Physicochemical Characterization of Moroccan Phosphate and Coke of a Solid Combustible

Ikbal Bouatba[1], M'barek Benchanaa[1], Mustapha El Hammioui[1], Latifa Bilali[1]

[1]Laboratoire de Recherche, Reactivite des Materiaux et Optimisation des Procedes: REMATOP, Faculte des Sciences Semlalia, Universite Cadi Ayyad, Avenue Prince Moulay Abdellah, B.P. 2390, 40000 Marrakech, Maroc

Correspondence: M'barek Benchanaa, Laboratoire de Recherche, Reactivite des Materiaux et Optimisation des Procedes: REMATOP, Faculte des Sciences Semlalia, Universite Cadi Ayyad, Avenue Prince Moulay Abdellah, B.P. 2390, 40000 Marrakech, Maroc. Tel: 212-6-61192039. E-mail: mbarek_benchanaa@yahoo.fr

Abstract

This paper concerns the study of the phosphate ore and a coke of solid combustible. The determination of their physicochemical characteristics and the study of their structural, textural and morphological aspects before and after thermal treatment are important and necessary for understanding of the reaction mechanisms and of the modelling of the processes of combustion and calcination.

The characterization of these materials was accomplished according to various experimental techniques such as: X-ray diffraction; infrared spectroscopy, scanning electron microscopy, porosimetry and the BET method. The results obtained show that the X-ray diffraction pattern of the coke presents only the crystalline phase of the graphite. The diffraction pattern of the raw phosphate as well as the crystallographic parameters at 25 °C
(a = 9.36 Å, c = 6.90 Å) are consistent with those given in the literature and indeed correspond to those of the crystal lattice of pure fluorapatite. The specific surface of natural phosphate is in the range of 13.36 m²g⁻¹ and that of the coke is 0.361 m²g⁻¹. The total pore volume of the phosphate ore measured by the condensation of nitrogen adsorbed was 0.178 mL and the mean opening diameter of the pores is 0.029 m. The real density of the phosphate (2.96 g.cm⁻³) and that of the coke (1.36 g.cm⁻³), were determined using an ultra pycnometer. Morphological observation of the grain surface shows fairly homogenous areas and a porous structure in the phosphate ore. The coke grains show on the contrary a difference in the grain size and a non-porous structure.

Keywords: phosphate ore, coke, characterisation, calcination, combustion, energy, industrial process

1. Introduction

Morocco has important reserves of phosphate ores. According to the chemical and granulometric characteristics of each phosphate type, the mineral extracted is subjected to treatments which are principally washing, drying, calcination and dry enrichment. All these processing operations are energy consuming.

In this context, we have initiated a research project that aims first to contribute to the energy optimization of industrial processes, particularly related to the calcination of phosphate ores, and second, to develop techniques for combustion, using coke as a solid fuel. Many authors have focused on the study of complex phenomena occurring during the combustion of coke (Dubuisson et al., 1995; Salvador et al., 2003; Slaoui & Bounahmidi, 2004). Others analysed the characterisation of the petroleum coke (Heintz, 1996; Suelves et al., 2002; Commandre & Salvador, 2005) and its application (Méndez et al., 2006; Murthy et al., 2014).

The present work is part of an extensive research and development program on energy optimization of the calcination process of the Moroccan phosphate ore using coke a solid fuel. We focused as a first step on the characterization of phosphate ore samples and coke samples used in the calcination of Moroccan phosphates. The main objective is to determine the physicochemical and mineralogical characteristics as well as the structural features, textural and morphological aspects of these samples before starting the study of their behavior in terms of combustion and calcination.

2. Materials and Experimental Techniques

The experimental study is based on two samples: the coke of a solid combustible and bright natural phosphate. These samples were provided by the CERPHOS (Center for studies and research on phosphates of the OCP group).

2.1 Sample Preparation

The homogeneity of the material and its particle size must be well controlled. For this, we subjected the samples to preparation operations such as:

- Coning and quartering

Sampling is an operation which splits a large sample into several smaller samples that are virtually identical. This operation can be accomplished using a splitter or manually through a series of divisions-mixtures.

- Granulometric separation

This operation consists of the separation of the desired elements from unwanted particles by sieving into three fractions: $_1 < 100$ µm, 100 µm $< _2 < 400$ µm and $_3 > 400$ µm. Only the fraction $_2$ was kept, because it represents a great part of the sample (nearly 80%).

2.2 Materials Characterisation Techniques

The characterization of the samples was achieved using different techniques and experimental processes such as: X-ray diffraction, infrared spectroscopy, scanning electron microscopy; porosimetry and the BET method.

3. Results & Discussion

3.1 Radiocrystallographic Analyses

The use of X-ray diffraction permits determination of the structure of the samples. It allows, at first, to control the different phases of the studied material, and subsequently the determination of its crystal parameters.

