

Cadmium Removal from Phosphates of Djebel-ONK by Thermal Treatments

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In this work, the calcination of Algerian phosphate by microwave radiation is studied. Obtained results show that the dielectric constants, ξ' and ξ'' , of these phosphates over the frequency range from 2.4 GHz to 3.65 GHz, were in order of 3.6 and 0.36, respectively, which could be considered as admissible values for applying microwave radiation on phosphate rock calcinations. Applying the microwave radiation on phosphate calcinations at laboratory scale allowed to reduce the concentration of cadmium down to 12 mg/kg and increase the P_2O_5 content up to 36.82%.

Key Words: Phosphate ore, Phosphoric fertilizers, Cadmium, Soil contamination.

INTRODUCTION

Commercial phosphate fertilizers contain small amounts of heavy metal contaminants originated from phosphate rocks. These heavy metals may accumulate in soil and plants with repeated fertilizer applications and may end up in the food chain.

It is known that cadmium is the heavy metal of highest toxicity and so its presence in the fertilizer could be a source of environmental pollution. In this respect various methods have been proposed for its elimination from the phosphate rock. Analyzing the calcination process of Algerian phosphate in fluidized-bed calcinators shows an increase in the P_2O_5 content from about 25% up to 35% and a decrease in the Cd concentration down to 12 mg/kg, which is considered as admissible but with very high cost and overall yield of about 50%.

During phosphate industrial processing 60–80% of the cadmium value in phosphate rocks passes into the fertilizer. Depending on the origin and the type of rock, the cadmium content varies from 0.15–5 ppm in rocks of volcanic origin to 5–300 ppm in sedimentary rocks¹. Furthermore, sedimentary ores represent about 96% of world reserves and supply about 79–80% of market concentrates². As the sedimentary rock with 28 ppm is used in Algeria for producing fertilizers, it could be a potential source of environmental pollution by cadmium.

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To face up to this pollution, research is being very actively pursued for development of phosphate treatment, on the industrial scale. Although the main objective of phosphate rocks processing is to produce concentrates with good quality for use in the production of phosphoric acid by wet process, which accounts for 80–90% of world phosphate fertilizer production, the concentrate specifications concern specially the P_2O_5 content ($> 30\%$), the maximum MgO content (0.4 to 0.8%), the maximum weight ratio for CaO/P_2O_5 (< 1.65) and cadmium content (< 20 ppm)^{2,3}.

The samples studied were obtained from the deposit of Djebel-Onk (Algeria); they are sedimentary carbonate phosphates.

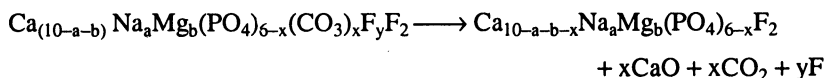
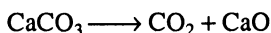
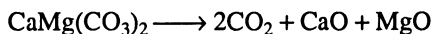
The aim of this study is (i) exploring the possibilities for applying microwave radiations on phosphate treatment, and (ii) establishing the optimal parameters for phosphate treatment, which can allow significant beneficiation and cadmium removal.

EXPERIMENTAL

Mechanical preparation and chemical analyses of raw phosphate ore

The mechanical preparation involved operations of crushing, grinding and sizing down to 0.15 mm. Then a sample was withdrawn and dried at 150°C. Then the sample was size classified and the contents of P_2O_5 and Cd were determined in each fraction. Mineralogical composition was determined by X-ray diffraction (XRD). For determining the chemical composition a sample of each fraction was ground (powdered) in an agate mortar and placed in a platinum crucible with a mixture of HNO_3 (65%) and $HClO_4$ (70%). Then it was heated on a hot plate until almost dry, followed by addition of 1 mL of HNO_3 (65%), which was evaporated until dryness. The addition of HNO_3 was repeated until obtaining a clear solution. This solution was transferred into a 100 mL flask and completed by double-distilled water. The resulting solution was used in the determination of cadmium with solvent extraction flame atomic absorption spectrometry (SEFAAS)^{4,5}, whilst Ca and Mg were determined by flame atomic absorption spectrometry (FAAS) and P_2O_5 content was determined by gravimetric method using phosphomolybdate of quinoline⁶.

