GRADIVA

Volume 63 | Issue 03 | March 2024
DOI: 10.5281/zenodo.10873901

Enhancing Djebel Onk Black Phosphate Processing Parameters for Phosphoric Acid Production

B. Benouis [1]*, H. Boutefnouchet [2], Z. Djemai [3] & B. Amara [4]

1. Laboratory of Mining, Metallurgy and Materials (L3M), National school of mining and metallurgy (ENSMM)
Amar Lakri, Annaba, Algeria. *Corresponding Author Email: bornia.benouis@univ-annaba.dz
2. Laboratory of Foundry Research (LRF), University of Badji Mokhtar, Annaba, Algeria.
3. Entreprise d'Exploitation des Mines d'or, Tamanrasset, Algeria.
4. Djebel Onk Mining Complex, SOMIPHOS Bir El Ater, Tebessa, Algeria.

Abstract

The objective of this study is to evaluate the potential behaviour of black phosphate in the production of phosphoric acid. A qualitative comparison of the two phosphates (black and beige) from Kef Essenoun de Djebel Onk was carried out during the first part of this study, with the aim of defining the differences between the two types of phosphate. Phosphate is the most widely exploited mineral currently, and is completely devoid of organic matter. In the second part, the studies focused on black phosphate samples ground to two particle sizes, 100 and 80 µm, in order to define the effect of grinding on the quality of the chemical composition of the ore to be etched. Etching parameters, such as phosphate flow rate, were adjusted. The effect of overflowing the tank was also considered.

Keywords: *Phosphoric Acid, Black Phosphate, Immersion Time, Etching Attack, Organic Matter, Dihydrate Process.*

INTRODUCTION

An essential chemical intermediate in the production of phosphate fertilisers is phosphoric acid. Generally, it is prepared by processing phosphate rock with sulphuric acid. The world production of phosphoric acid is around 30 million tonnes of P2O5, almost 90% being used in the fertiliser industry [1, 3]. As part of the production process, calcium sulphate (gypsum) is separated from the phosphoric acid by filtration, as are the other by-products of the reaction [4].

The phosphoric acid production process requires complex interactions between solid and liquid constituents, which are governed by a number of parameters including mineral characteristics, particle size, reagent composition, etching time and temperature conditions [5].

Algeria has significant phosphate deposits, particularly at Djebel Onk. The latter is composed of two distinct types of ore, which can be identified mineralogically, granulometrically and chemically [6, 7].

Dark colours indicate the presence of organic compounds. The presence of organic matter during the preparation of H_3PO_4 by etching with H_2SO_4 can lead to a number of drawbacks and complications, including the formation of undesirable compounds such as sulphur-containing hydrocarbons, volatile carbon compounds and various other decomposition products that can render phosphoric acid unsuitable for certain applications by reducing its purity and quality [8]. The presence of organic matter can reduce the reactivity of the etching solution and have a significant impact on phosphate yields. The presence of organic matter with sulphuric acid, when the reaction is slow, can lead to the sudden formation of gases such as carbon dioxide

(CO_2), sulphur dioxide (SO_2) and other volatile compounds, which will be trapped in the etching solution, leading to the formation of foam or froth. This increases the risk of the etching tank overflowing due to the increased liquid volume and reduced tank capacity [9, 10]. Therefore, if foams are not properly controlled, they result in tank overflow.

A number of studies have been carried out into the use of Algerian phosphate in the production of phosphoric acid, but none has experimentally investigated the problem of overflow from the etching tank during the preparation of phosphoric acid.

The aim of this study is to investigate the possibility of using Kef Essenoun black phosphate, which has until now been used as a second choice material after beige phosphate due to the presence of organic matter, for the development of Algeria's phosphate ore beneficiation megaproject.

Based on these considerations, this study first presents the chemical and physical characteristics of the two Algerian phosphates: black and beige, in order to indicate the similarities and differences that justify the choice of the ore selected as the subject of this study.

The second objective is to present an economic and practical study on the processing of black phosphate to obtain phosphoric acid, i.e. the granulometry of the phosphate as a function of the grinding time and the prevention of overflowing solutions during processing as a function of the sulphuric acid attack time.

THEORY

The basic reactions for the preparation of phosphoric acid, which result from the acidification of phosphate concentrates (1-3), are generally presented as follows [11, 12].

$$\mathbf{Ca_3(PO_4)_2 + 6H_2O + 3H_2SO_4 \rightarrow 2H_3PO_4 + 3(CaSO_4, 2H_2O)} \quad (1)$$

$$\mathbf{3CaF_2 + 3H_2SO_4 + 4H_2O + SiO_2 \rightarrow H_2SiF_6 + 3(CaSO_4, 2H_2O)} \quad (2)$$

$$\mathbf{CaCO_3 + H_2SO_4 + H_2O \rightarrow CO_2 + CaSO_4, 2H_2O} \quad (3)$$

The result is exothermic reactions and the formation of products, which then pass into solution before crystallising. There are two main phases:

- A liquid phase, an aqueous solution of phosphoric acid
- A solid phase, consisting of calcium sulphates.

