Treatment of Phosphogypsum Waste for Use as an Additive in the Manufacture of Cement and Ceramics

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Abstract: ***The present work aims to study the effect of two ways of phosphogypsum treatment using the organic and mineral solution to remove organic matter andP_2O_5 impregnated in phosphogypsum. The presence of these impurities in PG affect its application such as the non-dryness of the cement, i.e., the delayof setting, and the problem of tiles breakage.Actually, we carried out a solid-liquid extraction test at the laboratory scale, using an organic solution and comparing it at some time to leaching by the mineral solution method. The results obtained show that solid-liquid extraction by organic solvent improves the extraction efficiency of P_2O_5 and eliminate the organic matter without changing the crystallography structure of PG with a yield of 100%, and 47% for OM and P_2O_5 respectively.***

Keywords: Cement Industry, Ceramics, Organic Matter, P_2O_5, Phosphogypsum.

1. Introduction

The production of phosphoric acid is constantly increasing to ensure the fertilizer demand for the constantly increasing demand of the world for food [1]. The most used route for the production of phosphoric acid is that of the wet process using sulfuric acid because it is the most economically viable and allows the valuation of different grades of phosphate rock. Nevertheless, this process generates large amounts of phosphogypsum more than 140 million tons per year, of which only 5% worldwide recycled and the is sent to the sea or store in stack [2]. Valorization of this by-product by using it in cement and in the construction industry (is one of the most important trends in the field). The impurities removal process remains the most important step inphosphogypsum treatment [3]. The resulting suspension undergoes a filtration operation to separate the produced phosphoric acid from calcium sulfate dihydrate crystals thatcalled phosphogypsum. It is in the form of very fine powder with a humidity of 20 - 30% and mainly consists of calcium sulfate and syncrystallized or impregnated impurities from phosphate ore [1].

The manufacture of wet phosphoric acid involves attacking the natural phosphate ore with sulfuric acid. The main reaction is summed up in:

$$\mathbf{Ca_{10}(PO_4)6F_2 + 10H_2SO_4 + \ 20H_2O \rightarrow 6H_3PO_4 + 10CaSO_4.2H_2O + 2HF\ (1)}$$

This reaction (1), results in the formation of gypsum as a by-product. Indeed, for a ton of P_2O_5 produced, five tonnes of phosphogypsum are generated. It is estimated that around 60 million tonnes per year of the amount of phosphogypsum produced per year by the world [2].

The phosphogypsum present in the form of a very fine powder, where it is possible to distinguish different crystalline forms these crystals can be grouped into four or seven large groups according to the authors [3,4]: acicular crystals, mono dispermous tabular crystals, compact crystals, and crystals in polycrystalline aggregates, phosphogypsum has a fine to very fine particle size with a particle size distribution of less than 200 µm. The densities of phosphogypsum grains are slightly higher than those of natural gypsum (of the order of 2.32 g / cm3) according to Chang and Mantell [5], Gorlé [6], and Schaeffner[7]. For Tunisian phosphogypsum, we found slightly lower values. Schaeffner [7] also reports significantly higher values reaching 2.76 g / cm3 for some phosphogypsum from Seine-Maritime in France. This can be explained by the strong presence of impurities, the densities of which are generally higher than that of gypsum, or by the fact that phosphogypsum is in the form of a hemihydrate. Phosphogypsum is essentially composed of gypsum (75 to 78% for the dihydrate process) mixed with calcium phosphate in different forms, silica and other impurities such as oxides of iron, magnesium and aluminum, sulfides, organic matter, and traces of metals[8]. Table 1 shows the results of the analysis of phosphogypsum (dihydrate) from a common ore [9].

Phosphogypsum is mainly composed of calcium sulfate mixed with impurities such as iron oxide, magnesium, aluminum, organic matter, and traces of metals. , we find quartz and/or phyllosilicates, fluorides, phosphates, organics, and minerals of titanium, iron, and aluminum [10,11]. It contains two types of impurities such as soluble impurities; these are salts or acids, which are notremoved by washing process: mainly soluble $P_2O_5$and fluorine. These acids give the phosphogypsum a fairly low pH (generally between 2 and 4). And insoluble impurities, they come from the mineral without transformation, during the phosphoric attack (silica, unattacked ore, organic carbon, residue from the decomposition of living species that generated the phosphate, etc.); also: syncrystallized$P_2O_5$and trace elements, mainly heavy metals[12].