Figures 1 and 2 present the The diffraction pattern performed on powdered samples, obtained by grinding the raw samples (phosphate and cokeof a solid combustible) at 25 °C. The diffraction pattern of the raw phosphate sample (Figure 1) shows various lines. Some can be attributed to the carbonate fluorapatite $((CaF)Ca_4(PO_4)_3)$ contained in the ore and others correspond to the carbonate $CaCO_3$ phase.

The values of the crystallographic parameters of the phosphate ore analysed are: a = 9.36 Å and c = 6.90 Å at 25 °C. The X-ray diffraction pattern of the coke (Figure 2) shows a single line corresponding to the crystalline phase of graphite.
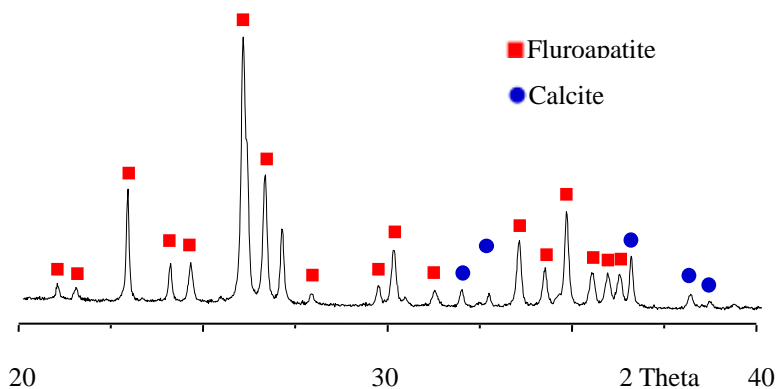

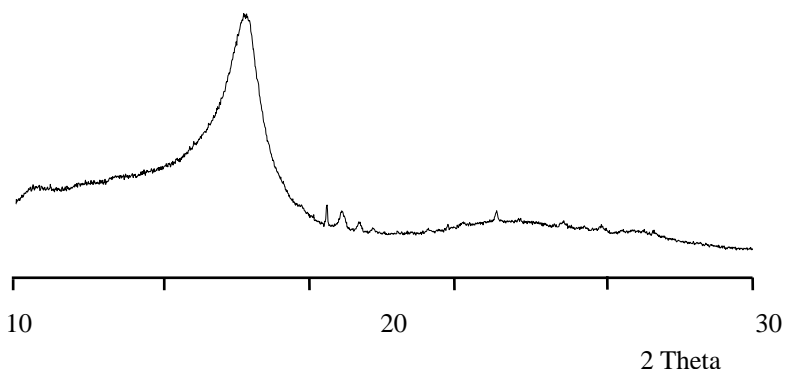Figure 1. X-ray diffraction pattern of the raw phosphate.

Figure 2. X-ray diffraction pattern of the coke of a solid combustible.

3.2 Infrared Spectroscopy

The presence of apatite and carbonate phases in bright phosphates are confirmedby infrared spectroscopy technique (Figure 3).
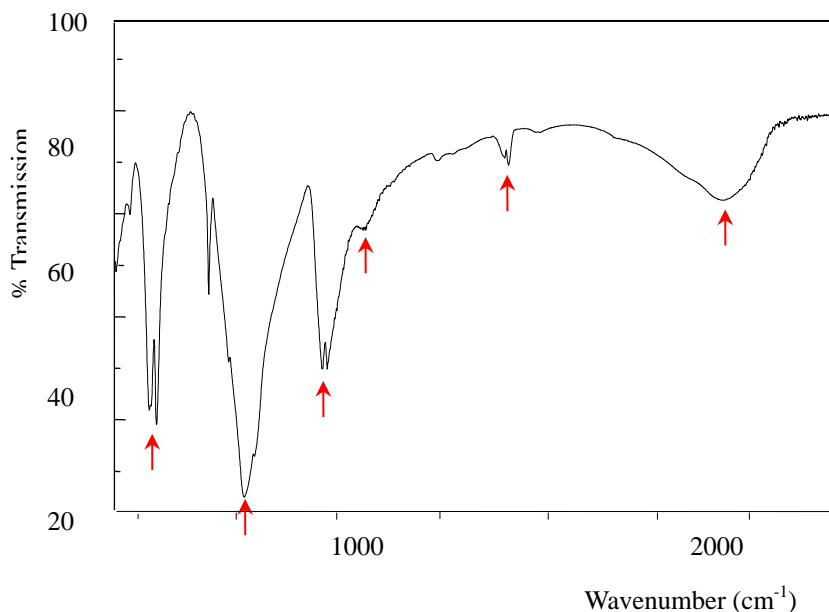

Figure 3. Infrared spectrum of natural phosphate before treatment.