Calcination: Calcination is based on the decomposition of exogangue and endogangue carbonates under thermal effect, in the temperature range between 700 and 1000°C, corresponding to endothermal decarbonatization first of dolomite followed by that of calcite and the conversion of francolite to fluorapatite⁷.



At Djebel-Onk the calcination process applied to phosphate consists of three stages: (i) drying-preheating at 280°C of scrubbed phosphate, (ii) calcination in fluidized-bed furnaces in the temperature range 600–900°C necessary for the

dissociation of carbonates, and (iii) cooling with wet hydration of the lime (extinction).

The P_2O_5 content and Cd concentration in the concentrates obtained at different temperatures *i.e.*, 600, 700, 800 and 900°C were determined and XRD spectra were registered.

Application of microwaves: It is well known that the phosphate rock is a mixture of various constituents and the microwave properties are influenced by the mass, shape and composition of each of these components. The dielectric properties (permittivity, ξ_r' ; dielectric drop, ξ_r'') of the phosphates were determined over the frequency range 2.4–3.65 GHz. This frequency range was chosen because it includes the frequencies of the most widely used microwave applicators for industrial purposes⁸.

The measurement system used (Fig. 1) was designed and calibrated in the electronic laboratory LEN7 of ENSEEIHT, INP Toulouse, France, and then verified by determining the relative permittivity of teflon (Fig. 2). The measured value of the real part of relative permittivity (ξ_r') of teflon agrees well with the value of 2.087 as

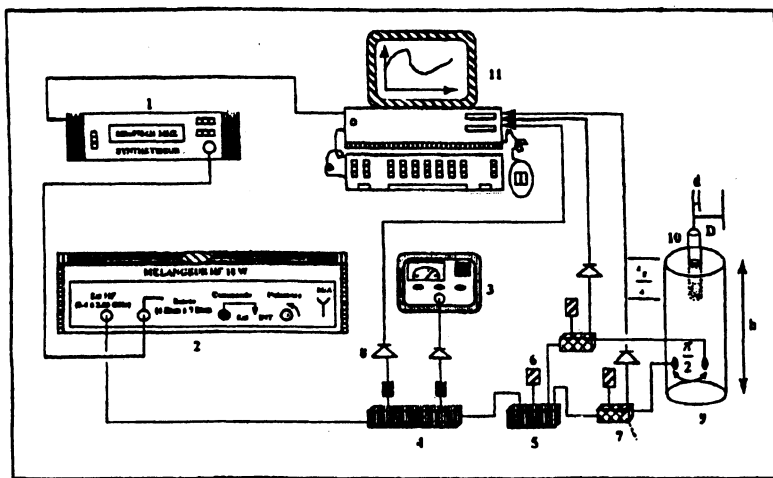


Fig. 1. System of measure

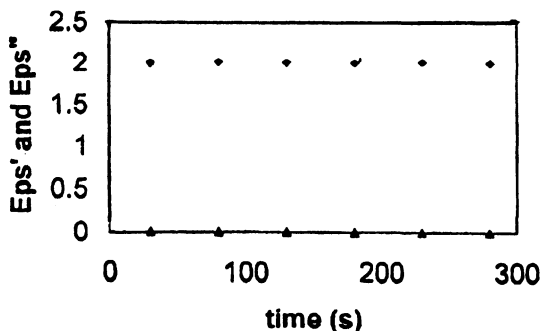


Fig. 2. Dielectric properties of teflon

obtained by Von Hippel⁹. The relative permittivity of phosphate rock was determined by a method based on the comparison of resonance frequencies and over tension coefficients of cavity with and without phosphate sample.