Many ways of recovering phosphogypsum have been explored, so the possibilities of using phosphogypsum can be separated into three categories: 3% between Application as raw material for chemical processes such as: ammonium sulphates, sodium sulphates, plastics and ceramics as well as the synthesis of ceramic glass. 70% in Application as materials especially in plaster industry, cement sector, building materials andthe utilization in road construction, and 7% of application in agriculture: as a fertilizer, for the rehabilitation of saline soils as well as for the improvement of the subsoils of acidic soils loaded with ammonium[15]. The construction industry is one of the most important industries in the world, it is growing in all countries and it finances several research projects on the development of new materials. It is therefore the most interesting recovery sector from an economic point of view. In addition, it could, on its own, absorb all annual production and eliminate the long-term storage of these tailings. In comparison, the amounts that could be used for agricultural applications are much less and will only ever represent a small percentage of the total phosphogypsum production [13,15].

For its use in various fields, phosphogypsum requires treatment to remove or neutralize various harmful impurities. Conventional treatments based on a simple washing are used to remove soluble impurities. However, syncrystallized impurities require specific treatments often inducing consequent modifications of the phosphoric acid production facilities and / or post-filtration units. It is at the level of the latter that the treatment of phosphogypsum takes place since the modification of the manufacturing process is very expensive. This work takes stock of the study and treatment of phosphogypsum by two methods. The first is to based on a solid liquid extraction using an organic solvent in the presence of an extractant (E36) that allows us to extract two solutes; organic (OM) and inorganic (P_2O_5) in aqueous solution. the second one is by acid leaching based on an acidic solution (sulfuric acid) to remove organic matter and reduce the percentage of P_2O_5. A comparison of the removal efficiency of organic carbon and $P_2O_5$was established to choose the best process necessary for the phosphogypsum upgrading.

2. Materials and methods

2.1 Materials

2.1.1 Characterization of phosphogypsum

In our experiments, we used phosphogypsum fordifferent tests of treatment. The phosphogypsum used is obtained from the attack of the phosphates by sulfuric acid according to a process of attack and dehydrated crystallization of the gypsum. For the characterization of phosphogypsum, knowledge of several parameters is required to identify and quantify the phases present. To do this, an operative process using several characterization techniques is proposed.

In one hand, plasma induction mass spectrometry has been used for the chemical characterization of existing elements. On the other hand, the quantities of total phosphorus were measured thanks to specific electrodes, as well as the Organic Carbon content which was determined by the TOC method (analysis of Total Organic Carbon). The main purpose of this analysis is to determine the amount of carbon present in the samples, which was difficult to confirm by X-ray diffraction because the carbon peaks are the same as in quartz. Besides, it was also impossible to determine its presence using X-ray microanalysis of a scanning electron microscope, due to the presence of the carbon pellets (they act as a weld between the sample and the sample holder). It was, therefore, necessary to resort to analyzes of total carbon and total organic carbon, to determine the presence and quality of carbon in the phosphogypsum. The chemical composition of phosphogypsum is reported in Table 1. From this table, we can see that phosphogypsum is formed mainly of 32% CaO and 46% SO_3, plus impurities which are mainly: fluorine (F), - silica (SiO_2), and 1.52% phosphorus.It can be seen that the organic carbon value is about 1.2%. The Corg comes largely from the portion of the residue not removed from the starting phosphate ore. And this may explain the black color and metallic texture of the sample as for its physical qualities.