The analysis of the infrared spectrum shows that:

- between 4000 and 3000 cm^{-1}, a large peak is observed around 3480 cm^{-1}corresponds to the water absorption band. It is a combination of antisymmetric stretching mode, symmetric stretching mode and an overtone of the bendingmode (Bernath, 2002 ; Tennyson et al., 2014),

- the 2360 cm^{-1} peak corresponds to the atmospheric CO_2,

- the 1644 cm^{-1} peak corresponds to the third vibration mode of adsorbed water molecule, known as angular deformity,

- the 1425 cm^{-1} doublet isfrom carbonate ν_3 and the 873 cm^{-1}peak is from carbonate ν_2. (Knubovets et al., 1997; Marshall et al., 1999).

- the1190-976 cm^{-1}peaks are from phosphate ν_3, 961 cm^{-1}shouldisfrom phosphate ν_1 and peaks around 660-520 cm^{-1} are from phosphate ν_4 (Pleshko et al., 1991; Gadaleta et al. 1996; Rehman & Bonfield, 1997).

3.3 Specific Area Measurement

The specific surface areas of the samples were measured by the BET method which consists of the adsorption of an inert gas at its liquefaction temperature on the solid. The specific surface of the solid is then calculated from conventional formulas proposed by Brunauer, Emmet & Teller (Brunauer et al., 1938).

The study of the adsorption-desorption isotherm is used to determine the distribution of the pore sizes. The isothermal adsorption-desorption of nitrogen on Youssoufia phosphate is reported in Figure 4.

The nitrogen adsorption-desorption isotherm on natural phosphate shows that it is of type II according to BDDT classification (Brunauer et al., 1940). It is characterized by a very gradual increase in the adsorbed amount based on the pressure equilibrium. This type of adsorption is a multimolecular adsorption characteristic, obtained during the adsorption on non-porous surfaces or macroporous adsorbents.

We also note the presence of a hysteresis between the desorption and the adsorption curves. This phenomenon is related primarily to the phase difference between adsorption and desorption of nitrogen in the solid pores. According to the IUPAC classification (Sing, 1985), the observed hysteresis is an H_3 type. It is observed in the case of an adsorbent that forms aggregates and can be attributed to capillary condensation taking place in a non rigid construction, but it is not a defined mesoporosity. Using this method, we have estimated for the phosphate mineral studied a specific surface area of about 13.37 m ^{2}g^{-1}.
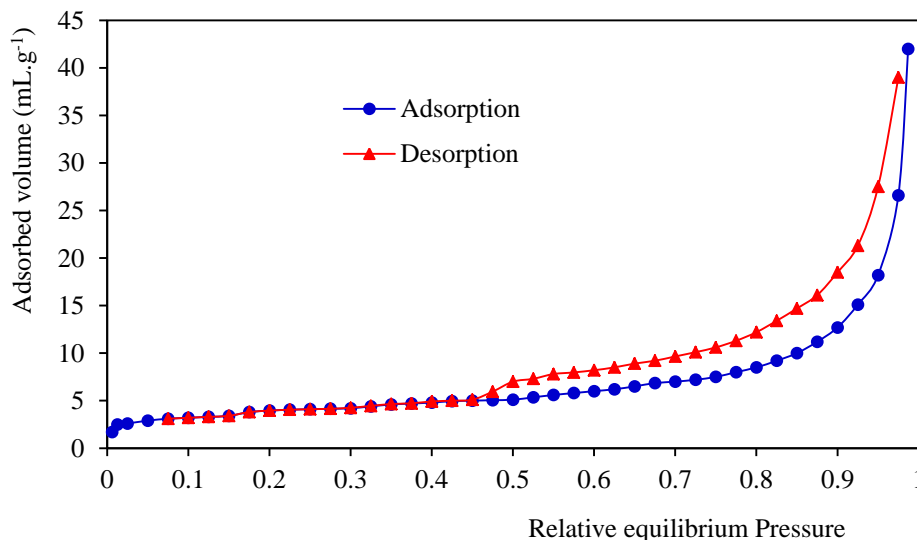
Figure 4. Natural Phosphate BET Isotherm.

3.4 Analyze of Phosphate Porosity

In any calcination process, it is very useful to know the distribution of pores on the material surface. The best method used to study the pore distribution is the BHJ method (Barrett et al., 1951). This technique is used to determine the ratio (volume/area) of the pore distribution taking into account the change in the thickness of the adsorbed layer and the condensation in the pores of the solid. As a function of pore diameter of the natural phosphate, we report the evolutions of the cumulative volume (Figure 5), the volume distribution of the pore size (Figure 6) and the cumulative surface pores (Figure 7).
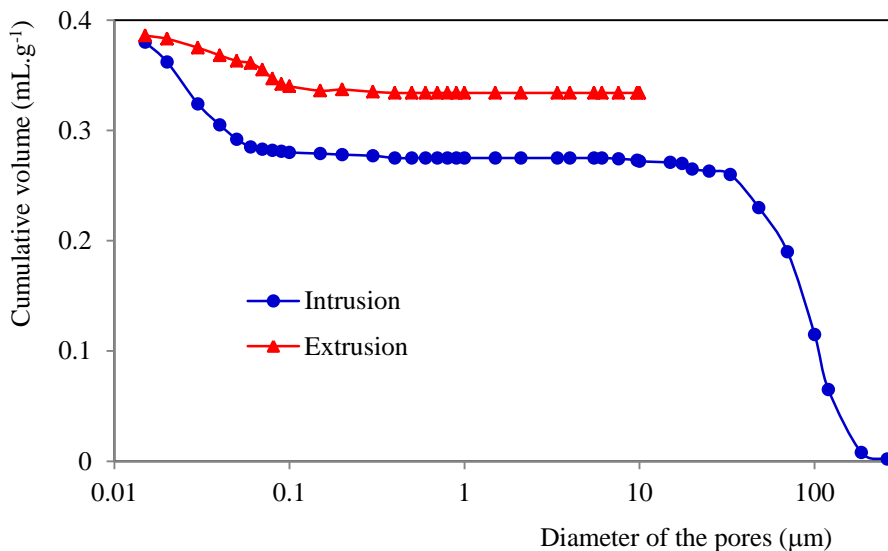

