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Decadmiation of Natural Phosphates by Heat Treatment and Hydrochloric Acid

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Natural phosphate is the product resulting from the exploitation of minerals containing phosphorus. In addition to the mineral containing phosphorus, phosphate rock contains several impurities including cadmium often with amounts above acceptable levels. The phosphate ore industry generally strives to improve product quality by eliminating this toxic element to avoid contamination of the soil after application of phosphate fertilizers in the long term. Therefore, it is better to use phosphate with a low concentration of cadmium. Currently there is no commercial way to remove the metal completely during the manufacturing process of phosphate fertilizers. The only way to reduce the contents of cadmium in fertilizer products is to use phosphates with a low concentration of this element. This study focuses on the elimination of cadmium from phosphate ore (decadmiation), by heat treatment using reagents such as chlorinating agents. The analysis was based on the amount of cadmium extracted and P_2O_5 losses. The results by ICP-AES analysis of the treated samples show the extraction between 90 and 98 % of cadmium at temperatures that vary from 750 to 900 °C, with consideration of the influence parameters such as the heat treatment time, the volume of the added acid and the temperature.

Keywords: Removal, Treatment, Temperature, Cadmium, Chlorine.

INTRODUCTION

Phosphate fertilizers contain traces of cadmium that accumulate from year to year in cultivated soils. This is not an essential trace element for the metabolism of living beings, on the contrary, its toxicity is strong and polymorphic and has a harmful effect on the kidneys, liver and prostate. Once ingested, it takes 30 years to get rid of. To prevent contamination of phosphate fertilizer by cadmium, it is essential to eliminate this element from the phosphate ore.

Currently, cadmium removal can be done in two ways, either by direct removal from the ore [1,2] or from phosphoric acid namely by precipitation [3], exchange of ions [4,5] solvent extraction [6,7] and membrane processes [8,9]. The decadmiation of phosphoric acid will lead to a significant increase in cadmium-rich gypsum waste. The gypsum waste presents a significant problem (because of cadmium content, other impurities and the radioactivity). In this way, the problem is therefore not solved in this way but merely transferred to another environment.

The present work is focused on the elimination of cadmium by the direct way using thermal treatment with the addition of a chlorinating agent. The existing studies prove that the thermal treatment of phosphate ores at 1100 °C allows a significant or total removal of cadmium.

The goal of our research is to decrease the temperature to about 800 °C by the addition of hydrochloric acid to phosphate ore.

EXPERIMENTAL

Procedure of extraction: Extraction tests were made in a melting pot of 25 g. 10 g of natural phosphate and a measured volume of hydrochloric acid and other agents such as NaCl, KCl, $CaCl_2$, $MgCl_2$ and NH_4Cl were mixed. The mixture is then transferred to an oven at a specific temperature ranges from 600 to 900 °C.

Methods of analysis and characterization: Elemental analysis of the main elements of the phosphate is made using a Horiba Jobin Yvonultima 2 spectrometer ICP-AES (analysis laboratory, Reminex Managem, Morocco) and confirmed by Thermo Scientific iCAP 6000 series (Materials Department Laboratory and Applied Chemistry College of Science and Technology Nihon University, Japan).

The X-ray diffraction measurements of the samples before and after pyrolysis were performed using a Philips X'Pert MPD diffractometer equipped with a Cu Ka (k = 1.54178) X-ray source (analysis laboratory, Reminex Managem, Morocco). The analysis of the data was carried out with the DIFFRACTINEL software.

The infrared spectra were obtained using an instrument of spectrometer Bruker tensor 27 in the Centre for analysis and characterization "CAC", Faculté des Sciences Semlalia, Cadi Ayyad Marrakech, Morocco). The pellets were prepared by mixing and grinding 2.5 mg of the raw phosphate with 200 mg of KBr. The spectra were recorded with a 2 cm resolution.

The morphology and the composition of the phosphate grains were studied by Miniscope TM3000 dedicated energy dispersive Analyzer X-ray QUANTAX70 (Hitachi High-Technologies Corporation) in Materials Department Laboratory and Applied Chemistry College of Science and Technology Nihon University, Japan).

RESULTS AND DISCUSSION

Physico-chemical characterizations of the phosphate samples before treatment: The phosphate used is black phosphate mining center of Youssoufia Morocco, rich in organic matter, located at an average depth of over 150 m which can sometimes reach 180 m. The general characteristics of the phosphate and the chemical composition of the mineral are summarized in Tables 1 and 2.