The dielectric properties (ξ'_r and ξ''_r) and reflection coefficient (R) were calculated employing the following equations:

$$\begin{aligned}\xi'_r &= 1 + 2(f_0 - f'_0)/Nf'_0 \\ \xi''_r &= 1/N (1/Q'_0 - 1/Q_0) \\ N &= 4V_e/V_c \\ P_{\text{abs}}/P_{\text{in}} &= 1 - |R|^2 \\ P_{\text{abs}} &= P_{\text{in}} - P_{\text{ref}}\end{aligned}$$

where f_0 = cavity frequency without phosphate ($f_0 = 2.54$ GHz); f'_0 = cavity frequency with phosphate; Q_0 = surtension coefficient of cavity without phosphate ($Q_0 = 2Q$); Q'_0 = overtension coefficient of cavity with phosphate; V_e = sample volume ($V_e = 0.8$ cm³); V_c = cavity volume ($D_c = 8.3$ cm, $L_c = 20.37$ cm); P_{abs} = absorbed power; P_{ref} = reflected power; P_{in} = incident power; R = reflection coefficient and N = filling coefficient.

Obtained results for ξ'_r , ξ''_r and R are represented in Figs. 6, 7 and 8 respectively. After determination of phosphate dielectric properties, phosphate samples were treated in microwave furnace at two different powers: 400 and 800 W. The heating time was varied between 1 to 10 min. Then they were analyzed and characterized by X-ray diffraction.

RESULTS AND DISCUSSION

Table-1 shows the chemical composition of raw phosphate and Fig. 3 its XRD

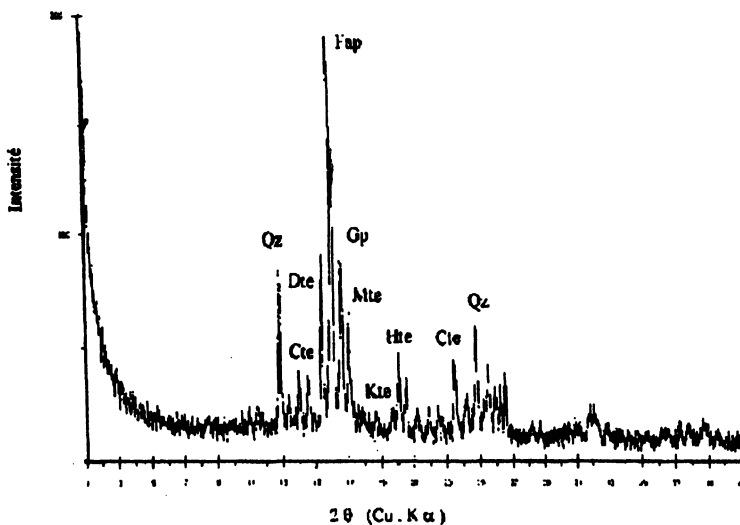


Fig. 3. XRD spectrum of raw phosphate

spectrum, whilst Table-2 shows the contents of P_2O_5 and Cd in different granulometric fractions and the weight % of each fraction.

TABLE-1
CHEMICAL ANALYSIS OF RAW PHOSPHATE

Element	Mass (%)	Element	Mass (%)
P_2O_5	25.70	Cl^-	0.012
CaO	46.50	F^-	3.25
MgO	2.74	CO_2	9.83
Fe_2O_3	0.50	MnO	48 ppm
Al_2O_3	0.85	Cd	28 ppm
SiO_2	4.40	As	10 ppm
Na_2O	1.30	Pb	60 ppm
K_2O	0.28	C	0.32
SO_3	2.67	Moisture	5.30

TABLE-2
GRANULOMETRIC ORDERING OF THE RAW PHOSPHATE ORE

Granulometric fraction (mm)	Differential (%)	P_2O_5 (%)	Cadmium (ppm)
+1.25	24.239	22.860	22.750
-1.25 + 1	08.057	25.500	28.500
-1 + 0.4	27.058	27.900	28.250
-0.4 + 0.25	03.289	26.976	23.500
-0.25 + 0.16	28.237	26.900	20.000
-0.16 + 0.063	07.928	24.183	19.500
-0.063 + 0.036	00.868	17.500	12.250
-0.036	00.185	17.500	11.750

In order to have a concentrate satisfying the marketing quality and based on obtained results, the fractions coarser than 1 mm and smaller than 0.16 mm were omitted, whilst the fractions between 1.00 and 0.16 mm were recovered.