Depending on the etching operating conditions, the calcium sulphates precipitate obtained may be a $CaSO_4, 2H_2O$ dihydrate or a $CaSO_4, 1/2H_2O$ hemihydrate. The phosphoric acid solution is then concentrated by evaporation [13].

The wet process for producing phosphoric acid from phosphate rock comprises various stages, as illustrated in Figure 1.

Volume 63 | Issue 03 | March 2024
DOI: 10.5281/zenodo.10873901

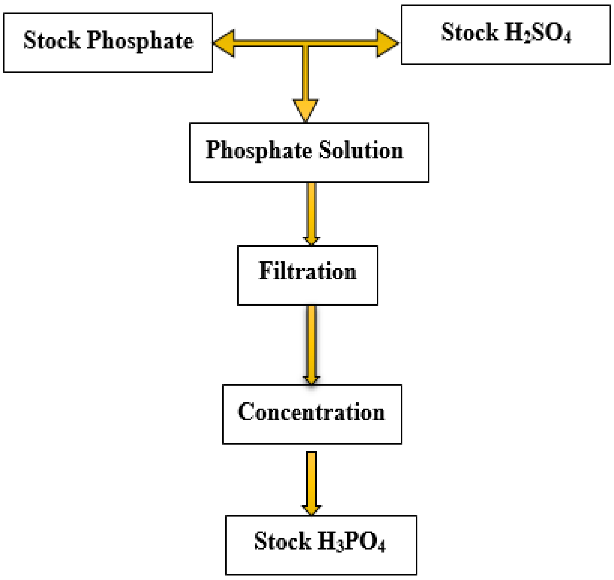


Figure 1: Phosphoric Acid production stages [14]

Experimental Procedure

Two types of phosphate, black and beige, are extracted from the Kef Essenoun ore deposit. Phosphoric acid is produced by extracting phosphate rock, which is then finely ground to a particle size below 500 µm. A wet process according to the process « dihydrate » produces the acid. Figure 1 gives a general description of the process [15]. However, it refers exclusively to black phosphate.

The production of phosphoric acid using black phosphate involves the extraction of phosphate rock, which is ground to obtain particle sizes of 100 and 80 µm. The phosphate used has a 30% P_2O_5 grade. It has an apparent density of 1.6 g/cm^3 and a moisture content of 0.8%. The sulphuric acid used is 98% H_2SO_4 and has a specific gravity of 1.84. The water used for washing is distilled water.

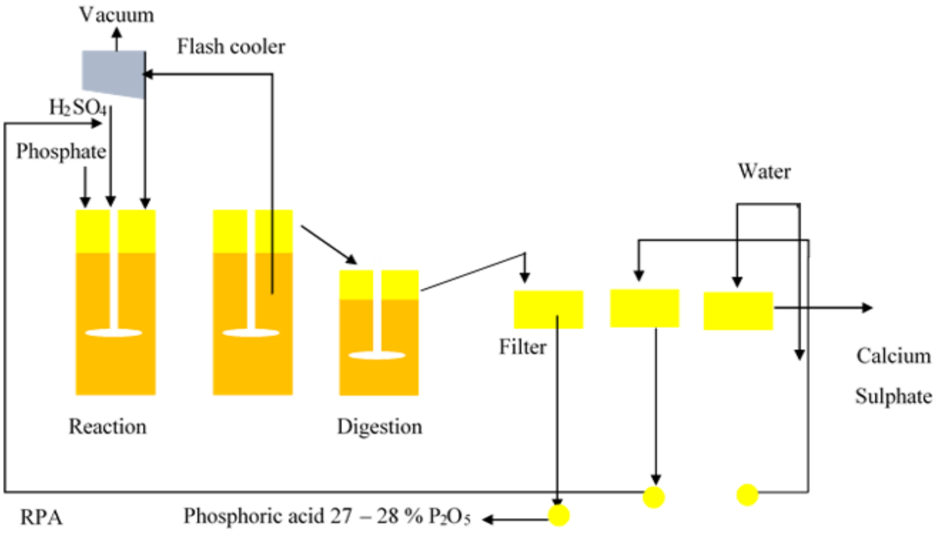


Figure 2: Production of phosphoric acid by dihydrate process according to T. Theys *et* al. [15]

Volume 63 | Issue 03 | March 2024
DOI: 10.5281/zenodo.10873901

The raw materials and quantities required to produce 1 kg of H_3PO_4 are presented in Table 1.