TABLE-1
CHEMICAL COMPOSITION OF PHOSPHATE

P_2O_5	33.11 %	TiO_2	0.03 %
CaO	46.81 %	F	3.36 %
SiO_2	2.65 %	MnO	< 0.01 %
Fe_2O_3	0.11 %	K_2O	0.48 %
Al_2O_3	< 0.10 %	Cd	61 ppm
MgO	1.02 %	–	–

TABLE-2
MINERALOGICAL PHOSPHATE ORE CHARACTERISTICS [Ref. 12]

Mineralogical characteristics	Weight (%)
Apatite	90
Calcite	2.6
Dolomite	1.8
Clays	1.2
Quartz	1.4
Organic substance	2.8
Amorphous silica	0.2

X-ray diffractogram of phosphate (Fig. 1) shows very sharp diffraction peaks. Analysis of this diagram, which is similar to the diagrams in reference [10,11], shows that the ore consists of a fluorapatite as the main constituent, accompanied by calcite in large quantities and quartz.

The difference in lattice parameters (Table-3) can be attributed to the substitution in the apatite, network of Ca^{2+} cations by Na^+, K^+, Cd^{2+}, Mg^{2+} cations and also by the partial substitution of phosphates ions by the carbonate ions.

These substitutions will be subsequently confirmed by other techniques in particular IR spectroscopy, EDAX analysis (Fig. 3; Table-4) and chemical analyses.

The analysis of the infrared spectra of Fig. 2 shows: an important peak around 3480 cm^{-1}, which corresponds to the hydroxyl group of water adsorbed by the material. The peak at 2360 cm^{-1} corresponds to atmospheric CO_2.

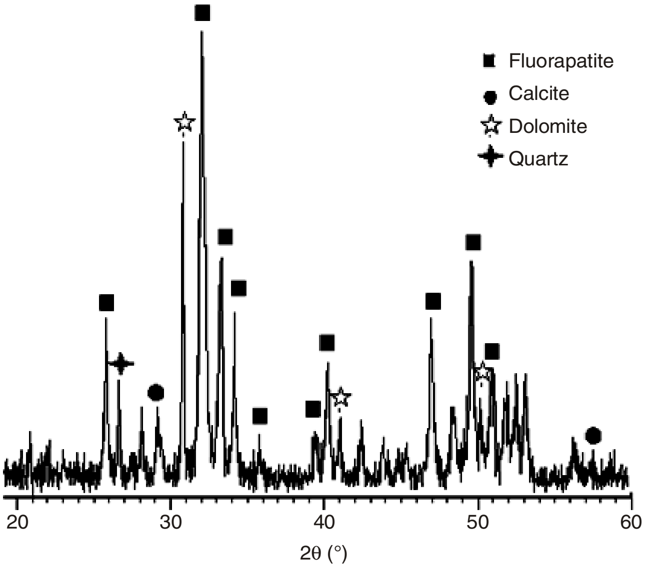


Fig. 1. X-ray diffractogram of natural phosphate

TABLE-3
CRYSTALLOGRAPHIC PARAMETERS OF THE MATERIAL USED (PHOSPHATES)

Parameter	Phosphates	Hydroxy-Ap [Ref. 10,11]	Fluoro-Ap [Ref. 10,11]	Francolite [Ref. 10,11]
a	9.320	9.421	9.372	9.360
b	9.320	9.421	9.372	9.360
c	6.894	6.882	6.888	6.890

TABLE-4
CHEMICAL COMPONENTS STUDIED NATURAL PHOSPHATE ANALYZED BY EDAX

Atomic number			Weight (%)	Atomic (%)
Ca	20	A	77.09	72.29
		B	78.16	73.65
		C	76.51	71.61
P	15	A	22.81	27.68
		B	21.53	26.25
		C	23.43	28.37
Cd	48	A	0.10	0.03
		B	0.31	0.11
		C	0.06	0.02