Scanning electron microscope is also used, it constitutes an additional means to validatetheother results of twoprevious techniques. Indeed, it allows an approach at the microscopic scale with visualization of the texture, shape, and size of crystallites. It can also highlight the different minority phases, using X microanalysis, not detectable by X diffraction. For analysis with a scanning electron microscope with a Tecnai G2 120 kV microscope, the powders were sprayed onto small carbon pellets, stuck on sample holders.
The figure 1and 2; gives an overview of the shape and level of organization of crystals. The photograph of the figure made it possible to visualize the physical structure of the phosphogypsum and to qualitatively assess the size of its grains. It can be observed that the particle size of the sample is well spread with particles between 1 µm and 500 µm. Smaller particles may be present. It can be noted that the crystal morphology is of the tabulartype of different sizes, oriented randomly[1,3,8].The figure 3, shows that the SEM-EDX analysis of the composition of the phosphogypsum helped us to identify that the PGcontains various elements such as Ca, S, O, P, and Carbon (figure 3).

Table 1: Chemical compositions of the main elements of phosphogypsum

Elements	CaO	SO_3	F^-	SiO_2	Na_2O	$\mathbf{P_2O_5}$	$\mathbf{C_{org}}$
%	32.2	46.1	3.5	0.93	0.51	**1.52**	**1.2**

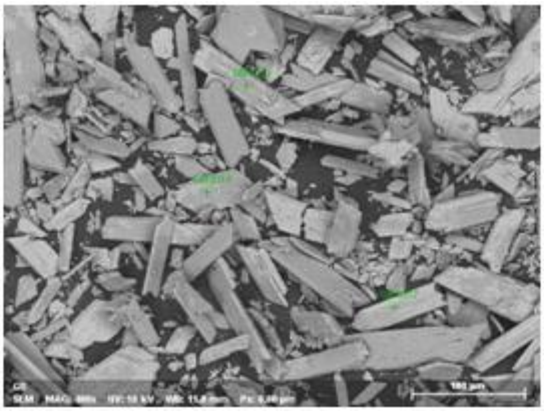


Figure 1: SEMphotomicrograph of phosphogypsum with 400 magnification

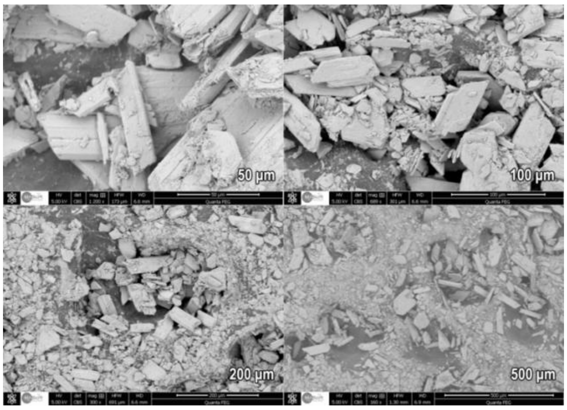
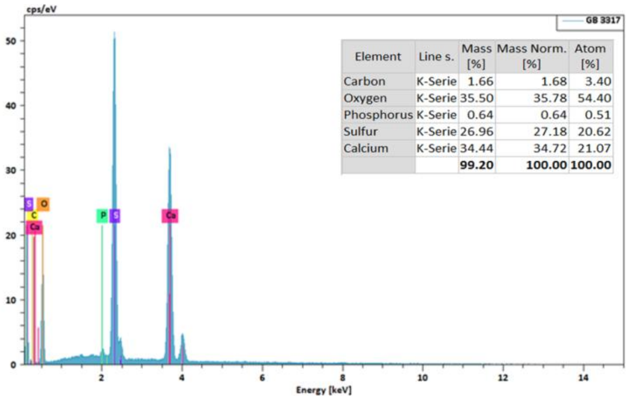


Figure 2: SEMphotomicrograph of phosphogypsumat different magnification



Element	Line s.	Mass [%]	Mass Norm. [%]	Atom [%]
Carbon	K-Serie	1.66	1.68	3.40
Oxygen	K-Serie	35.50	35.78	54.40
Phosphorus	K-Serie	0.64	0.64	0.51
Sulfur	K-Serie	26.96	27.18	20.62
Calcium	K-Serie	34.44	34.72	21.07
		99.20	**100.00**	**100.00**

Figure 3: Elemental composition of phosphogypsum measured by EDX-MEB

Thermal analysis methods for solids (DSC, TGA) are complementary 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).Figure 4 shows the thermogravimetric analysis curve of phosphogypsum. According to the curve TGA of the sample, two stages of weight loss were observed. The first weight loss occurs from ambient temperature to 150°C whose peak is located towards 80°C and can be attributed to the departure of moisture. The second weight, Weak exothermic phenomenon which starts around 200°C and is spreading out until 600°C probably due to the combustion of the Organic Matter.