In Fig. 4, the concentration of P_2O_5 and cadmium as function of calcination temperature are plotted. From this figure, it is evident that the content of cadmium decreases slightly, while the P_2O_5 content increases with increasing the calcination temperature up to 35%. The increasing of P_2O_5 content is a consequence of dissociation of the dolomite and magnesium carbonates that started at 650 to 800°C, then of the calcite carbonates at 900°C.

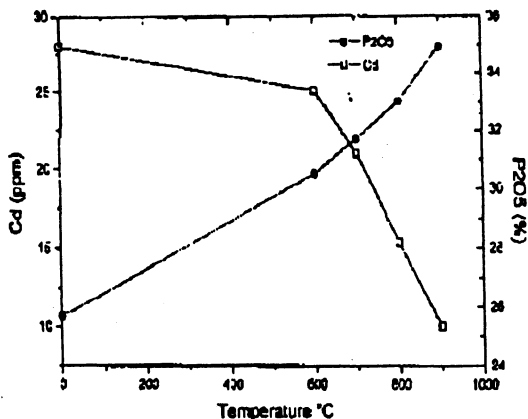


Fig. 4. Variation of P₂O₅ percentage and Cd level according to calcination temperature

The examination of XRD spectra (Fig. 5) of phosphate samples calcinated at 600, 700, 800 and 900°C revealed that effectively, the dolomite dissociation starts at 600°C. The intensity of peak relative to dolomite decreases progressively with increasing the calcination temperature, until its disappearance at 700°C.

Carbonates dissociation is described by the following reactions:

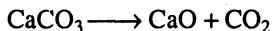
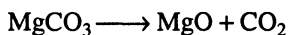
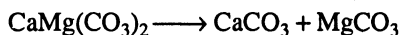


Table-3 shows that at 900°C, MgO content and CaO/P₂O₅ ratio were respectively 0.67% and 1.56. Thus the concentrate obtained at this temperature fits the criteria required for concentrate of marketing quality.