Tableau 1: Raw materials and process operating conditions

Material	Quantity
Phosphate	2.8 à 3.8 Kg
Sulphuric acid (H2SO4)	2.5 à 2.85 Kg
Process ater	5 à 7 L
Cooling water	30 à 50 L
Low - pressure process steam	0.3 à 2.2 Kg
Electrical energy	110 à 180 KWh

The slurry generated by the acid attack goes through flat vacuum filters in order to separate the solids (gypsum) from the liquid (phosphoric acid).

Then the acid is heated to its boiling point, which is between 120°C and 150°C, under a pressure ranging from 80 to 150 mbar.

RESULTS

Mineralogical analysis by X-ray diffraction

The X-ray diffraction results for the two raw phosphates, beige and black, are shown in Figure 3. These results show a similarity in phase composition in terms of the main minerals, such as phosphate minerals ($Ca_5(PO_4)_3F$, $Ca_5(PO_4)_{2.5}(CO_3)_{0.5}F$) and $Ca_{10}(PO_4)_5(CO_3)_3(OH)_2$) and dolomite ($CaMg(CO_3)_2$). These results are in good agreement with the literature [16-19]. According to a study by N. Bezzi et al [7] carried out on Djemi-Djema black phosphate (another Djebel Onk deposit), after acid etching, the ore revealed, in addition to the main phosphate components, the presence of minute quantities of potassium feldspar, montmorillonite and clays. According to the same authors, these clays combined with haematite give the phosphate its black colour, whereas other authors believe that it is organic matter, which gives the phosphate its black colour.

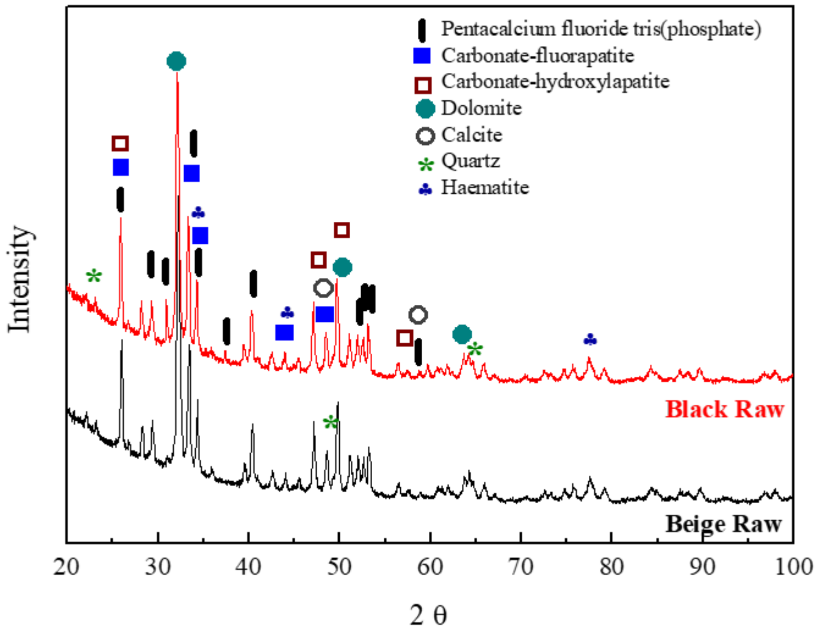


Figure 3: X-ray diffractogrammes of beige and black raw phosphates

Volume 63 | Issue 03 | March 2024
DOI: 10.5281/zenodo.10873901

Scanning electron microscopy analysis

The observations in SEM of the two samples of beige and black phosphates (Figure 4) reveal in the first place the presence of the principal phosphate minerals required [16] and in the second place a similarity in the size and shape of the grains of the two phosphates. On a larger scale, fine particles are observed in both microstructures. Bezzi et al [7] attribute the presence of these fine particles to the organic matter that characterises black phosphate, but the presence of these fine particles in beige phosphate does not suggest that these fines are due to organic matter. The presence of organic matter in black phosphate is subsequently confirmed by additional tests, although it is likely to be composed of dolomite, calcite, quartz, feldspar and eventually of gypsum [17].