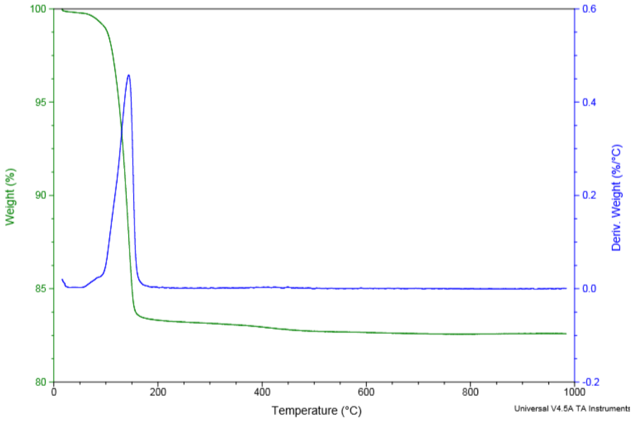


Figure4: Elemental composition of phosphogypsum measured by EDX-MEB

The particle size distribution of phosphogypsumwas carried out by Granulomètre Malvern Mastersizer 2000, and the results are shown in Figure 5. The particle size distribution of the sample particles of this PG, contains 14.92% below 37 µm. Most of the particle size (95.3%) is between 70 and 900 microns.And figure 6, shows that the phosphogypsum generated during the production of phosphoric acid has a specific surface area towards the15,4012 m²/g, Pore Volume of 0.020257 cm³ / g, and pore size 5.1519 nm.

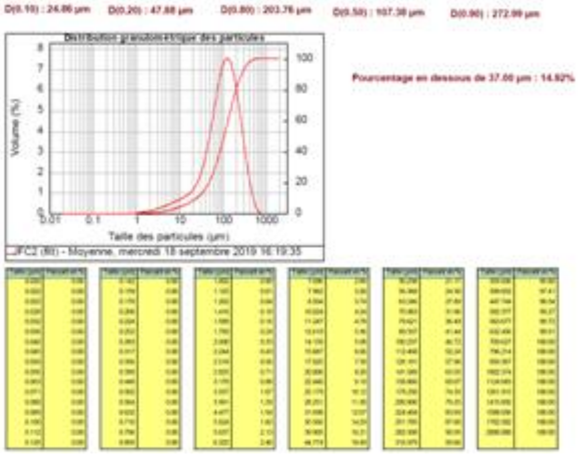


Figure 5: The particle size distribution of particles

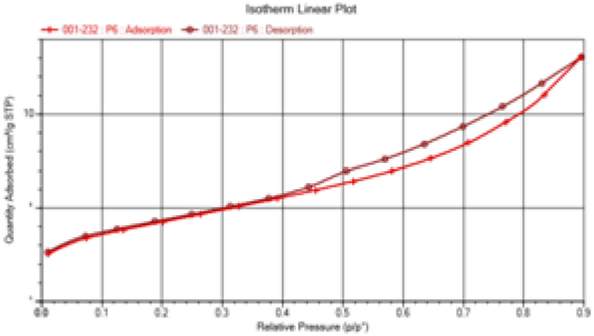


Figure 6:PG adsorption and desorption phase

2.2 Methods

The phosphogypsum treatment tests are carried out on a laboratory scale using the following equipment: Double-walled reactor, Thermostat bath to regulate the temperature, Stirrer motor to ensure the homogenization of the mixture, and Filtration bench for the separation (S /L). The experimental parameters taken into considerations in our tests are :

*Temperature: Raising the temperature usually increases the solubility, diffusivity of the solute, and decreases the viscosity of the solution. The various investigations were carried out in the range of 25 - 60 ° C. The upper limit is set by the risk of extracting harmful compounds, the corrosion resistance of the materials used, and, in some cases, by the safety of the installation (risk of explosion).