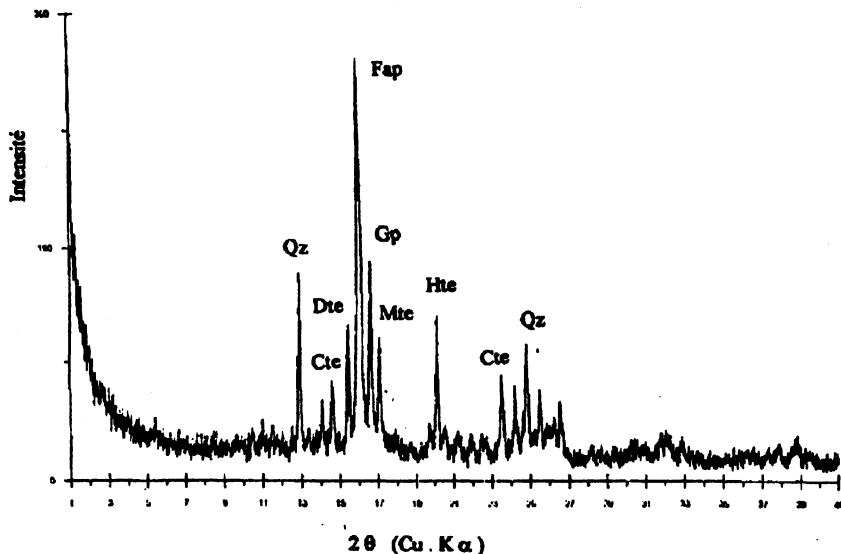


Fig. 5. XRD spectra calcinated phosphate at (a) 600°C,

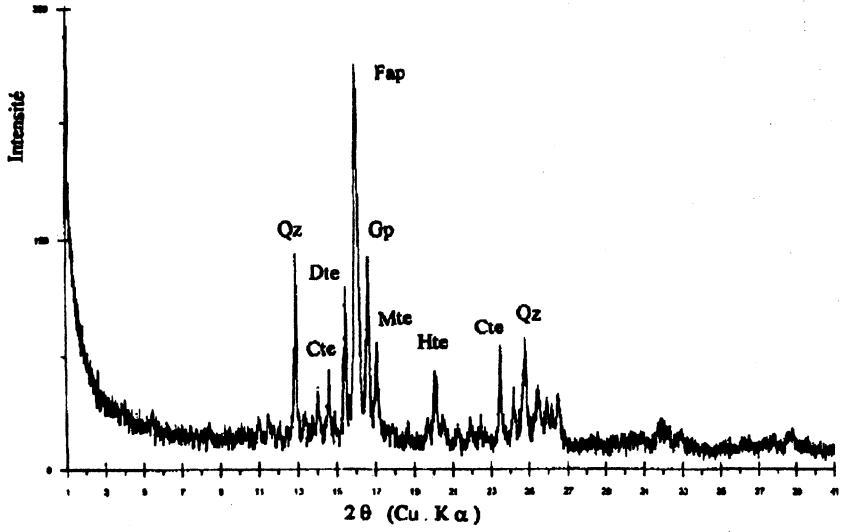


Fig. 5. (b) 700°C,

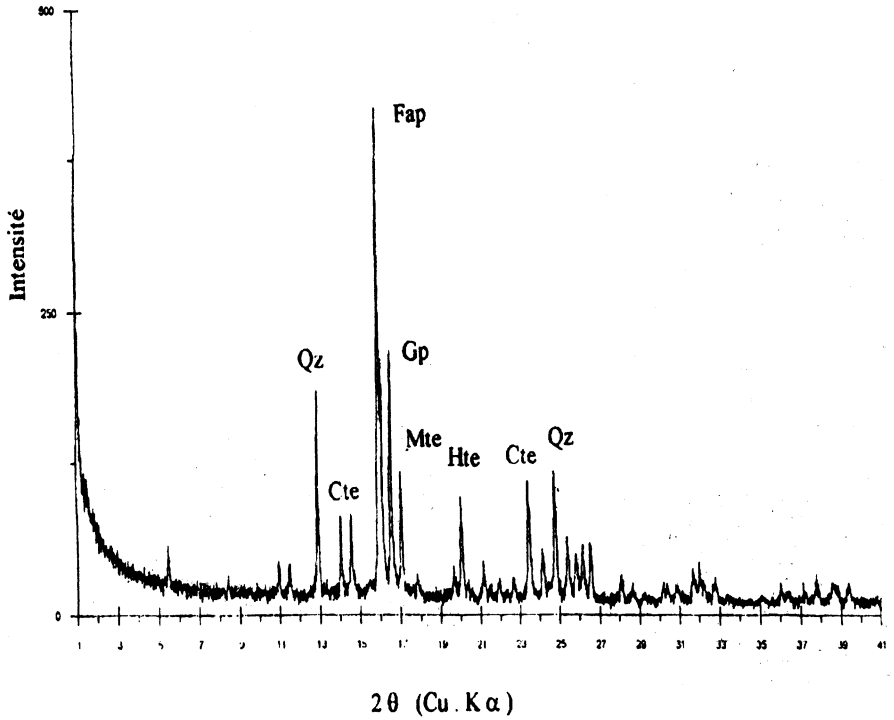


Fig. 5. (c) 800°C,

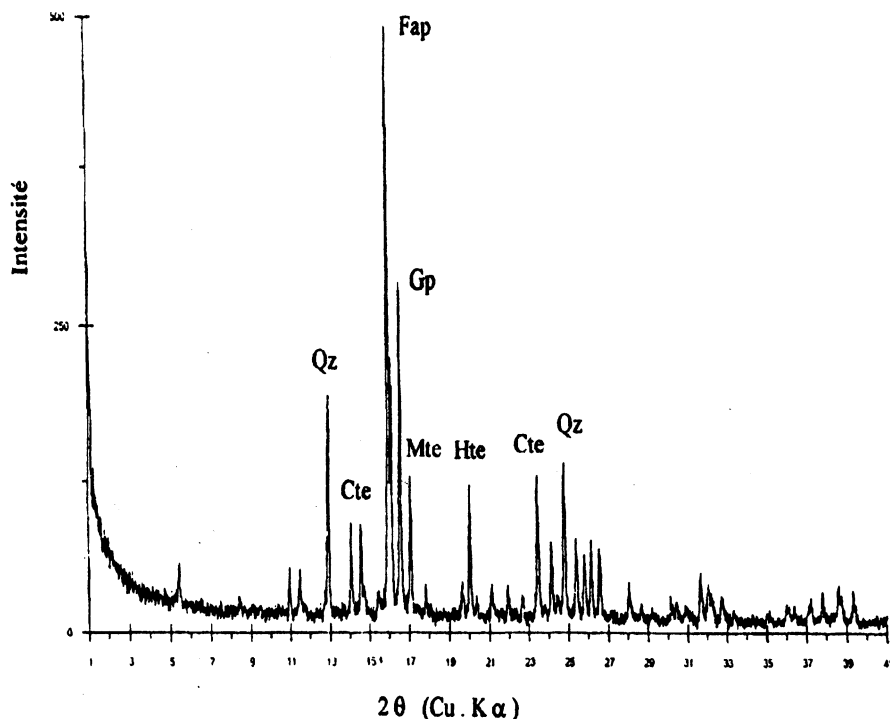


Fig. 5. (d) 900°C

TABLE-3
ANALYSES RESULTS OF PHOSPHATE CONCENTRATES AT 600, 700, 800 and 900°C

T°C	Cd (ppm)	P ₂ O ₅ (%)	TPL (%)	MgO (%)	CaO/P ₂ O ₅
0	28.00	25.70	54.62	2.740	1.80
600	25.06	30.50	66.64	0.760	1.69
700	21.00	31.70	69.26	0.760	1.67
800	15.35	33.00	72.10	0.674	1.62
900	10.00	34.95	76.36	0.674	1.56

The determination of the cadmium concentration in samples calcined at 600, 700, 800 and 900°C shows a light reduction for a temperature lower than or equal to 700°C. This decrease can be assigned to the elimination of the CdO and Cd(NO₃)₂.

Beyond 700°C the decrease of Cd concentration is more remarkable. This can be explained by the fact that metal, as soon as it reaches its boiling point 766°C, is volatilized.