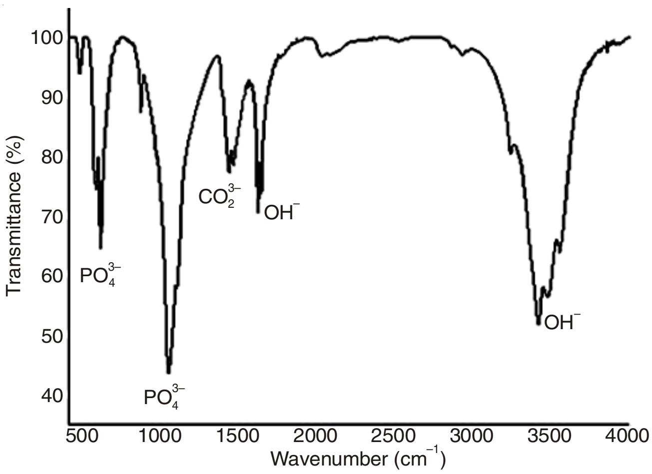


Fig. 2. Infrared spectrum of phosphate

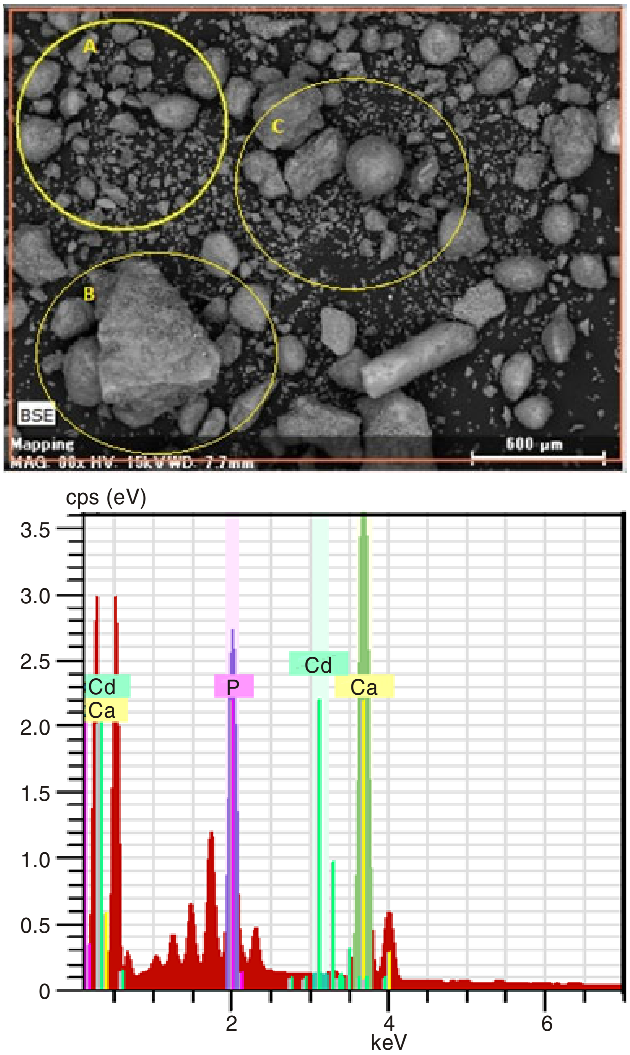


Fig. 3. Morphology and energy dispersive X-ray (EDAX) of the chemical elements of natural phosphate studied

The peak at 1644 cm^{-1} corresponds to the bending mode of the adsorbed water molecule. The double peak on 1425 cm^{-1} is due to the substitution of ions PO_4^{3-} ion CO_3^{2-} in apatite. An intense band in the region of 900 to 1200 cm^{-1}, centered at 1040 cm^{-1}, as well as the bands of average intensity at 570 and 608 cm^{-1} which characteristic of apatites.

The studied natural phosphate ore is a carbonate fluorapatite. This physico-chemical characterization allows mastering the chemical composition of natural phosphate and the nature of impurities in the ore.

Extraction of cadmium using hydrochloric acid: The results of the analysis of certain elements of the studied phosphate ore are presented in Table-1. Cadmium contents in the phosphate is 61 ppm. This content is higher than the recommended value 10 ppm [3]. In this work, the possibility of reducing the content of cadmium by heat treatment was studied.

Calcination by simple heat treatment of the studied ore at 800 and 900 °C did not allow the extraction of cadmium [2,13]. This is the reason why we will process the ore with a chlorinating agent namely hydrochloric acid at temperatures ranging from 600 to 900 °C with a variation of volume the acid and the duration of treatment.