*Degree of agitation: The mechanical agitation of the particles in the solvent allows them to be kept in suspension and the homogenization of the medium and always has a favorable effect on the operation. This parameter is expressed as a relative solvent-particle velocity or surface velocity.

*Solid/liquid ratio: The solubilization in a two-phase medium of a species in a solid phase depends on the solid/liquid ratio. Therefore,to obtain the maximum solubilization,we optimized our work with a ratio equal to 20%.

*Dwell time: Depending on the kinetics of the reaction, the solubilization of a species requires a more or less long time. Optimization of the residence time is therefore of the utmost importance [16].

3. Results and discussion

3.1 Treatment by solid/liquid extraction

To complete H. El-Didamonywork [16], were carried out ~~a~~ series of experiments, using kerosene as an organic solvent (diluent), in the presence of the different concentration of extraction agent E36. Table 2 represents the different factors studied. One can note that each given factor, a low level (-), and a high level (+) have an impact on the efficiency of the process. Table 3 presents the experimental plan adopted as well as the various observations noted during the tests.

Table 2: The levels of factors used in treatment

N°	Factor	Unit	Level (-)	Level (+)
1	Temperature	°C	25	60
2	Concentration	g/l	5	10
3	Dwell time	h	2	4

Table 3: Organic solvent treatment process with existing extractant E36

N° tests	Temperature (C°)	Dwell time (h)	The concentration of extractant (g/l)	Observation
1	25	2	5	Gray cake
2	60	2	5	White cake
3	25	2	10	Gray cake
4	60	2	10	White cake
5	25	4	5	Gray cake
6	60	4	5	White cake
7	25	4	10	Gray cake
8	60	4	10	Gray cake

Figure 7.A and 7.B represent the removal efficiency in terms of% P_2O_5 and% OM respectively. From figure 7.A, it can be seen that theP_2O_5 elimination yield is maximum for the high levels of the various factors. It can be concluded, that the optimal conditions for the elimination of P_2O_5 are a temperature of 60 °C, a ten-gram per literas the concentration of the oxidant during 4 hours. According to figure 7.B, we notice that to have a maximum elimination of theOM, we need only to use 5% of extractant, at 60 °C for 2 hours. Under these conditions, all of the organic matter is eliminated (figure8).

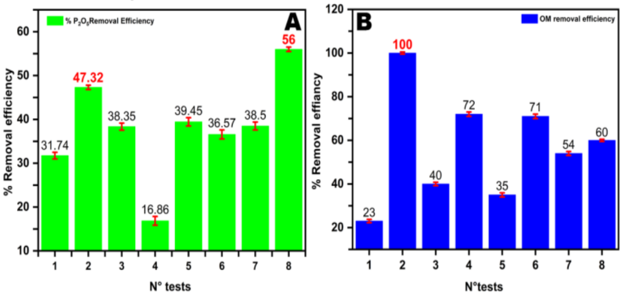


Figure 7:P_2O_5 and OM removal efficiency by organic solvent

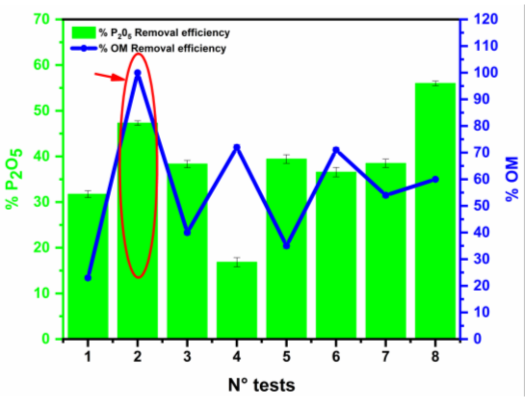


Figure 8:P_2O_5 and OM removal efficiency at different conditions

3.2 Acid treatment

An experiment was performed to investigate the effect of acid treatment on the removal efficiency of OM and $P_2O_5$from PG. The choice of sulphuric acid with a low concentration was optimized by its removal efficiency, and its costs [17]. One type of oxidant dissolved (almost 2%) in sulfuric acid experimented. The processes were carried out at: room temperature (25 °C); contact time = 2 h; solid: liquid ratio = 20% . The results were graphically presented in Fig. 9. By the addition of sulfuric acid, the removal efficiency of OM reach 100%, and of P_2O_5% exceed 55%.