In summary, the volatilization of the Cd from the phosphate ore can be divided into two stages in which the ion metallic Cd²⁺ is reduced (Cd⁰), after which it is volatilized quickly as soon as the boiling point (766°C) is reached.

Effect of microwaves

After calculation of ξ_r' and ξ_r'' , the results were plotted on Figs. 6 and 7 respectively. They show an increase of permittivity and dielectric drop during a heating time estimated to 300 s. After this time ξ_r' and ξ_r'' reach values of 3.6 and 0.36 respectively. These values are related to those found by Van der Berg *et al.*, 1992: 4.0 and 0.4 for a phosphate with 80% BPL (36.5% P_2O_5 , 52.0% CaO, 1.5% MgO) in the same frequency range (2.4 to 3.6 GHz).

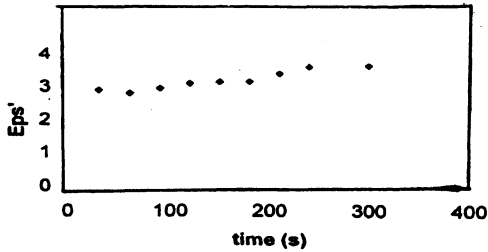


Fig. 6. Relative permittivity ξ_r' of phosphate

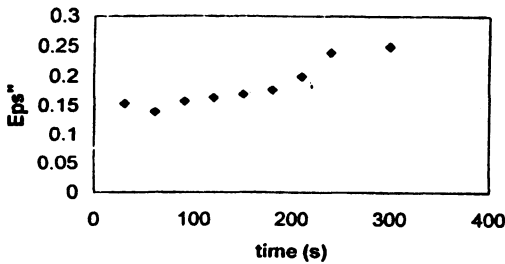


Fig. 7. Dielectric drop ξ_r'' of phosphate

Furthermore, the calculation of reflection coefficient R (Fig. 8) from reflected powers revealed low values which explains that if *dissipative* properties increase, the reflected power decreases and vice versa.