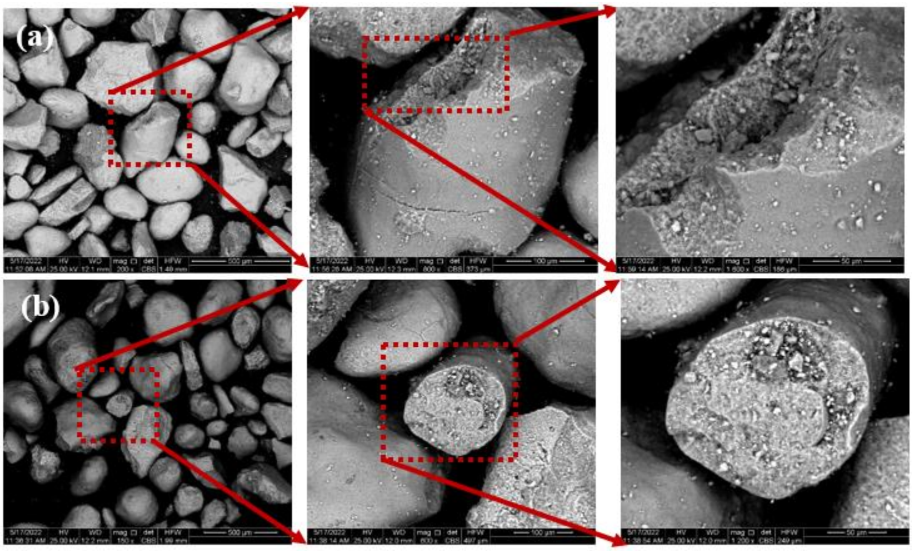
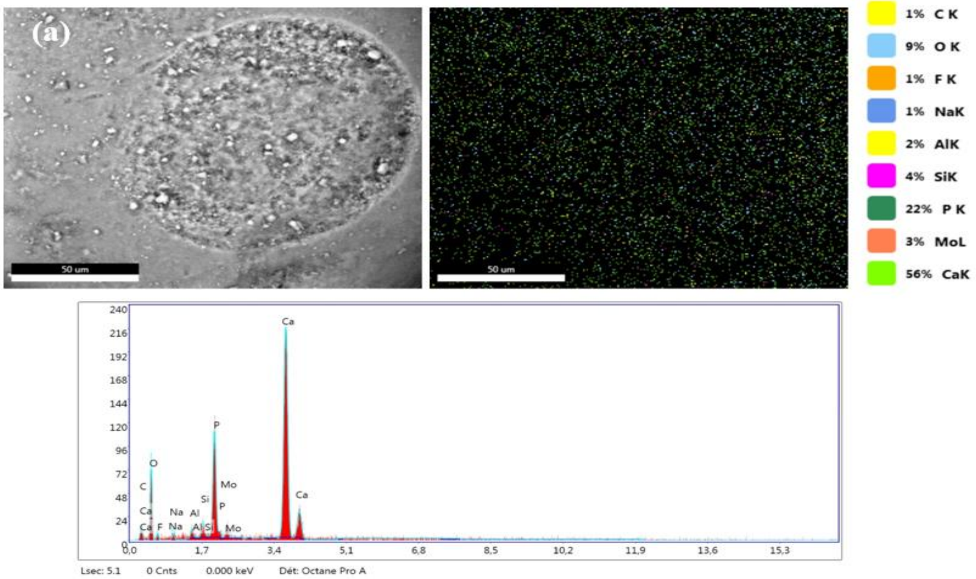


Figure 4: SEM microscopic observation: (a) black raw phosphate sample (b) beige raw

The Energy Dispersive X-Ray Analysis (EDX) presented in figure 5, shows the presence of a tiny quantity of carbon in the black phosphate (figure 5.a), which suggests the presence of organic matter in the phosphate.