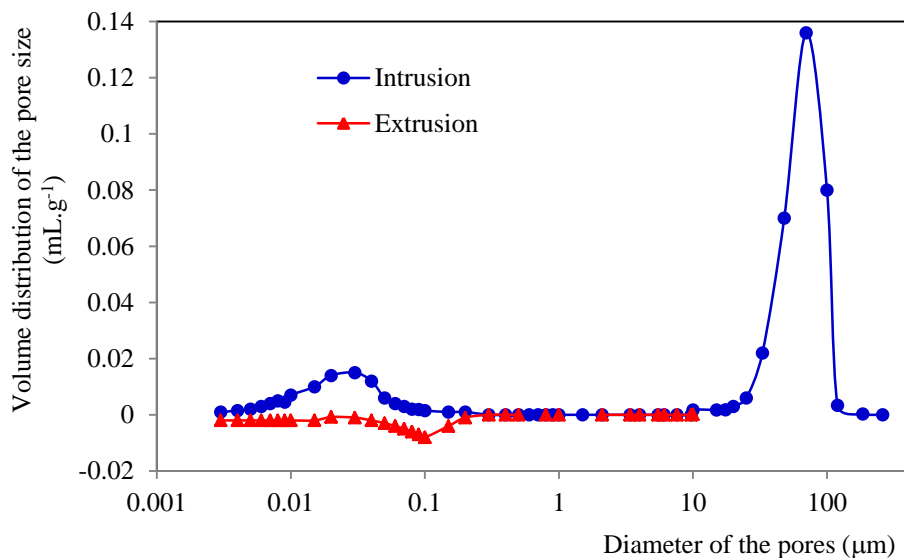Figure 5. Cumulative volume versus the pore diameterin the natural phosphate.

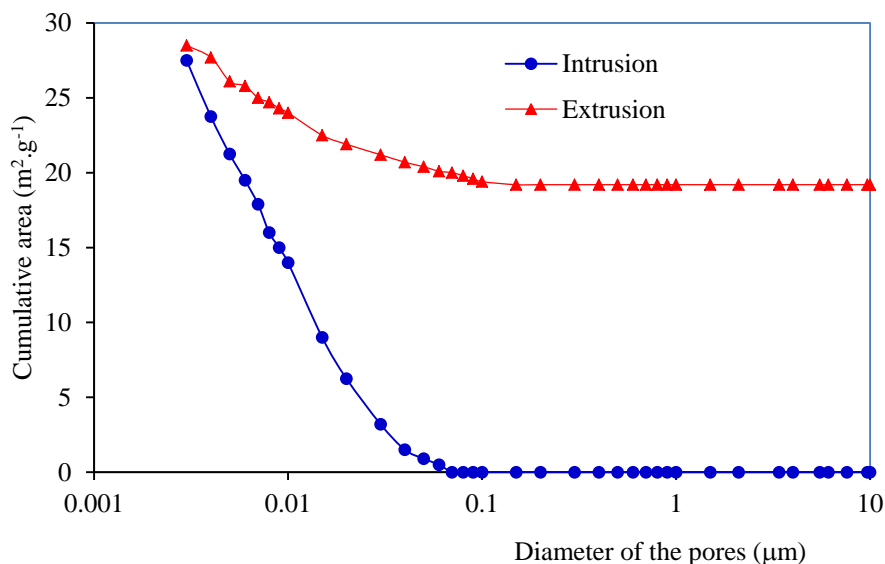Figure 6. Volume distribution of the pore size in the natural phosphate.

Figure 7. Cumulative surface versus the pore diameter in the natural phosphate.

We can also see the evolutions of the cumulative volume and volume distribution as functions of the equilibrium pressure (Figures 8 and 9).

The analysis of these curves show that:

- for a pore size between 30 μm and 320 μm, there is a progressive gas adsorption until the recovery of the monolayer,

- for a pore size between 0.1 μm and 31 μm, there is a saturation stage indicating no adsorption despite the increase in the equilibrium pressure. This is interpreted by the fact that the mesopores, in which capillary condensation is occurred, are no longer available for adsorption.