Four series of experiments were carried out with the 2 mL of hydrochloric acid, heat treatment for 1 h and the 10 g of studied phosphate at 800 and 900 °C. After the treatment, the remaining cadmium level and the P_2O_5 concentration are practically the same for the four series (Table-5).

TABLE-5
CONTENT OF CADMIUM AND P_2O_5 TESTED

Sample	Cd (ppm)	P_2O_5 (%)
S_0 (initial sample)	61	33.11
S_1 (800 °C)	1	34.03
S_2 (900 °C)	< 1	37.56
S_A (800 °C)	1	36.71
S_B (900 °C)	< 1	35.15
$S_{1'}$ (800 °C)	1	35.79
$S_{2'}$ (900 °C)	< 1	34.90
$S_{A'}$ (800 °C)	1	35.15
$S_{B'}$ (900 °C)	< 1	35.47

Influence of temperature: The phosphate ore processing studied at temperatures between 600-900 °C with the addition of 2 mL of HCl for 1 h allowed the reduction of cadmium from 57 ppm at 600 to < 1 ppm at 900 °C (Fig. 4). So it is suggested that the extraction of 18.03 % of cadmium at 600 °C, 26.22 % of cadmium 700 °C, 90.16 % at 750 °C, 98.3 % at 800 °C and over 98.3 % of cadmium at 900 °C.

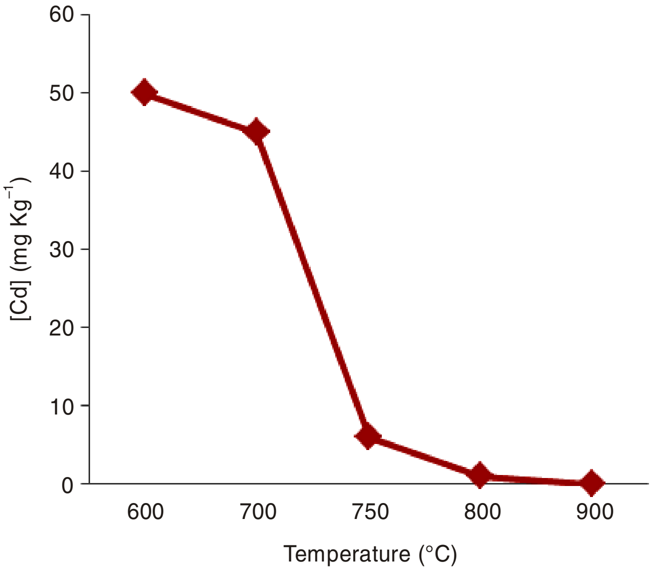


Fig. 4. Variation of the cadmium content with the extraction temperature (Duration = 1 h; V_{HCl} = 2 mL)

When the temperature is varied between 600 and 800 °C, the content of the samples in P_2O_5 decreased from 35.15 to 34.02 %, which is still greater than the initial content of sample 33.11 %. At 900 °C, where a significant extraction of cadmium is obtained (Fig. 4), an increase of P_2O_5 up 35.47 % (Fig. 5) is also observed.

The infrared spectra corresponding to samples of phosphates treated with the chlorinating agent at temperatures of 750, 800 and 900 °C are presented in Fig. 6. These spectra are characteristic of apatite in general and more particularly a fluorapatite.

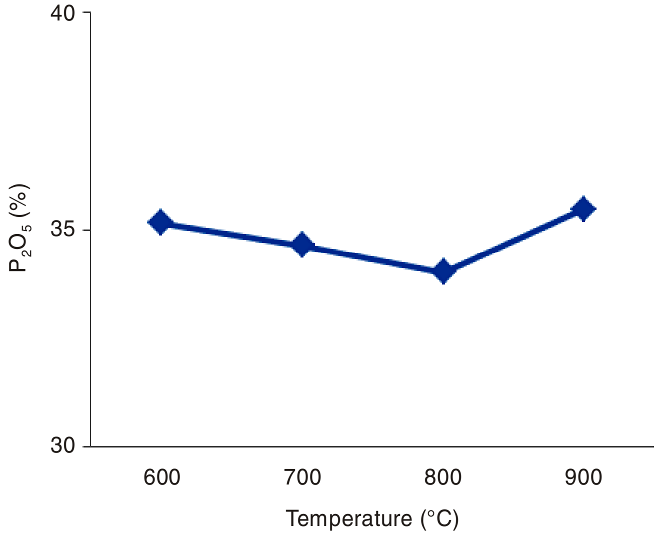


Fig. 5. Evolution of P_2O_5 content with temperature (Duration = 1 h; V_{HCl} = 2 mL)