The obtained values of ξ_r' , ξ_r'' and R for phosphate confirm its dissipative nature, so it can be treated in microwave furnace without fear of wave reflection.

Phosphate treatment was realized at two mean powers: 800 and 400 W, during a heating time varying between 1 and 10 min.

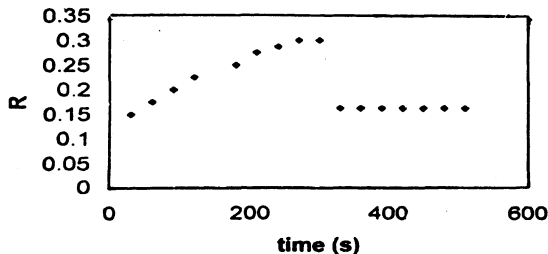


Fig. 8. Reflection coefficient R of phosphate

Experimental results presented in Table-4 show a significant difference between results obtained at 800 W and those obtained at 400 W, so after 10 min, the Cd concentrations are reduced down to 12 and 16 ppm and the P₂O₅ contents increased up to 36.82 and 31.04% respectively.

TABLE-4
ANALYSES RESULTS OF PHOSPHATE AFTER MICROWAVE HEATING

Heating time (min)	P = 800 W				P = 400 W			
	Cd (ppm)	P ₂ O ₅ (%)	MgO (%)	CaO/P ₂ O ₅	Cd (ppm)	P ₂ O ₅ (%)	MgO (%)	CaO/P ₂ O ₅
0	28	25.70	2.74	1.81	28	25.70	2.74	1.81
1	26	28.22	0.71	1.70	28	26.50	0.44	2.07
2	21	32.09	0.76	1.49	26	27.70	0.41	1.89
3	19	32.07	0.68	1.65	24	28.05	0.35	1.80
4	14	33.35	0.55	1.56	19	29.00	0.29	1.72
6	12	36.05	0.31	1.49	17	30.75	0.25	1.60
10	12	36.82	0.28	1.60	16	31.04	0.21	1.58

The XRD spectra of samples treated (Fig. 9) show that dolomite dissociation starts after 4 min, which is expressed by a decrease of corresponding ray intensity. All these results reveal the effect of microwaves on the improvement of phosphate quality. Thus, at 10 min and 800 W, 57.2% of Cd was removed and phosphate got satisfied values of P₂O₅, MgO and CaO/P₂O₅ which were 36.82%, 0.28% and 1.6, respectively.

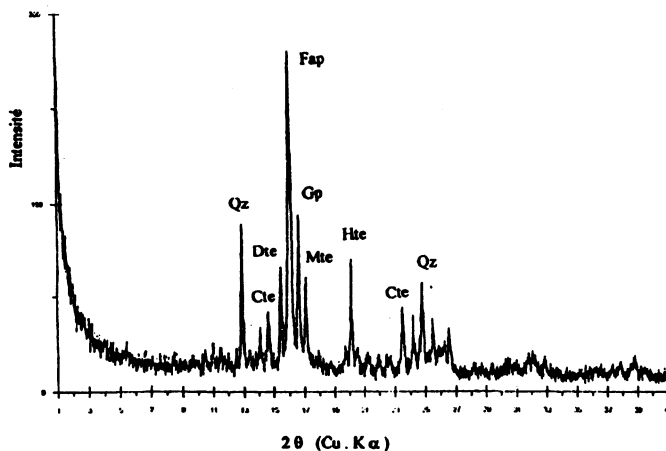


Fig. 9. XRD spectra of phosphate samples treated with microwaves at 800 W: (a) 1 min