- when the pore size is between 31 μ m and 0.1 μ m, there is a saturation level that indicates a lack of adsorption despite the increased pressure balance. This is interpreted by the fact that the mesopores under which took place capillary condensation is no longer available for adsorption,

- for a pore size less than 0.1 μm, the adsorption is produced at so high pressures and the pores are not large enough and do not substantially contribute to the specific surface area.
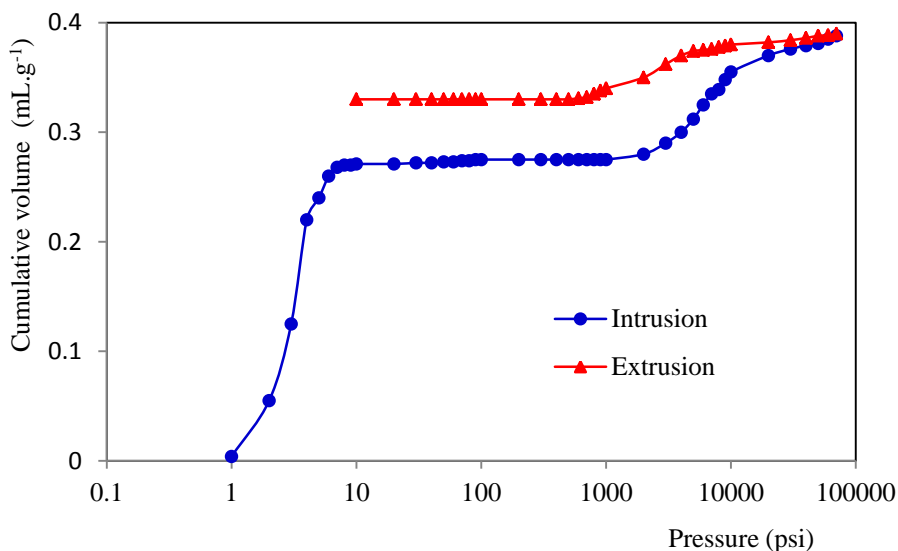
Figure 8. Change in cumulative volume as a function of the relative equilibrium pressure.
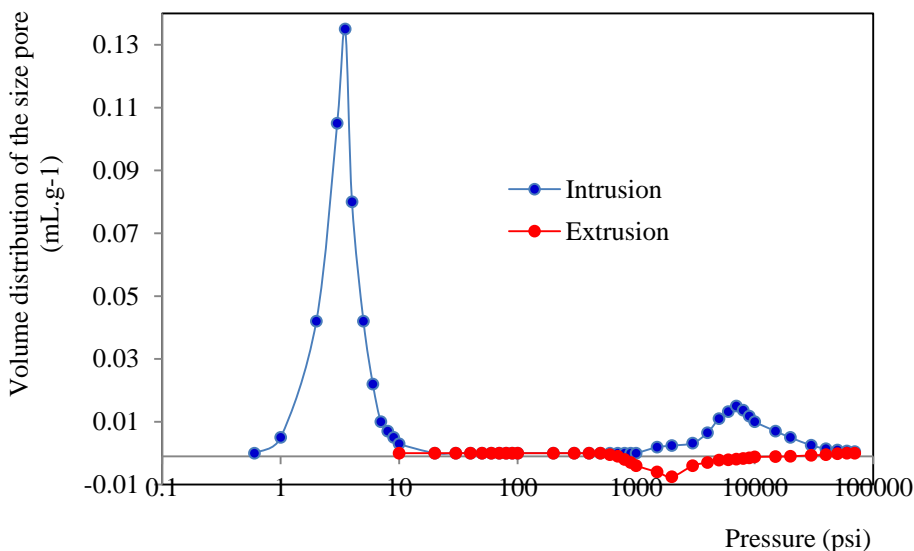

Figure 9. Volume distribution of the poresize as a function of the relative equilibrium pressure in the natural phosphate.

From these results, we can deduce the total pore volume of the natural phosphate measured by the condensation of adsorbed nitrogen: $V_T = 111$ mm^3.g^{-1} and the mean pore opening diameter is: d = 0.029 µm.