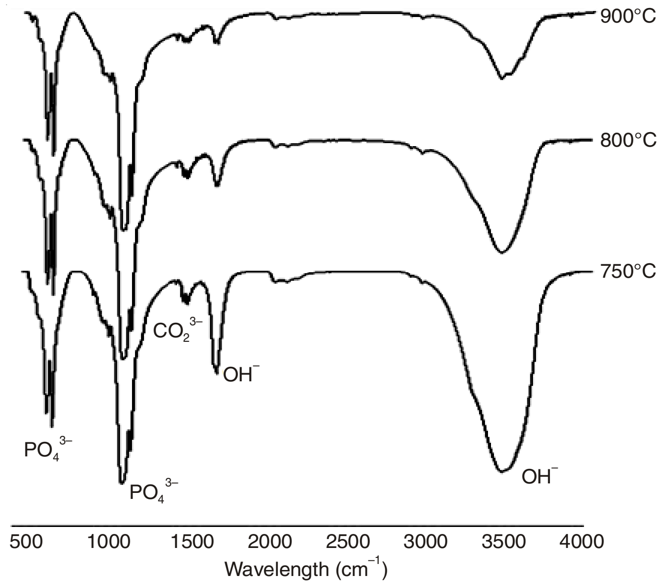


Fig. 6. Infrared spectra of after phosphate treatment studied at temperatures of 750 °C and 800-900 °C

After the heat treatment, there is a decrease in the intensity of the peaks corresponding to the OH^- vibrations of the adsorbed water molecule and of the peak located at 1425 cm^{-1} corresponds to CO_2^{3-}.

Influence of hydrochloric acid: At 800-900 °C, the extraction rate is greater than 98 % regardless of the volume of HCl mixed with the ore. At 600 and 700 °C the rate of extraction of cadmium is increased with the increase of HCl volume (Fig. 7).

The P_2O_5 content at 900 °C varies from 37.16 to 35.96 %, with a maximum concentration observed for the sample treated with 1.5 mL of HCl and a minimum content for the sample treated with 2 mL of HCl at 800 °C. The P_2O_5 content of samples treated with 1 mL; 1.5 mL and 2 mL is still lower than that of samples that were treated with the same volumes at 900 °C and ranges from 33.65 % to 34.02 %, but the sample treated with a volume of 3 mL has a higher content compared to those treated at 900 °C (Fig. 8).

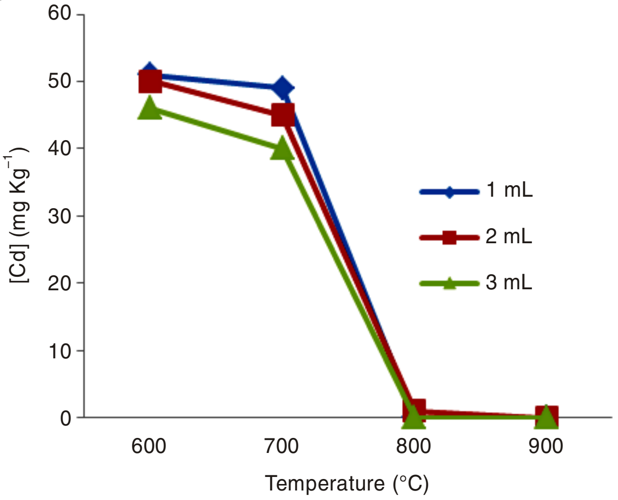


Fig. 7. Variation of the cadmium content on the basis of the volume of HCl with: duration = 1 h

