Revista Colombiana de Materiales
ISSN 2256-1013, No 18, pp. 54-68, 2021. https://doi.org/10.17533/RCM/udea.rcm.n18a05

CALCINATION OF PHOSPHORIC ROCK BY PLASMA TORCH, TO OBTAIN THERMOPHOSPHATES FERTILIZERS

N. M. Espinel Pérez [1], M. C. Pazos [2], E. Parra [3], D. Martínez [4]

1: MSc. Chemistry, Pedagogical and Technological University of Colombia, Tunja, Colombia; National Learning Service Sena, Mining Center, Sogamoso, Colombia.
2: PhD. Chemical Sciences, Pedagogical and Technological University of Colombia, Tunja, Colombia.
3: Technologist in Chemistry, National Learning Service Sena, Mining Center, Sogamoso, Colombia.
4: PhD. Sciences of Materials, Pedagogical and Technological University of Colombia, Sogamoso, Colombia.

* E-Mail: nespinelp@sena.edu.co; espienlson@misena.edu.co

PALABRAS CLAVE

Reactor de antorcha de plasma, apatitas, fertilizantes, termofosfatos.

RESUMEN

Se utilizó un reactor provisto de una antorcha de plasma para la obtención de termofosfatos para su uso como fertilizantes, a partir de la calcinación de la roca fosfórica de la región centro oriente del departamento de Boyacá, Colombia, proveniente de los municipios de Iza y Sogamoso. Para lo anterior, se utilizó un equipo de corte por plasma marca Victor Cut Master A60^{TM}, con una potencia nominal de 7.6 kW, que le permite alcanzar temperaturas de proceso superiores a 10000 °C. El tamaño de partícula del mineral tratado fue de 0.075 mm, el cual fue calcinado durante un tiempo entre 30 s y 40 s. Como resultado experimental se obtuvieron concentraciones máximas de fósforo total y fósforo asimilable correspondientes a 27.0 y 3.07 % de P_2O_5, respectivamente, a partir de los termofosfatos de Iza. Por su parte, los resultados para los termofosfatos de Sogamoso fueron 33.12 y 4.83 % en peso de P_2O_5. Los análisis de fósforo total se realizaron por fluorescencia de rayos X y para la determinación del fósforo asimilable se realizó primero la extracción con solución neutra de citrato de amonio y posteriormente la determinación cuantitativa por espectrofotometría ultravioleta visible. Mediante difracción de rayos X se determinó que la fase cristalina predominante fue el carbonato de fluorapatita, que osciló entre 53.0 y 87.0 % para los termofosfatos de Iza y entre 60.6 y 93.7 % para los termofosfatos de Sogamoso. El consumo energético para la obtención de los termofosfatos fue muy bajo, del orden de 0.64 kW-h/Kg – 1.14 kW-h/Kg, usando una corriente eléctrica de 30 A y 45 A, respectivamente.

KEYWORDS

Plasma torch reactor, apatites, fertilizers, thermophosphates.

ABSTRACT

A plasma torch reactor was used to obtain thermo phosphate fertilizers by subjecting the phosphoric rock (PR) from the central eastern region of the Boyacá Department, Colombia, in the municipalities of Iza and Sogamoso. A plasma torch equipment Victor Cut Master A60^{TM}, with 7.6 kW as nominal power, reaching temperatures of process higher than 10000 °C, was used. The particle size of mineral treated was 0.075 mm, which was calcined during 30 s and 40 s. The experimental results show a maximum concentrations of total phosphorus and assimilable phosphorus corresponding to 27.0 and 3.07 % P_2O_5 respectively for Iza sample, while the results for the Sogamoso one were 33.12 and 4.83 % P_2O_5, respectively. The total phosphorus analyses were carried out by X ray fluorescence, while the assimilable phosphorus was determined from the extraction with neutral ammonium citrate solution and quantified by visible ultraviolet spectrophotometry. The main crystalline phase in each sample was determined by X ray diffraction. The results indicate that the samples are constituted mainly by fluorapatite carbonate, ranged between 53.0 and 87.0 % for the Iza one and between 60.6 and 93.7 % for that from Sogamoso. The energy consumption to obtain the thermophosphates was very low, ranged between 0.64 kW-h/Kg and 1.14 kW-h/Kg, for electrical current of 30 A and 45 A, respectively.