The adsorption-desorption isotherm of nitrogen on coke of a solid combustible is illustrated in Figure 10. According to the BDDT classification (Brunauer et al., 1940), it shows that it is a type III and it is different from the adsorption isotherms of type II at low pressure. This change at the beginning of the adsorption isotherm is due to the weaknesses of the adsorbent/adsorbate interactions. Using this method, we found out that the specific surface of the coke of a solid combustible is approximately 0.36 m²g^{-1}.
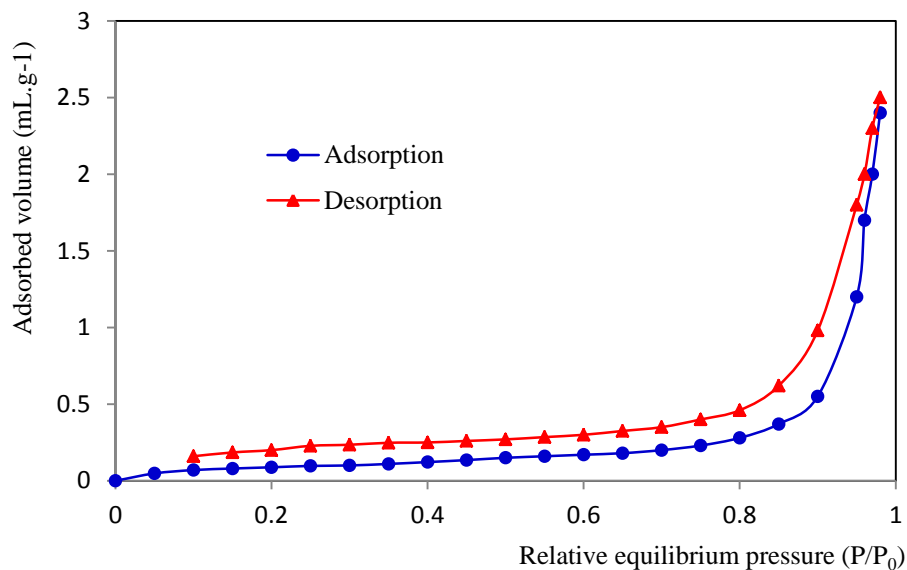
Figure 10. Coke BET Isotherm.

3.5 Scanning Electron Microscopy

This technique allows the observation of the sample morphology before treatment. The morphological observation of phosphate grains before treatment shows a fairly homogeneous zones and a porous structure. The morphology observation of the grain surface of coke of a solid combustible shows that there are different sizes of grains, heterogeneous areas and non-porous structure and anisotropic.
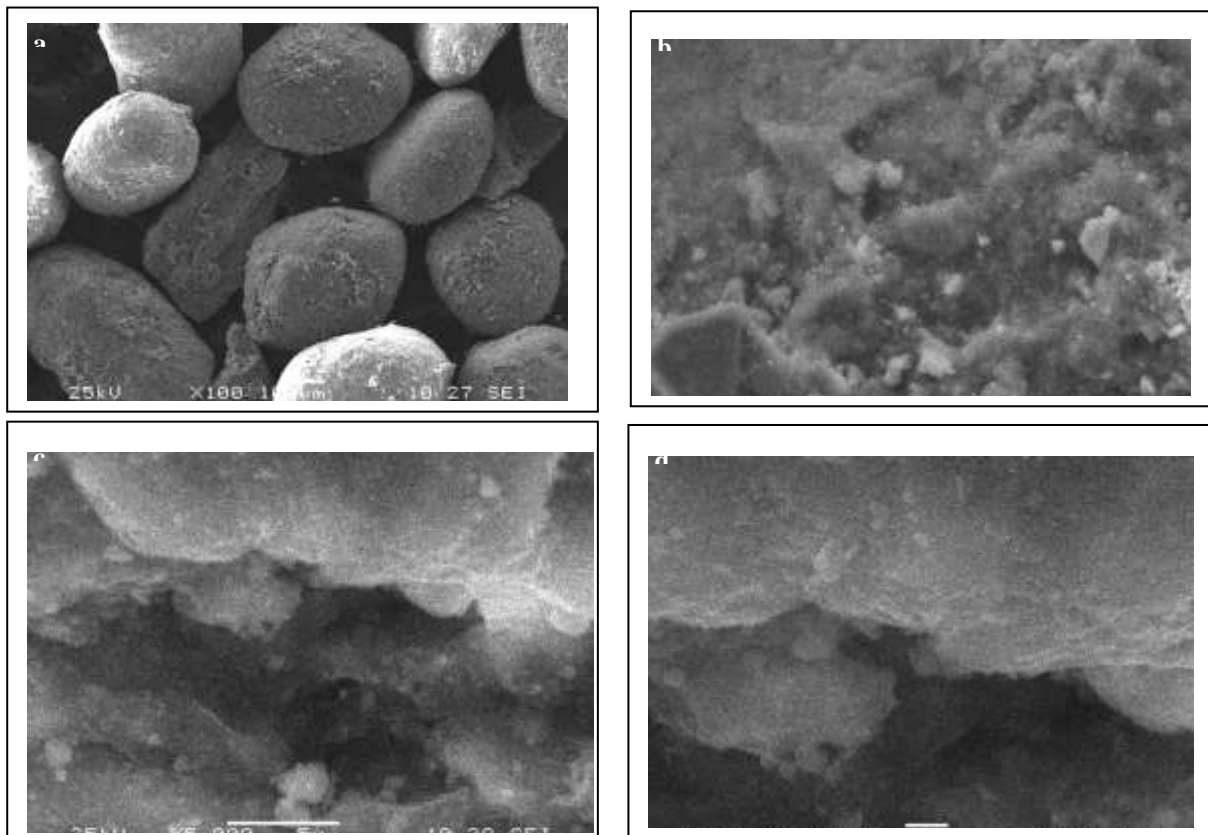