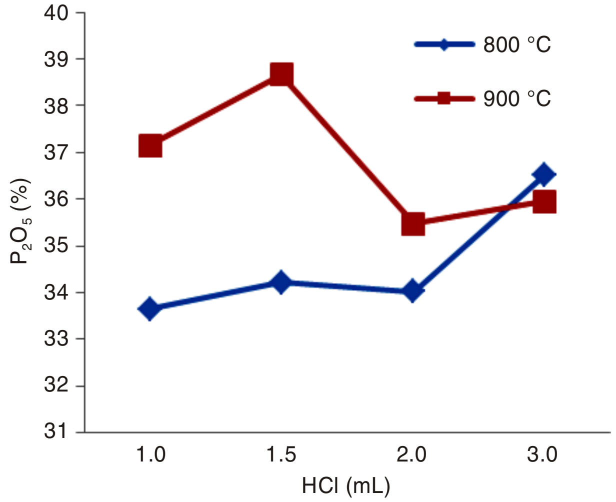


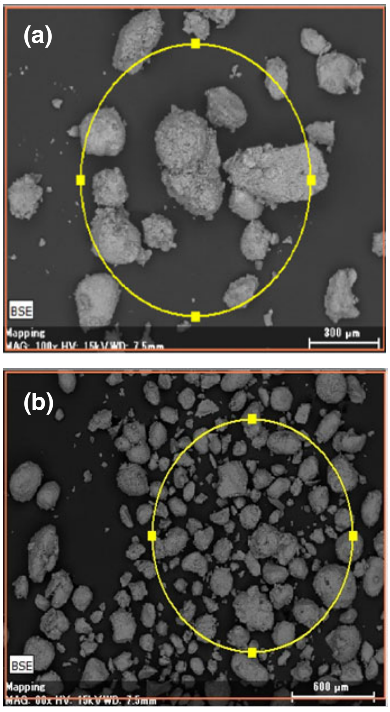
Fig. 8. Evolution of content of P_2O_5 based on volume of HCl

The analyses by the EDAX, confirm that in samples treated at 800 and 900 °C (Fig. 9) no cadmium is present.

Influence of time: As it can be seen in Fig. 10, at 800 °C, the cadmium content decreases with heat treatment time. Specifically, it decreased from 16 ppm at 15 min of calcination at a lower content of 1 ppm at 60 min of calcination. In other words, we have reached the extraction of 73.77 % of cadmium at 15 min, 80.32 % at 30 min, 96.72 % and 98.3 % at 45 min and 60 min of calcination. An increase of the temperature to 900 °C leads to an increase of the cadmium extraction rate independently of the thermal treatment time.

The P_2O_5 contents of the samples treated at 800 °C and those treated at 900 °C are very close for treatment duration of 15 to 45 min. For samples treated at 900 °C for 60 min an increase in content of P_2O_5 is observed (Fig. 11).

Extraction of cadmium using other chlorinating agents: The rate of cadmium extraction by other chlorinating agents such as NaCl, KCl, $CaCl_2$, $MgCl_2$, NH_4Cl for 1 h of treatment at 800 °C and 900 °C is greater than 98 %. While the content of P_2O_5 showed a decrease from the initial content 33.11 %. It is noted that the higher value of P_2O_5 '30.41 %' of samples treated with these agents is observed for the sample treated with $CaCl_2$ at 900 °C for 1 h (Fig. 12).



	Atomic number	Weight (%)	Atomic (%)	Error
Ca	20	68.91	64.54	1.03
P	15	16.59	20.11	0.33
Cl	17	14.50	15.35	0.26
Cd	48	0.00	0.00	0.00

	Atomic number	Weight (%)	Atomic (%)	Error
Ca	20	79.23	64.73	1.38
P	15	20.76	19.78	0.48
Cd	48	0.00	0.00	0.00

Fig. 9. Morphology and chemical constituents analyzed by EDAX of phosphate treated A) at 800 °C and B) at 900 °C

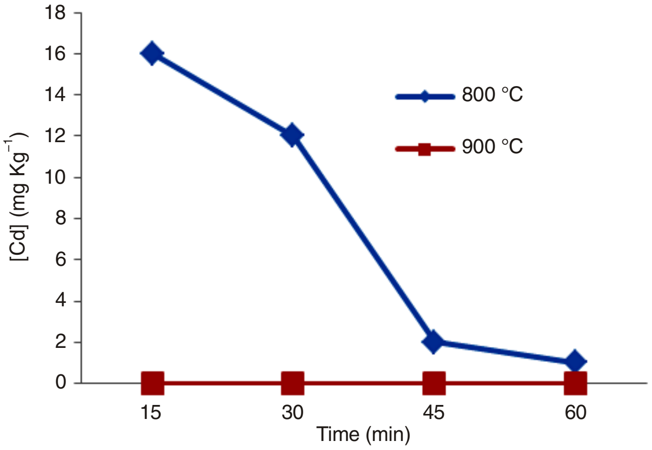


Fig. 10. Variation in rate of extraction of cadmium based on time (Temp. = 800 and 900 °C and V_{HCl} = 2 mL)