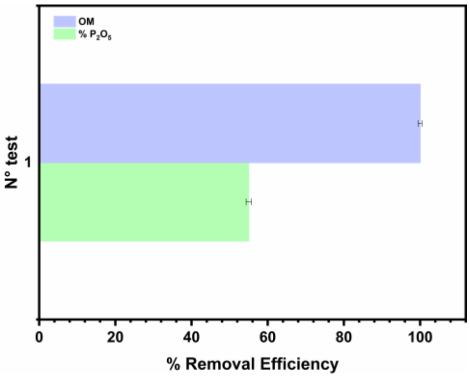


Figure 9:OM and P_2O_5 removal efficiency by acid treatment

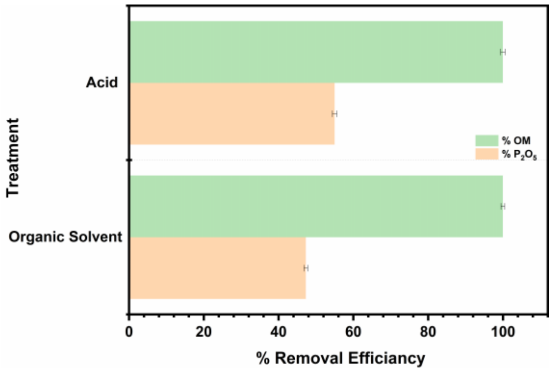


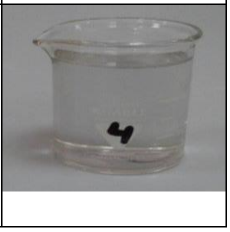
Figure 10: Comparisons between removal efficiency by acid treatment and solvent extraction

According to our results (presented in figure 10). we note that the two treatment routes have the same efficiency of elimination of organic matter and decreaseof the P_2O_5. We recommend the treatment of PG with an organic solvent, and under our founded optimal experimental conditions.The choice is reinforced by the fact that the mineral solution reacts with the phosphogypsum cake by changing its crystallographic structure, however, the organic solvent does not change anything, and it is easy to recycle.

3.3 Recycling of Organic Solvent

To reutilise the organic solvent in other process,we need to use an activated carbon. In various measuring beakers of 250 ml, a quantity of 160 g of the charged solvent, with an approximately 16 g of the activated carbon (solid/liquid ratio equal to 10%) at room temperature and a mixing of 30 min. Finally we filterit and undergo it through UV-Visible to measure the percentage of organic matter (Table 5).

Table 5: Solvent after and before filtration with activated carbon

	Before Filtration	After Filtration
% OM	0.4%	0.0001%
Visual comparison		

4. Conclusion

In the present work, we developed a new technique of for phosphogypsum treatment namely the liquid-solid extraction, using an organic solvent. We compared this new approach, with a leaching in mineral solution one. Based on the results of this work we were able to summarize that Liquid solid extraction of PG using extractants with the presence of an organic solvent (kerosene as a diluent), improves the efficiency of total OM removal and decreases the existing of P_2O_5 content. The removal efficiency expects 100% and 55% for MO and P_2O_5 respectively. As a conclusion we can say also that,the best kerosene treatment conditions are: the use of five gram per liter at 60 ° C, with a stirring time of two hours, and a solid: liquid ratio of 20%. The treatment of phosphogypsum by leaching with a mineral solution (20% sulfuric acid) allows us to extract 55.9% of P_2O_5 and 100% of the organic matter under the following conditions, ambient temperature and a residence time of 2 hours. Finally, to obtain the best performance and ensure that the structure of the phosphogypsum does not change, we must use this new technology - solid-liquid extraction - instead of leaching with the mineral solution.

5. Conflicts of interest

The authors declared that there are no conflicts of interest.

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