Figure 11. Morphological observation the surface of natural phosphate before treatment

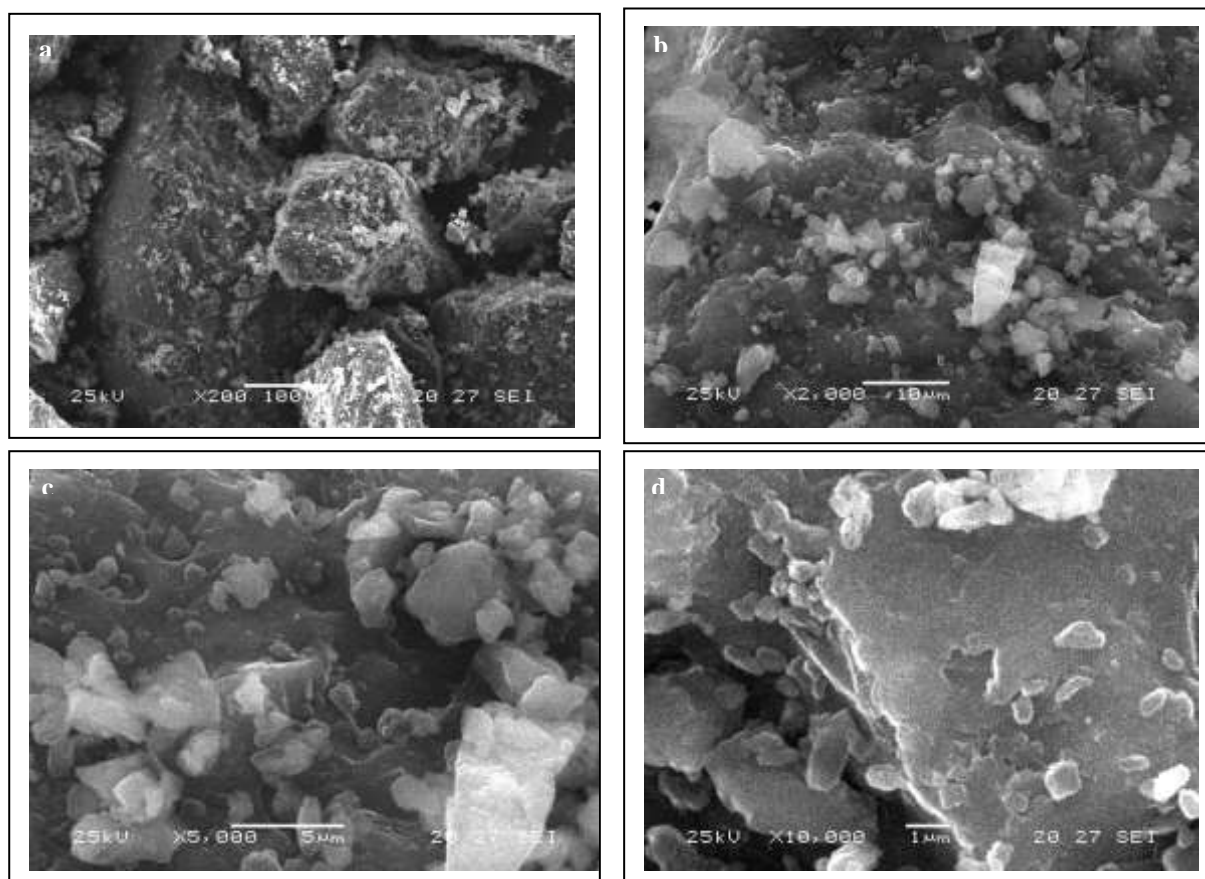(a) 100 μm, (b) 10 μm, (c) 5 μm, (d) 1 μm.

Figure 12. Morphological observation the surface of coke of a solid combustible before treatment

(a) 100 μm, (b) 10 μm, (c) 5 μm, (d) 1 μm.

4. Conclusion

We determine the physicochemical and morphological characteristics of the phosphate and coke of a solid combustible in order to know the properties of these materials. This will help when it comes to analyse its behaviours during the phosphate thermal treatment process as well as during the different reaction mechanisms involved in the process of combustion of coke of a solid combustible and phosphate calcinations.