Volume 63 | Issue 03 | March 2024
DOI: 10.5281/zenodo.10873901

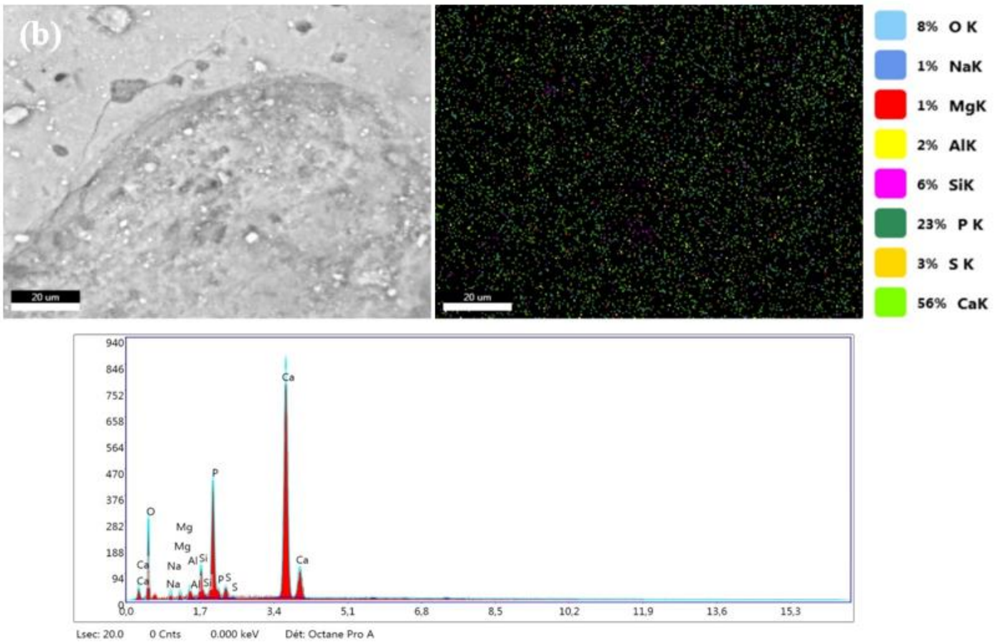


Figure 5: SEM microscopic observation: (a) black raw phosphate sample (b) beige raw phosphate sample

Thermal analysis: GTA- DTA

In this test carried out on black phosphate, thermal behaviour is analysed using GTA and DTA to determine the temperature and operating conditions. Figure 6 illustrates the principal transformations that take place during heating.

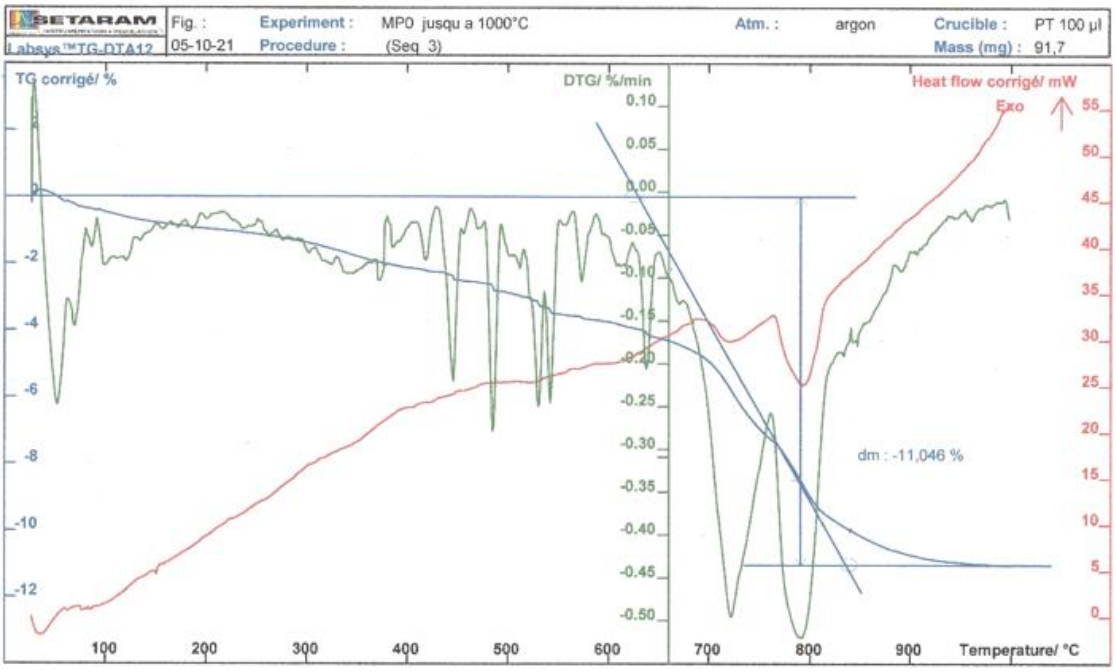


Figure 6: GTA – DTA Thermogramme of black phosphate

The corresponding GTA graph indicates four major mass losses due successively to:

- The first concerns the removal of physisorbed water (moisture) between 100 and 120°C.
- The second is attributed to the decomposition of the water of crystallisation and organic matter between 350 and 480°C
- The decomposition of the carbonates of the exogangue between 530 and 620°C.
- The decomposition of carbonates from the endogangue between 710 and 830°C.

These data elements suggest that the elimination of CO_2 is not instantaneous, but takes place progressively during heating. According to previous work [17], the slow elimination of apatitic CO_2 extends beyond 840°C to 1000°C. The DTA graph shows endothermic peaks attributed successively to the evaporation of physisorbed water and water of crystallisation, organic matter and carbonates from the exogangue and endogangue. The results obtained are consistent with the literature [7, 16, 17, 20, 21].

Utilisation of black phosphate in the preparation of phosphoric acid

Chemical composition of the raw material

The technical data sheet for Kef Essenoun black phosphate 63/65% BPL as established by the phosphate mining company SOMIPHOS is presented in table 2.