1. INTRODUCTION

Phosphate rock is the basic component for the production of fertilizers and its global demand has growth projections of 207 Mton in 2018 / to 263 Mton in 2035 [1]; this type of commodity was considered in Colombia's mining development plan [2] as one of the strategic minerals, with 20 million hectares of reserves and with great potential for extraction [3]. An efficient way to obtain thermophosphates fertilizers is the application of thermal treatments, which facilitate the decomposition of phosphate rock (PR) at high temperatures, incorporating in some cases additives to improve its performance. There are three types of heat treatments applied to raw PR: calcination, sintering, and melting. "During calcination, carbonates are decomposed, and CO_2 is eliminated, while in the sintering stage, the agglomeration of small particles occurs to form larger ones and, in the fusion, the crude mineral is heated above the melting point" [4]. According to [5], more than 10 % of the world fertilizer market is produced by calcination and a novel technology to carry out this operation is by means of plasma torch, which implies the creation of an electric arc sustained by the passage of an electric current through a gas, there by stripping the electrons of gas molecules, results in a current of ionized gas or plasma [6]. As the electrical resistivity in the entire system increases, the temperatures also increase (> 10,000 °C), facilitating the calcination of the phosphate rock and transforming it into thermophosphates. The objective of this work is the obtaining and physicochemical characterization of thermophosphates fertilizers from the heat treatment of minerals by plasma torch, which implied the design of a plasma reactor for the benefit of phosphate rock.

2. EXPERIMENTAL METHODOLOGY

2.1 Collection and preparation of samples

The phosphate rock samples were supplied from Colombia, Boyacá Department, specifically in the municipalities of Iza (San Miguel village) and Sogamoso (Pilar and Ceibita village). Subsequently, the benefit of minerals was carried out through unit operations of crushing, grinding and sieving until a particle size ≤ 0.075 mm was obtained as a result of a granulometric analysis that passes 200 mesh. Prior to size reduction, the samples were taken to a drying oven for 8 hours at 50 °C, subsequently they were ground using a Retsch planetary ball mill Pm 400 for 5 minutes – 250 rpm and then, classified using a Fritsch Analysette 3 Pro vibratory sieve and a sieve Tyler normalized series number 8, 16, 30, 50, 100, 200 and -200 for 5 minutes.

According to [7] the particles with a size distribution ≤ 0.075 mm are considered fine particles, and have greater mechanical durability (resistance to crumbling) in briquettes, favoring agglomeration. Since each original mineral treated [phosphoric rock of Iza (PRIZA) and phosphoric rock of Pilar and Ceibita Sogamoso (PRPC)] was mixed with a wheat flour in water paste in proportions of 65 wt.% - 70 wt.% PR and 35 wt.% - 30 wt.% wheat flour in water paste. Subsequently, each material was homogenized to form a mass and then, hydraulically pressed (119.84 MPa) into circular briquettes of 2.5 cm in diameter and 1.2 cm in height were obtained.

According to [8], lignin in wheat flour is present, which is considered a thermoplastic polymer and binder, activating with pressures equal to or greater than 100 MPa [9], facilitating the formation the phosphate rock briquettes. The humidity was eliminated by taking the briquettes to an electric oven at 105 °C, for 2 days.

2.2 Description of calcination process in the plasma torch reactor

The sample was placed in an internal stainless-steel crucible (4 briquettes per experiment), the reactor was hermetically sealed, the cooling system was started feeding cold water to the top of the jacketed reactor and drawing hot water from the bottom of it. The experimental conditions were established (equipment Victor Cut Master A60^{TM}, transferred arc, 20 A – 80 A current output, plasma gas air and secondary gas air, working pressure 4.1 Bar – 6.5 Bar, gas flow 142 L/min – 235 L/min) and then, the calcination was carried out during 30 s – 40 s in the stainless-steel crucible, obtaining a uniform calcination of the material due the high temperatures supplied by the plasma.

The treatment performed to each sample, as well as the code assigned to each of them is shown in Table 1.

Subsequently, the thermophosphates obtained were allowed to cool and were then ground using Retsch planetary ball mill Pm 400 for 5 minutes and then using Fritsch Analysette 3 Pro they re-sieved through 200 mesh for 5 minutes, to obtain the particle size ≤ 0.075 mm. Figure 1 describes the characteristics of the plasma reactor used.

***Table 1**. Experimental parameters of treatments carried out by plasma torch.*

Description of sample	Sample code	Current intensity [A]	Mineral:WFP[1] [wt.%:wt.%]	Time [s]
Thermophosphates obtained by plasma torch treatment from Iza phosphoric rock (TPPT – IZA)	M1	30	65:35	30
	M2		65:35	40
	M3		70:30	30
	M4		70:30	40
	M5	45	70:30	40
	M6		65:35	30
	M7		70:30	30
	M8		65:35	40
Thermophosphates obtained by plasma torch treatment from Pilar and Ceibita Sogamoso phosphoric rock (TPPT – PC)	M9	30	65:35	40
	M10		65:35	30
	M11		70:30	30
	M12		70:30	40
	M13	45	70:30	30
	M14		70:30	40
	M15		65:35	30
	M16		65:35	40

[1] Mineral: Wheat flour paste.