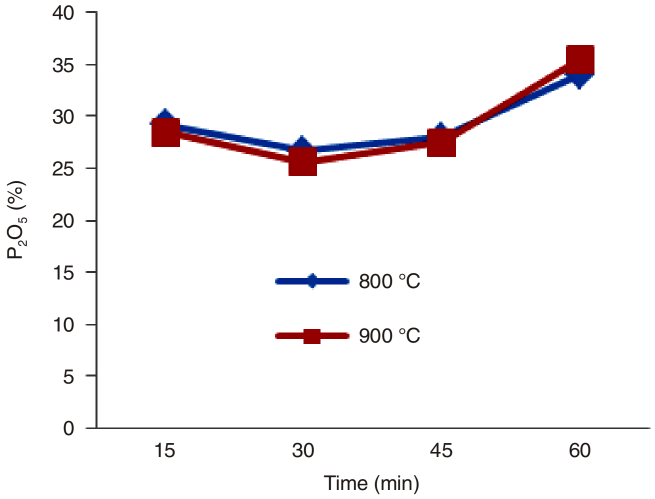


Fig. 11. Evolution of P_2O_5 content depending on the duration of treatment

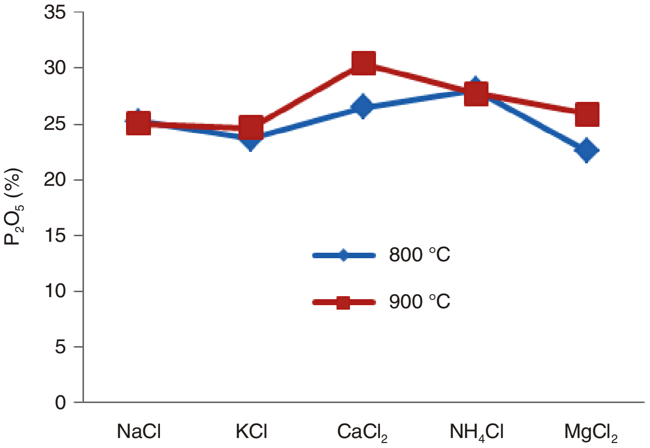


Fig. 12. Histogram of P_2O_5 % concentrations

It should be noted that the analysis by the X-ray diffraction of the ore after treatment with both NH_4Cl and $MgCl_2$ reagents revealed the presence of a new phase which is the Rorisite '$CaClF$' (Fig. 13).

