cm), and decreases with time (less than 1cm).

But when the carbon contents are initially less than 3%, and with the existence of organic carbon which does not exceed 0.1% (the case of Fig. 5H), the foam is formed in small quantities and disappears quickly without any addition or effort.

According to Fig. 6, which gathers the foam generated for the different phosphate grades used, we can deduce that the foam decreased with time and with the nature of phosphate (carbonate and organic carbon contents). It becomes more and more stable and compact with the increase of the rate of the C_{org} and CO₂ screws towards his. The volume, size bubble, and time of disappearance for the foam released during the phosphate attack by sulphuric are directly related to the percentage of organic matter and the rate of CO₂ in phosphates.

In order to evaluate the effect of OM on foam behaviour of the phosphate, we select a phosphate samples with fixed content of carbonate and variable carbon organic content (Table 4, Fig. 7).

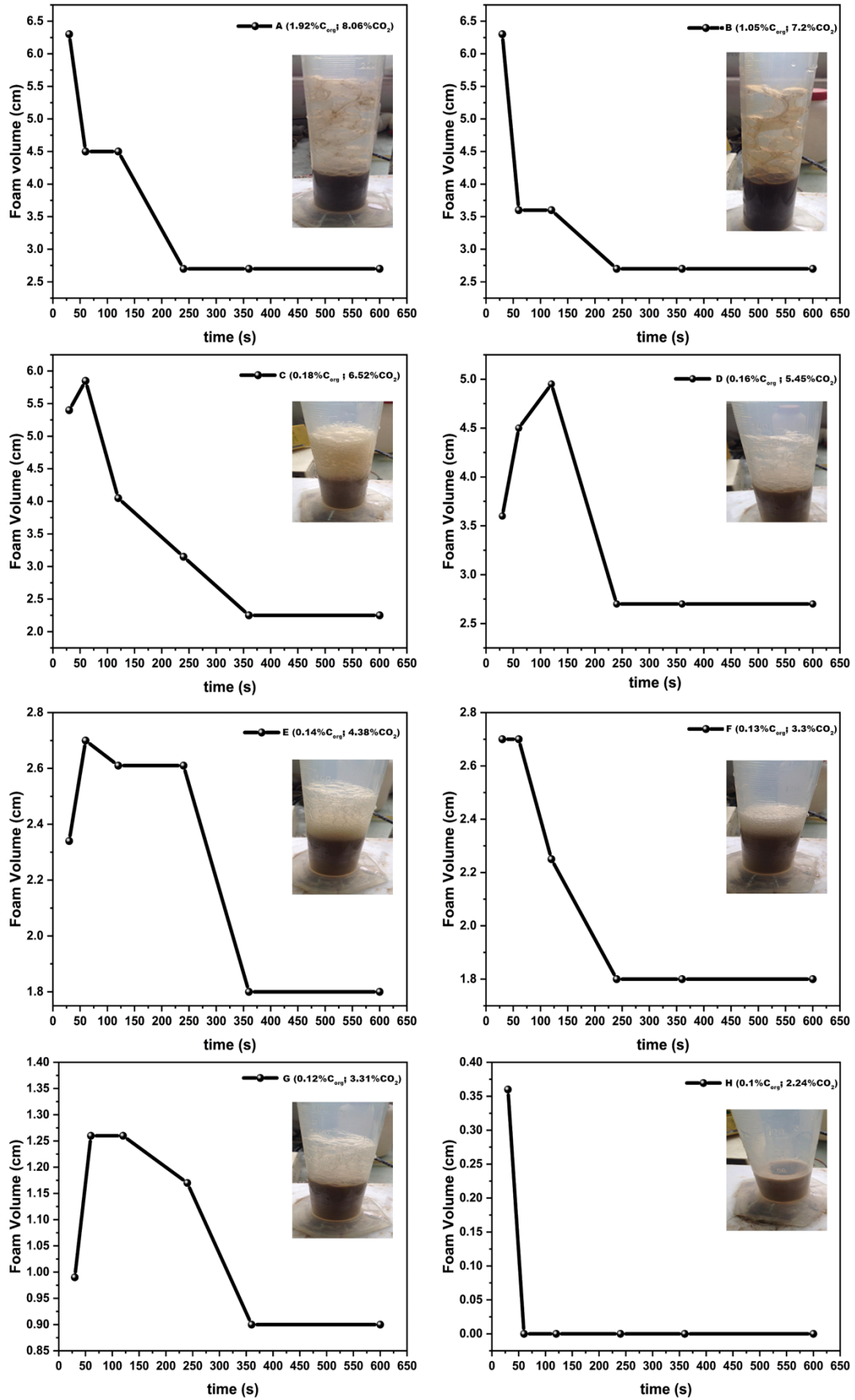


Fig. 5. Curves of the variation of the foam for different qualities of phosphates

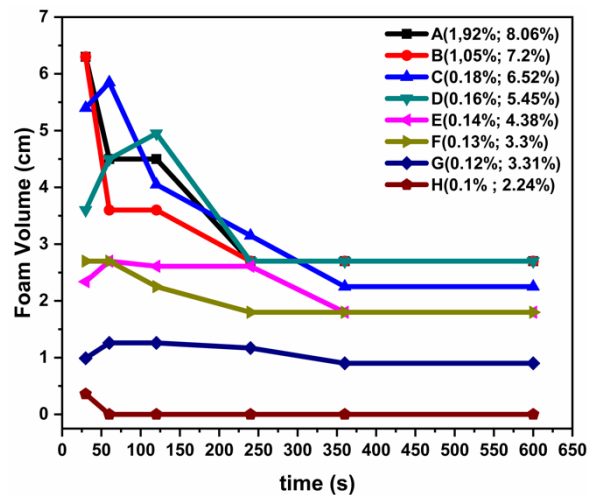
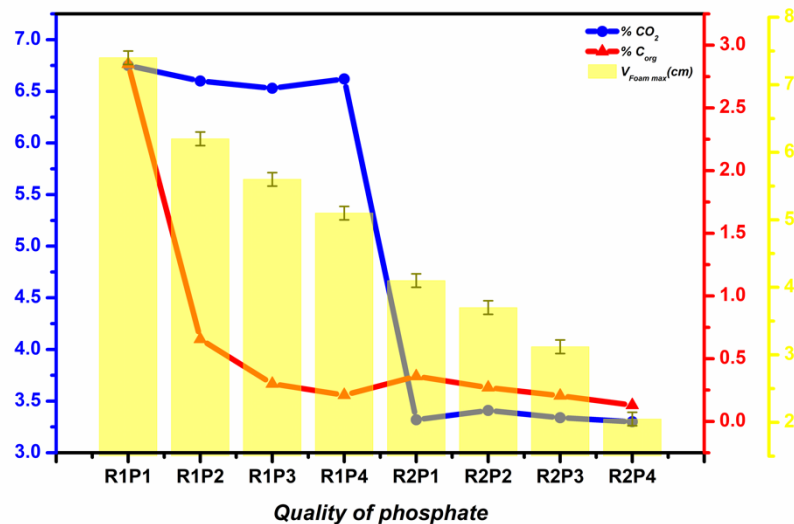


Fig. 6. Variation of the foam height for different phosphates tested

Table 4. Characteristic of the selected phosphate samples

| Range | Quality of phosphate | %P ₂ O ₅ | %CO ₂ | %C _{org} | V _{Foam max} (cm) |
|---------|----------------------|--------------------------------|------------------|-------------------|----------------------------|
| Range 1 | R1P1 | 29.9 | 6.75 | 2.85 | 7.4 |
| | R1P2 | 29.85 | 6.6 | 0.656 | 6.2 |
| | R1P3 | 29.83 | 6.53 | 0.3 | 5.6 |
| | R1P4 | 29.92 | 6.62 | 0.21 | 5.1 |
| Range 2 | R2P1 | 29.44 | 3.32 | 0.36 | 4.1 |
| | R2P2 | 29.6 | 3.41 | 0.27 | 3.7 |
| | R2P3 | 29.77 | 3.34 | 0.205 | 3.12 |
| | R2P4 | 29.65 | 3.3 | 0.13 | 2.05 |