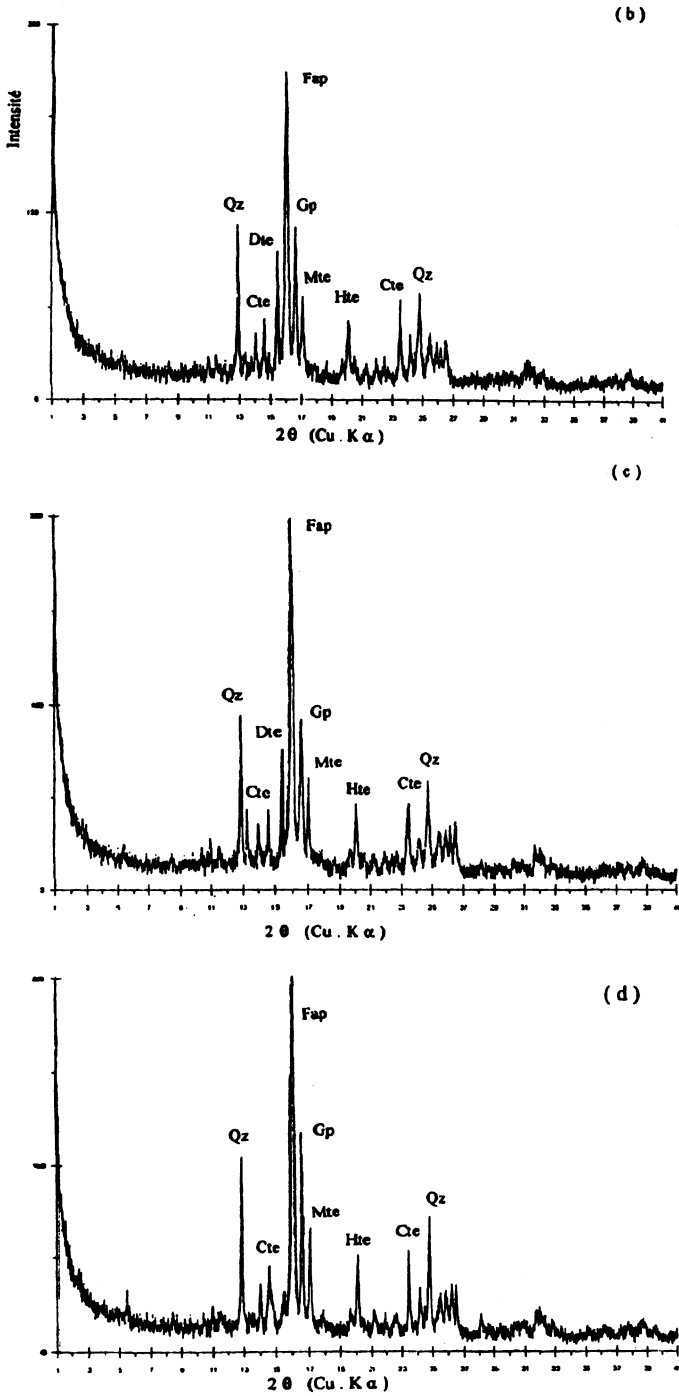


Fig. 9. (b) 2 min, (c) 3 min, (d) 4 min

Conclusion

From this study, it is concluded that the treatment of phosphate can be used to produce phosphate fertilizers of good quality in order to minimize risks of soil contamination by cadmium. Though the classical calcination of phosphate in fluidized-bed calcinators leads to good results, which can satisfy the requirements of the market (35% P_2O_5 and 10 ppm of Cd), however a set of important factors, *e.g.*, excessive cost price, a weak output, a poor global recuperation yield in the order of 50% in P_2O_5 with respect to the raw ore, the complexity and the slowness of the process, lead to orient our attention toward the choice of other processes.

Microwaves is a technology with a very rapid kinetics (the rise in temperature is very fast). In the period of time between 6 and 10 min, the phosphate is enriched to 36.82% in P_2O_5 and the Cd concentration is reduced to 57.3% (12 ppm) without preheating-drying.

The industrial application of microwaves for the treatment of phosphate seems to be currently impossible; there would be, therefore, a field of research, in order to implement the pilot tests that will permit us to be closer to real conditions.

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