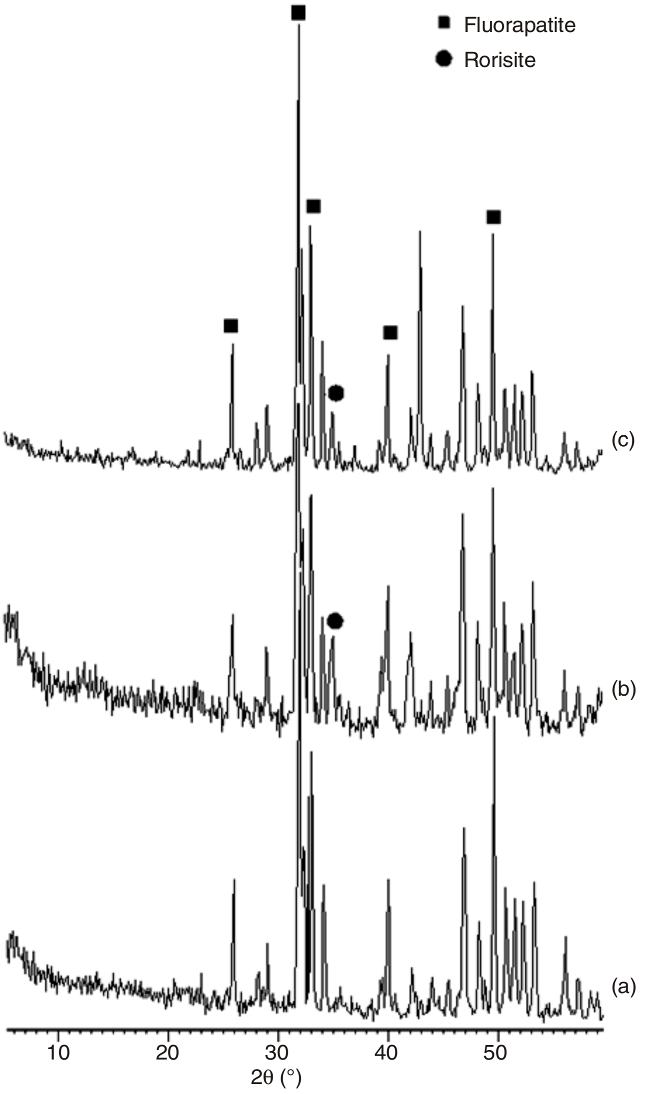


Fig. 13. X-ray diffractograms of phosphate ore treated with (a) HCl (b) NH_4Cl (c) $MgCl_2$ at 900 °C

Table-6 shows the lattice parameters of the samples after the chlorination treatment. Such treatments may lead to the substitution of the fluoride ions in the apatite by chloride ions at elevated temperatures, in the presence of chlorinated agents namely HCl, NaCl, Ca_2Cl, NH_4Cl and $MgCl_2$. This substitution of an ion by another ion of the same charge, but of different size, leads to a distortion of the crystal lattice and therefore a variation of the lattice parameters [14].

TABLE-6
CRYSTALLOGRAPHIC PHOSPHATE BEFORE AND AFTER TREATMENT PARAMETERS

Parameter	Natural phosphate ^{a}	HCl^b	NH_4Cl^b	$MgCl_2^b$
a	9.320	9.397	9.380	9.378
b	9.320	9.397	9.380	9.378
c	6.894	6.884	6.890	6.883

^{a}Before treatment; ^{b}After treatment

Conclusion

This study focused on the removal of cadmium from phosphate ore by thermal treatment in the presence of chlorinating reagents (HCl, NaCl, KCl, $CaCl_2$, $MgCl_2$ and NH_4Cl). This procedure allowed the extraction of cadmium at relatively low temperatures (750-900 °C) compared with simple thermal treatment at 1100 °C. The results showed that the use of hydrochloric acid solution allows extraction of 90.16 % at 750 °C. The values of extraction rates can be improved by seeking other extraction reagents and optimize other physical and chemical parameters.

REFERENCES

1. A. Nounah, Ph.D. Thesis, Contribution to the Study of Extracting Cadmium Vapométallurgie set of Synthetic Natural Apatites, Université Mohammed V-Agdal, Rabat, Morocco (1995).
2. Z. Benredjem, R. Delimi and A. Khelalfa, *Arabian J. Chem*.,; **doi:10.1016/j.arabjc.2011.05.016**.
3. Et. Ennaassia, K. El Kacemi, A. Kossir and G. Cote, *Hydrometallurgy*, **64**, 101 (2002).
4. C. Koopman and G.J. Witkamp, *Sep. Sci. Technol.*, **37**, 1273 (2002).
5. A. Almela, M.P. Elizalde and J.M. Gomez, *Fluid Phase Equilib.*, **145**, 301 (1998).
6. A. Elyahyaoui and S. Bouhlassa, *Appl. Radiat. Isot.*, **54**, 921 (2001).
7. A. Mellah and D. Bauer, *Hydrometallurgy*, **37**, 117 (1995).
8. C. Basualto, M. Poblete, J. Marchese, A. Ochoa, A. Acosta, J. Sapag and F. Valenzuela, *J. Braz. Chem. Soc.*, **17**, 1347 (2006).
9. A.M. Urtiaga, S. Zamacona and M.I. Ortiz, *Sep. Sci. Technol.*, **34**, 3279 (1999).
10. R.A. Young *Coll. Int. CNRS, Paris*, **230**, 21 (1973).
11. J.C. Trombe, *Ann. Chim. (Paris)*, **8**, 251 (1973).
12. L. Bilali, A. Aouad, K. El harfi, M. Benchanâa and A. Mokhlisse, *J. Anal. Appl. Pyrolysis*, **65**, 221 (2002).
13. J.K. Syers, Progress in the Development of Decadmiation of Fertilizer Phosphorus Fertilizer Industry, Federation of Australia (2001).
14. J.C. Elliott, Structure and Chemistry of the Apatites and Other Calcium Orthophosphates, Elsevier, Amsterdam (1994).