Table 2: Kef Essenoun black phosphate data sheet

Element	%
Phosphoric anhydride (P_2O_5)	29 - 29.50
Anhydride carbonic (CO_2)	7.2 - 7.8
Sulphuric anhydride (SO_3)	2.80 - 3.50
Calcium Oxide (CaO)	47.5 - 49.00
Magnesium (MgO)	1.20 - 1.60
Fer oxide (Fe_2O_3)	0.30 - 0.50
Aluminium oxide (Al_2O_3)	0.30 - 0.50
Sodium oxide (Na_2O)	1.00 - 1.30
Potassium (K_2O)	0.07 - 0. 15
Silicium oxide (SiO_2)	2.00 - 3.00
Humidity (H_2O)	0.80 - 2.00
Fire loss (excluding CO_2)	4.00 - 8.00
Fluor (F)	2.50 - 3.50
Chlorine (Cl) in ppm	500 - 900
C-Org	0.20 - 2.00
P_2O_5 soluble in citric acid at 2%.	9.00 - 11.0
P_2O_5 soluble in formic acid at 2%	18.00 - 21.00

I. Before Attack

The black ore is ground to an appropriate particle size, previously fixed at 80 µm. The coarser particle size is chosen to minimise grinding time and thus reduce energy consumption. The ore grinding results are shown in the following table:

Table 3: Phosphate ore after grinding

Size (µm)	Chemical composition (%)												
	P_2O_5	CO_2	CaO	MgO	Fe_2O_3	Al_2O_3	Na_2O	K_2O	SiO_2	F	C-Org	H_2O	LOI
80	30.20	6.0	50.13	0.95	0.35	0.45	1.20	0.10	2.30	3.65	0.20	1.00	2.50
100	29.80	6.9	49.50	0.95	0.35	0.40	1.19	0.09	2.60	3.65	0.15	1.00	2.75
Trace Elements (ppm)*										Bulk phosphate density			
Cl		Zn		Cu		Pb		Cd		1.6			
350		145		30		15		18					

* Values obtained in the two samples analysed.

Volume 63 | Issue 03 | March 2024
DOI: 10.5281/zenodo.10873901

These results show that for a particle size of 100 µm the component content is basically the same. The P_2O_5 content, as the principal component, is significantly lower than that of the sample with a particle size of 80 µm, the difference being only 0.4 %.

During processing, the two samples analysed underwent a sulphuric acid attack with phosphoric acid from the bottom of the tank as a recycling (reuse) agent, the composition of which is shown in Table 4.

Table 4: Phosphoric acid from the tank bottom (the two samples analysed)

Element (%)		Density
P_2O_5	SO_3	1.16
15	38	

II. After attack

The qualitative analysis of the phosphoric acid (H_3PO_4) obtained after etching the two samples (80 and 100 µm) is presented in Table 5.

Table 5: Quality of phosphoric acid after etching with H_2SO_4

Acid Phosphoric Quality (H_3PO_4)														
Duration attack (mn)	80 µm							100 µm						
	V_{Min} (g/mn)	V_{Aci} (ml/mn)	Element				ρ (g/cm^3)	V_{Min} (g/mn)	V_{Aci} (ml/mn)	Element				ρ (g/cm^3)
			(%)			ppm				(%)			ppm	
			P_2O_5	MgO	SO_3	Cd				P_2O_5	MgO	SO_3	Cd	
180	6.0	2.6	30.1	0.70	1.87	17	1.35	6.0	2.6	28.7	0.9	2.75	17	1.27
150	7.3	3.1	29.7	0.70	1.95	17	1.30	7.3	3.1	28.0	0.9	2.75	17	1.25
120	9.1	3.9	29.0	0.75	2.0	17	1.25	9.1	3.9	27.5	0.95	2.80	17	1.24
90	12.1	5.2	28.8	0.90	2.20	17	1.20	12.1	5.2	27.0	0.95	2.85	17	1.23
60	18.1	7.7	27.9	0.95	2.10	17	1.18	18.1	7.7	26.6	0.95	2.80	17	1.21