Fig. 7. Variation of Foam volume compared to C_{org} for the same value of CO₂

From the Fig. 7, we saw that the volume of the foam generated from phosphate rock samples with same value of P₂O₅ and CO₂, decrease with the decreasing of organic carbon (% C_{org}) content. From table 4, in case of samples with CO₂ content with average of 6.62, the variation of % C_{org} in phosphate rock from 0.21% to 2.85 increase the foam volume by 45%. While, in case of CO₂ content in the average of 3.34% the volume increase by 80% when the C_{org} content increase from 2.05% to 4.1%. This confirm the direct correlation between foam generated and C_{org} content in the phosphate rock for the same content

of CO₂, also higher foam volume obtained with low CO₂ range when changing Corg content in the phosphate rock.

Surface tension measurements were carried out with a 'Dataphysics DCAT 11' brand tensiometer, according to the Wilhelmy submerged vertical blade method. As the name of this method indicates, the measurements are made using a platinum-iridium according to DIN 53914, previously flamed, suspended from the plate of a balance, and which comes flush with the surface of the tested liquid contained in a bowl. Its weight is determined when dry and then when it comes into contact with the sample. This difference in weight is equivalent to the measured force which is proportional to the surface tension (in general, if the blade has been properly cleaned, the coefficient of proportionality is 1). We carried out the experiments at 20°C, on 4 different samples from Table 4 (R1P1, R1P3, R2P2, R2P4), which we had chosen according to the volume of the foam generated during their attack. The results we obtained are listed in the following Table 5.

Table 5. Surface tension of different quality of phosphate

| Quality of phosphate | %P ₂ O ₅ | %CO ₂ | %C _{org} | V _{Foam max} (cm) | Surface tension (mN / m) |
|----------------------|--------------------------------|------------------|-------------------|----------------------------|--------------------------|
| R1P1 | 29.9 | 6.75 | 2.85 | 7.4 | 0.094±0.575 |
| R1P3 | 29.83 | 6.53 | 0.3 | 5.6 | 29.587±0.824 |
| R2P2 | 29.6 | 3.41 | 0.27 | 3.7 | 38.029±0.024 |
| R2P4 | 29.65 | 3.3 | 0.13 | 2.05 | 42.310±0.81 |

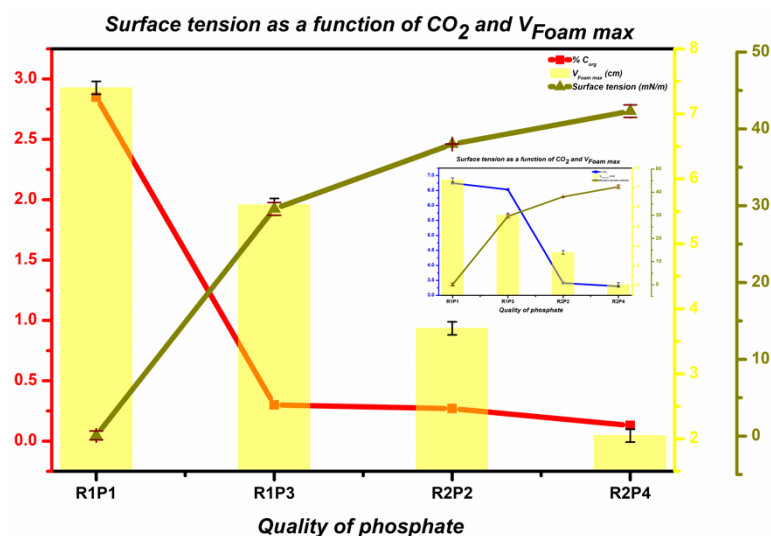


Fig. 8. Curve of the variation of surface tension as a function of C_{org}, CO₂, and V_{Foam}

It would therefore seem that the sample having high Corg and carbonate (R1P1) contents has a much lower surface tension than that characterized by low contents (R2P4). So we concluded that the presence of organic matter affects the foaming capacities of the phosphate (increases the volume of the foam or decreases it, depending on their content). These results showed that the high organic carbon content leads to a reduction in surface tension which promotes the formation of bubbles in the presence of carbonate.