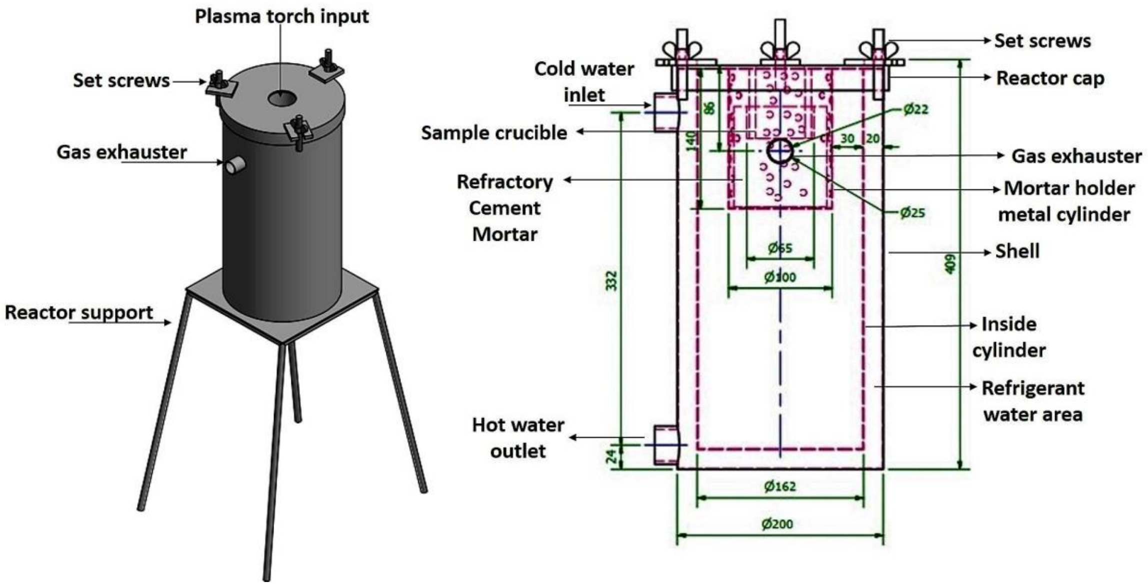

***Figure 1.** Schematic of the Plasma Torch reactor.*

2.3 Analytics methods

Using an X-ray diffractometer GNR XRD 600 of Cu Kα radiation (λ=1.5418Å), the samples were scanned in the diffraction angle range (*2Θ*) varying from *20° to 70°*, with step of 0.02 and integration time 35 min, the crystal structure of the thermophosphates was examined. This process was used to identify and quantify the crystalline phases present in thermophosphates with the Xpert Highscore version 3.0 software of PANalytical. The quantification of phases was carried out by Rietveld refinement method.

The elemental chemical composition was determined by X-Ray Fluorescence (XRF) using the Epsilon 4^{TM} equipment of Malvern PANalytical and the Omnian software, and then, the results reported as most probable oxides content.

The assimilable phosphorus quantification was carried out taking as reference the AOAC standards: 963.03, 960.02 960.03 and 993.31 [10]. The Shimadzu spectrophotometer UV-VIS 1601^{TM} was used as an analytical instrument, with a wavelength of 400 nm, a double beam of light and photodiode detector silicon.

3. RESULTS AND DISCUSSION

3.1 Crystalline phases analyses by XRD

In order to analyze the XRD diffraction peaks of thermophosphates obtained from different treatment carried out with the plasma torch to the Iza (TPPT – IZA) and the Pilar and Ceibita Sogamoso (TPPT – PC) samples, the following PDF and ICSD database standards were used: fluorapatite carbonate (PDF 33-1161), apatite – (CaOH) (PDF 24-33), apatite – CaF (ICSD 94082), feldspar alkaline (ICSD 158304), fosterite (ICSD 64741), calcite (ICSD 18165) and quartz low (PDF 46-1045).