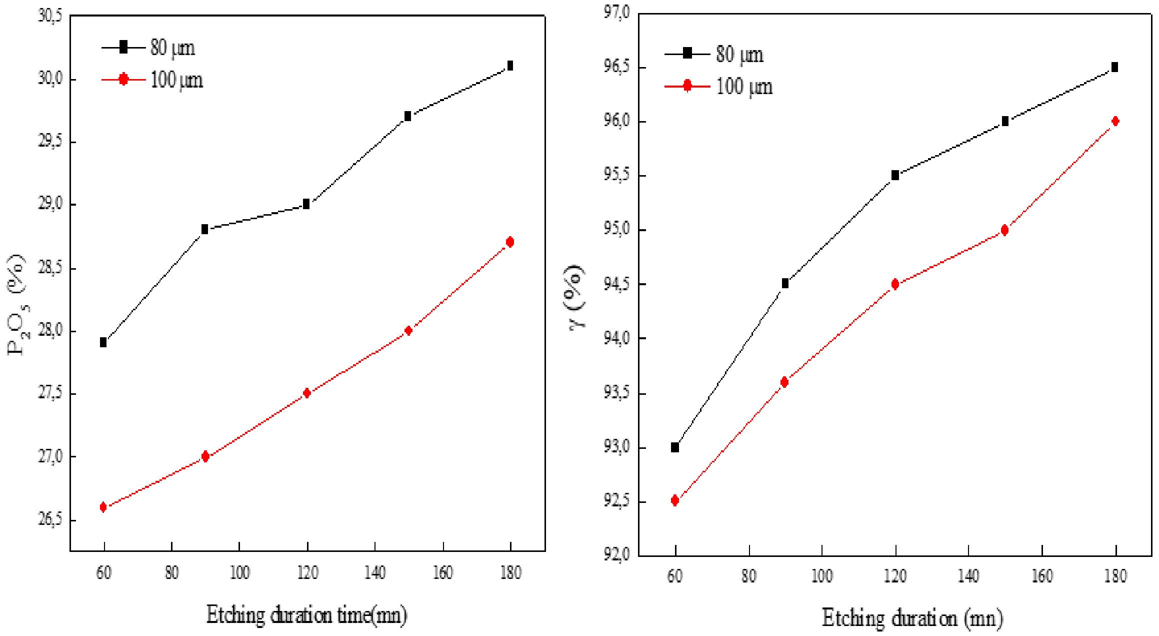


Figure 7: Attack results (a) P2O5 content (b) Yield

Table 6: Chemical analysis of phospho-gypsum obtained from the treatment process

Phospho-Gypsum analysis								
Duration attaqk (mn)	**80 µm**				**100 µm**			
	Element (%)				**Element (%)**			
	H_2O	**P_2O_5 Ins**	**P_2O_5 Syn**	**CaO**	**H_2O**	**P_2O_5 Ins**	**P_2O_5 Syn**	**CaO**
180	25.15	0.70	0.65	33.20	24.00	0.90	0.85	32.00
150	23.47	0.78	0.70	32.21	23.00	0.92	0.85	31.70
120	21.00	0.84	0.70	31.00	22.00	0.93	0.80	31.00
90	20.50	0.99	0.90	30.00	21.00	1.12	0.98	30.50
60	19.10	1.20	0.93	29.00	20.00	1.35	1.10	28.70

CONCLUSION

The objective of this investigation is to reduce the particle size of the grinded phosphate to an appropriate size so that the grinding time can be minimised and the etching operation become more efficient by improving performance and avoiding tank overflow. The effect of tank overflow is effectively controlled by adjusting the chemical etching parameters applied to the black phosphate, i.e.:

- Phosphate flow rate
- Sulphuric acid flow rate (etching solution)

The results achieved are described below:

The best yields and P_2O_5 concentrations results were observed for an immersion time of 3h00 with a particle size of 80 µm. However, the fluctuations in P_2O_5 in the phosphoric acid of ground phosphate at 80 µm (passing) and 100 µ (passing) for the selected times are not as significant, nor are the etching yields during these same periods. Overflowing of the tank was observed when both samples were etched for a period of 1 hour 00 minutes. The operating conditions in this particular case were inappropriate. The results obtained from etching ground phosphate at 80 µm (passing) and 100 µm (passing) for 1h 30 resulted in unsatisfactory yields, which leads us to consider tests involving extended etching times.

Immersion times of 2h 00 and 2h 30 for a particle size of 100µm give a high quality performance and a reduction in energy consumption. These conditions for treating black phosphate in terms of granulometry and attack time are applicable at industrial level without condition. SOMIPHOS' Kef Essenoun black phosphate accounts for more than 80% of the deposit. It is at the cause of the problems of tank overflow during phosphoric acid production and energy consumption during grinding and chemical attack. It is important to consider that the results obtained at 100 µm passing could be applied at an industrial level, since they are similar to those obtained at 80 µm (passing).

Finally, the SOMIPHOS mining company as marketing support to defend their products when faced with complaints from its phosphoric acid manufacturing customers could use these results. It should not be forgotten that this study is included in our country's strategic objective, which consists of focusing on phosphate processing and phosphoric acid production as part of a mega project.