From Fig. (7, 8), and Table (4, 5), we confirmed that the presence of organic matter affects the volume of the foam generated and also its stability. And in general, Foams are only dispersions of a gas in a liquid, stabilized by surfactants, which are essential for the formation and stabilization of the liquid films formed between the gas bubbles (Salager and Choplin, 2008) (Fig. 9). In our case, the % CO₂ generates bubble wish stabilized by the presence of organic matter from phosphate. It leads to the formation of emulsion then foam. In the case of foams generated from the production of phosphoric acid:

- The liquid is boiled,

- Gas is CO₂ released from apatite attack
- Surfactants are the organic matter which contains a large percentage of lipids which are hydrocarbon chains constituting the hydrophobic part.

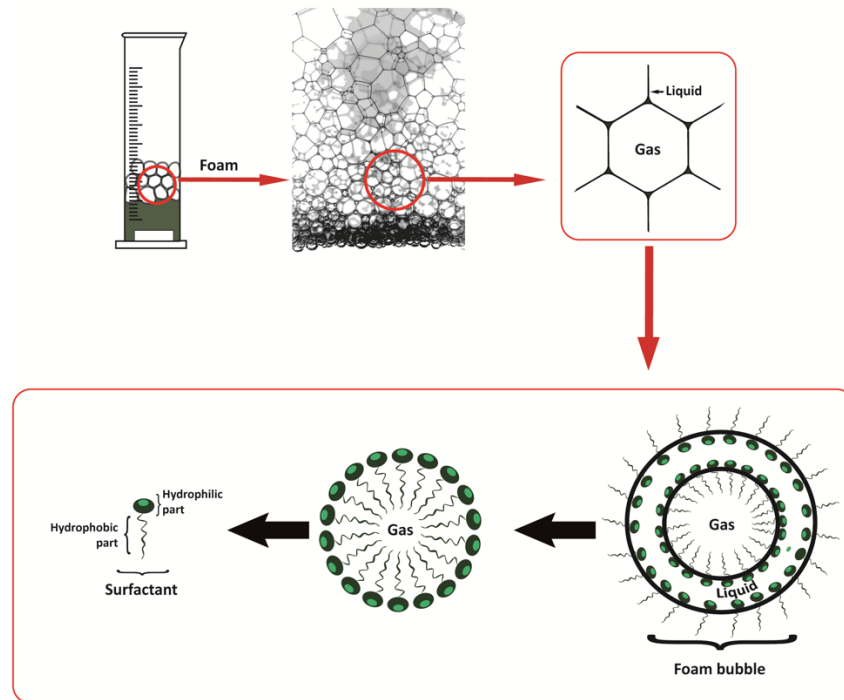


Fig. 9. Generation of foam and their stabilization by surfactants

4. Conclusions

In this work, after studying the foaming aptitude of different phosphates qualities, which showed that the volume, size bubble, and time of disappearance for the foam released during the phosphate attack by sulphuric, are directly related to the percentage of organic matter and the rate of CO₂ in phosphates, we conclude that:

The existence of the relationship between the volume of the foam generated during the manufacture of phosphoric acid and the contents of C_{org} and CO₂ in the phosphate rock.

The foamability has revealed that the volume of the foam is related to several parameters such as time, agitation, and the rate of C_{org} and CO₂, which specifies the shape, size, and nature of the bubble released during the phosphate attack by sulfuric acid.

The foamability of the phosphate rock can be controlled by controlling its contents in carbonate and organic carbon.

According to our work, we confirmed that foam generation during phosphoric acid production can be reduced or eliminated if the contents in phosphate rock are lower than 0.1% for the C_{org} and 3% for the CO₂. These conclusions allow us to draw that the volume and the nature of foam are associated with the quality of phosphate rock (precisely the contents of organic carbon and carbonate), and to reduce this problem, it is necessary to reduce these contents.

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