The XRD patterns obtained for TPPT – IZA samples treated applying 30 A to plasma torch are presented in the Figure 2. Additionally, the percentage of phases identified for these samples are presented in Table 2. It is evident that the percentages of the apatite phases are 60.3, 58.2, 61.3 and 53.7 % for M1, M2, M3 and M4 respectively. The M1 sample presented one of the highest conversions of fluorapatite carbonate and additionally the results of the XRF analyses presented in Table 4, shows the highest concentration of P_2O_5, corresponding to 27.0 wt.%, indicating that the best experimental conditions for obtaining this type of thermophosphate were (30 A, 30 s, 65 wt. % of PRIZA).

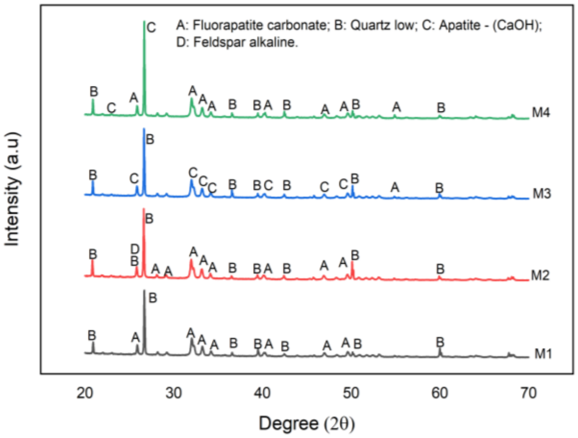

Figure 2. *Diffractograms of thermophosphates obtained by plasma torch (TPPT – IZA), applying 30 A.*

The crystalline phases identified in M1 and M2 were fluorapatite carbonate, while in M3 and M4, appear the phases apatite – (CaF) and apatite – (CaOH), all determined by experimental conditions, thermal stability and the stoichiometric ratio Ca/P, according to [11], are those that establish the structural substitutions. In the M2 sample additionally were identified the phases of quartz low and feldspar alkaline ($Al_1K_{0.8}Na_{0.2}O_8Si_3$), the first being the product of the thermal decomposition of the second, according to the mechanism proposed by [12].

The presence of secondary phases such as aluminophosphates is attributed to the geological conditions of phosphoric rocks, which due to weathering processes release orthophosphate ions, forming the secondary phases [13]. The thermal treatment of phosphoric rocks that contain aluminophosphates form new structures in response to the loss of water of hydration which is caused by their structural collapse [14] and this would explain the presence of carbonate phases of fluorapatite, apatite-(CaOH) and apatite–CaF, as well as quartz and quartz low [15-16].

Table 2. *Results of crystalline phases quantification carried out by Rietveld method to IZA samples after treatment with the plasma torch.*

Sample	Rexp	Rwp	GOF	Crystalline phases	Percentage [%]
M1	4.28	6.03	4.11	Fluorapatite carbonate	60.3
				Quartz low	39.7
M2	4.18	6.07	4.63	Fluorapatite carbonate	58.2
				Quartz low	40.4
				Feldspar alkaline	1.4
M3	4.32	5.45	3.31	Apatite – (CaOH) %,	61.3
				Quartz low	38.7
M4	4.23	5.82	4.07	Apatite – (CaOH) %,	53.7
				Quartz low	46.3
M5	4.24	5.39	2.98	Apatite –(CaF)	58.3
				quartz low	41.6
				fosterite	0.1
M6	4.20	5.03	3.84	Fluorapatite carbonate	64.3
				Quartz low	35.7
M7	4.28	5.26	3.21	Apatite – (CaOH)	60.6
				Quartz low	39.4
M8	4.43	5.68	3.32	Fluorapatite carbonate %	87.3
				Quartz low	9.0
				Calcite	3.7

For its part, the XRD patterns obtained for TPPT–IZA samples treated applying 45 A to plasma torch are presented in the Figure 3 and the percentage of phases identified for these samples are presented in Table 2. The results indicate that the highest conversion occurred in M6 and M8, obtaining the carbonates of fluorapatite, while conversions were low in the other phases (≤ 64 %).

According to [14], this is due to the progressive concentration of fluorapatite carbonate after calcination and the combination of carbon dioxide which increase the degree of phosphate in calcined products [15].

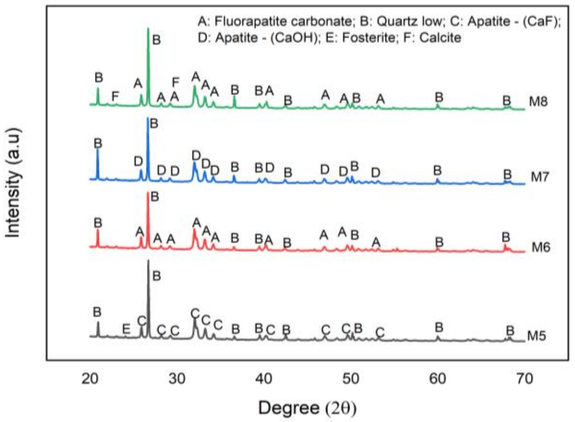

Figure 3. *Diffractograms of thermophosphates obtained by plasma torch (TPPT – IZA), applying 45 A.*

On the other hand, the results of crystalline phases identified by XRD analyses carried out on samples M9 to M16 (TPPT-PC) are shown in Figure 4 and Figure 5. The quantification of phases identified in theses samples are shown in Table 3.