References

1) K., Schrödter, G., Bettermann, T., Staffel, F., Wahl, Klein, T., Hofmann, “Phosphoric Acid and Phosphates”, In Ullmann’s Encyclopedia of Industrial Chemistry, Wiley, Vol. 26, pp. 679−724, 2008.

2) H., Diskowski, T., Hofmann, “Phosphorus”, Ullmann’s Encyclopaedia of Industrial Chemistry, Wiley, 2000.

3) Ms., G., Bharathi kannamma, Dr. D., Prabhakaran, Dr. T., Kannadasan, “Analysis and Simulation of Dihydrate Process for the Production of Phosphoric Acid” (Reactor Section), American Journal of Engineering Research (AJER), e-ISSN: 2320-0847 p-ISSN: 2320-0936 Volume-02, Issue-07, pp. 01-08, 2013.

4) A.B., Amin, and M.A., Larson, “Crystallization of calcium sulphate from phosphoric acid”, Ind. Eng. Chem. Process. Des. Dev, pp. 133-137, 1968.

5) P., Becker, “Phosphates and Phosphoric acid”, 2nd Ed, Chapter 8, Marcel Dekker Inc., NY, 1989.

6) S. Chabou - Mostefai, “Etude de la série phosphatée tertiaire du Djebel Onk”, Université Paul Cézanne (Aix-Marseille), Faculté des sciences et techniques de Saint-Jérôme, 1987.

7) N., Bezzi, D., Merabet, J-Y., Pivan, “ Etude comparative des minerais de phosphate noir (Djemi-Djema) et beige (Kef Essenoun) ” - Djebel Onk (Algérie). Les Techniques de l’industrie Minérale, N°19, 2003.

8) R. Gilmour, Phosphoric Acid: “Purification, Uses, Technology and Economics”, Taylor & Francis, Boca Raton, FL, Chap. 1, 2014.

9) A-A, E.A., “Industrial Simulation of Wet Process Phosphoric Acid Production”, Ph.D. Thesis, Faculty of Science, Cairo University, 1989.

10) W. H. Waggaman, “Phosphoric Acid, Phosphates and Phosphatic Fertilisers”, 2nd ed., Reinhold Publishing Corp., New York, 2002.

11) D. E. C. Corbridge, “Phosphorus: Chemistry, Biochemistry and Technology”, 6th ed., CRC Press, Inc., Boca Raton, FL, 2013.

12) Theys, T. “Influence of the rock impurities on the phosphoric acid process, products and some downstream uses”, IFA Technical Committee Meeting, 2003.

13) Leruth, H. Phos. “Acid Process Choices Fertilizer” Int. 481, 2017.

14) R. Gilmour, “Phosphoric Acid: Purification, Uses, Technology and Economics”, Taylor & Francis, Boca Raton, FL, 2014.

15) T. Theys, N. Van Lierde, A. Wareille “Water management in phosphoric acid: a processes comparaison”, 3rdInt. Symp. Innov. and Techn. In the phosphate industry, 2015.

16) N. Bezzi, D. Merabet, N. Benabdeslem, H.Arkoub, “Caractérisation physico-chimique du minera de Phosphate de Bled El Hadba - Tébessa” Ann. Chim. Sci Mat, 26 (6), pp. 5-23, 2001.

Volume 63 | Issue 03 | March 2024
DOI: 10.5281/zenodo.10873901

17) D., Merabet, N., Benabdeslam, N., Bezzi, T., Ikhlef, H., Arkoub. “Influence de la composition chimique et minéralogique du phosphate noir du gisement de Djebel Onk (Tebessa) sur le procédé de traitement”. Ann. Chim. ScL Mat., 29 (5), pp. 69-85, 2004.

18) N., Bezzi, T., Aıfa, D., Merabet, J-Y., Pivan, “Magnetic properties of the Bled El Hadba phosphate-bearing formation (Djebel Onk, Algeria): Consequences of the enrichment of the phosphate ore deposit”, Journal of African Earth Sciences 50, pp. 255-267, 2008.

19) N., Bezzi, T., Aïfa, S., Hamoudi, D. Merabet, “Trace elements of Kef Es Sennoun natural Phosphate (Djebel Onk, Algeria) and how they affect the various mineralurgic modes of treatment”, Procedia Engineering 42, pp. 1915-1927, 2012.

20) A. Z. M., Abouzeid, “Physical and thermal treatment of phosphate ores” - An overview, Int. J. Miner. Process, pp. 59-84, 2008.

21) I., Matveyeva, N., Nursapina, A., Bakhadur, S., Nazarkulova, B.r., Shynybek and O., Ponomarenko, “Simultaneous thermal analysis of mineral fertilizers, purchased in Almaty.” BIO Web Conferences 30: 02009, 2021.