References

Barrett, E. P., Joyner, L. G., & Halenda, P. P. (1951). The determination of pore volume and area distributions in porous substances. I. Computation from nitrogen isotherms. *Journal of the American Chemical Society*, *73*(1), 373-380. http://dx.doi.org/10.1021/ja01145a126

Bernath, P. F. (2002). The spectroscopy of water vapour: Experiment, theory and applications. *Physical Chemistry Chemical Physics*, *4*, 1501-1509. http://dx.doi.org/10.1039/b200372d

Brunauer, S., Deming, L. S., Deming, W. E., & Teller, E. (1940). On a theory of the van der Waals adsorption of gases. *Journal of the American Chemical Society*, *62*(7), 1723-1732. http://dx.doi.org/10.1021/ja01864a025

Brunauer, S., Emmett, P. H., & Teller, E. (1938). Adsorption of gases in multimolecular layers. *Journal of the American Chemical Society*, *60*(2), 309-319. http://dx.doi.org/10.1021/ja01269a023

Commandre, J. M., & Salvador, S. (2005). Lack of correlation between the properties of a petroleum coke and its behaviour during combustion. *Fuel Processing Technology*, *86*(7), 795-808. http://dx.doi.org/10.1016/j.fuproc.2004.08.001

Dubuisson, C., Charrette, A., & Kocaefe, D. (1995). Kinetic of the calcination of petroleum coke in neutral and oxidizing atmospheres. *The Canadian Journal of Chemical Engineering*, *73*(1), 110-119. http://dx.doi.org/10.1002/cjce.5450730112

Gadaleta, S. J., Paschalis, E. P., Betts, F., Mendelsohn, R., & Boskey, A. L. (1996). Fourier transform infrared spectroscopy of the solution-mediated conversion of amorphous calcium phosphate to hydroxyapatite: New correlationsbetween X-ray diffraction and infrared data. *Calcif Tissue Int.*, *58*(1), 9-16. PMID: 8825233

Heintz, E. A. (1996). The characterization of petroleum coke. *Carbon*, *34*(6), 699-709. http://dx.doi.org/10.1016/0008-6223(96)00037-1

Knubovets, R., Nathan, Y., Shoval, S., & Rabinowitz, J. (1997). Thermal transformations in phosphorites. *Journal of Thermal Analysis*, *50*(1-2), 229-239. http://dx.doi.org/10.1007/BF01979564

Marshall, C. P., Rose, H. R., Lee, G. S. H., Mur, G. L., & Wilson, M. A. (1999). Structure of organic matter in conodonts with different colour alteration indexes. *Organic Geochemistry*, *30*(10), 1339-1352. http://dx.doi.org/10.1016/S0146-6380(99)00106-0

Mendez, M. O. A., Lisboa, A. C. L., Coutinho, A. R., & Otani, C. (2006).Activated petroleum coke for natural gas storage. *The Journal of the Brazilain Chemical Society*, *17*(6), 1144-1150. http://dx.doi.org/10.1590/S0103-50532006000600011

Murthy, B. N., Sawarkar, A. N., Deshmukh, N. A., Mathew, T., & Joshi, J. B. (2014). Petroleum coke gasification: A review. *The Canadian Journal of Chemical Engineering*, *92*(3), 441-468. http://dx.doi.org/10.1002/cjce.21908

Pleshko, N., Boskey, A., & Mendelsohn, R. (1991). Novel infrared spectroscopic method for the determination of crystallinity of hydroxyapatite minerals. *Biophysical Journal*, *60*(4), 786-793. http://dx.doi.org/10.1016/S0006-3495(91)82113-0

Rehman, I., & Bonfield, W. (1997). Characterization of hydroxyapatite and carbonated apatite by photo acoustic FTIR spectroscopy. *Journal of Materials Sciences: Materials in Medecine, 8*, 1-4. http://dx.doi.org/10.1023/A:1018570213546

Salvador, S., Commandre, J. M., & Stanmore, B. R. (2003). Reactionrates fort he oxidation of highly sulphurised petroleum cokes: the influence of thermogravimetric conditions and some coke properties. *Fuel*, *82*(6), 715-720. http://dx.doi.org/10.1016/S0016-2361(02)00363-0

Sing, K. S. W. (1985). Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. *Pure and Applied Chemistry*, *57*(4), 603-619. http://dx.doi.org/10.1351/pac198557040603

Slaoui, S., & Bounahmidi, T. (2004). Experimental study and modeling of coke combustion kinetics. *Comptes Rendus Chimie*, *7*(5), 547-557. http://dx.doi.org/10.1016/j.crci.2004.01.010

Suelves, I., Lazaro, M. J., Diez M. A., & Moliner R. (2002). Characterization of chars obtained from co-pyrolysis of coal and petroleum residues. *Energy & Fuels*, *16*(4), 878-886. http://dx.doi.org/10.1021/ef010264m

Tennyson, J., Bernath, P. F., Brown, L. R., Campargue, A., Csaszar, A. G., Daumont, L., Gamache, R. R., Hodges, J. T., Naumenko, O. V., Polyansky, O. L., Rothman, L. S., Vandaele, A. C., & Zobov, N. F. (2014). A database of water transitions fromexperiment and theory (IUPAC Technical Report). *Pure and Applied Chemistry*, *86*, 71-83. http://dx.doi.org/10.1515/pac-2014-5012