The standard of the PDF and ICSD database used to identify the main phases in these samples are: fluorapatite carbonate (ICSD 71855 – ICSD 71854), apatite – (CaOH) (PDF 24-33, ICSD 1711), apatite – CaF (ICSD 94082), feldspar alkaline (ICSD 158304), fosterite (ICSD 64741), calcite (ICSD 18165 – ICSD 18166), hatrurite (ICSD 81100), coesite (ICSD 172295) and quartz low (ICSD 83849 – ICSD 62406 – ICSD 200726).

The results of the identification of crystalline phases indicate the presence of calcite, which is typical of the original source, according to [16], define it as phosphate quartz sands with the presence of carbonates.

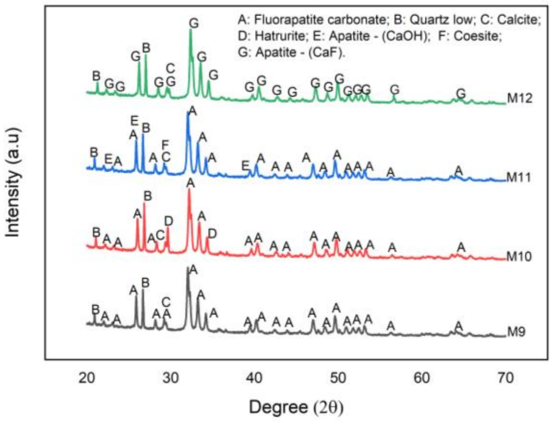

Figure 4. *Diffractograms of thermophosphates obtained by plasma torch (TPPT – PC) applying 30 A.*

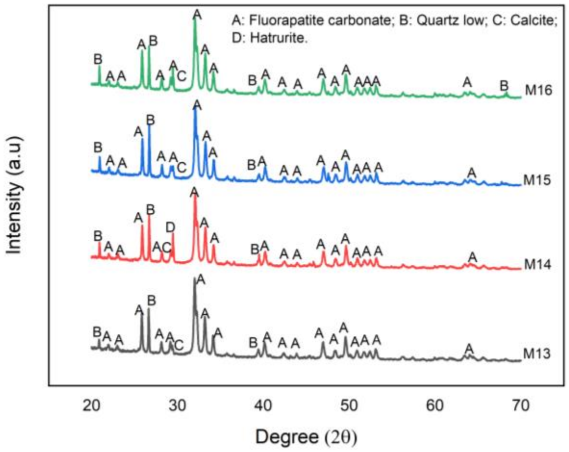

Figure 5. *Diffractograms of thermophosphates obtained by plasma torch (TPPT – PC) applying 45 A.*

According with the Figure 4 and the Figure 5, as well as with the Table 3, the conversion to apatites in M9, M10, M11, M12, M13, M14, M15 and M16 samples is: 88.1 %, 83.1 %, 60.6 %, 88.1 %, 89.2 %, 82.0 %, 87.7 % and 88.0 %, respectively. All of them in weight percentages. The M12 sample shows one of the highest conversion to apatite-(CaF) and according to the XRF analyses shown in Table 6, obtained the highest concentration, corresponding to 33.12 wt.% P_2O_5, indicating that the best experimental conditions for obtaining this

Table 3. *Results of crystalline phases quantification to PC samples after treatment with the plasma torch.*

Sample	Rexp	Rwp	GOF	Crystalline phases	Percentage [%]
M9	4.50	5.46	3.00	Fluorapatite carbonate	88.1
				Quartz low	9.8
				Calcite	2.1
M10	4.44	5.59	3.60	Fluorapatite carbonate	83.1
				Quartz low	10.1
				Calcite	4.9
				Hatrurite	1.9
M11	4.48	6.10	3.80	Fluorapatite carbonate	60.6
				Apatite – (CaOH)	26.0
				Quartz low	8.7
				Calcite	1.2
				Coesite	3.6
M12	4.66	5.46	3.02	Apatite – (CaF)	88.1
				Quartz low	10.3
				Calcite	1.6
M13	4.51	5.04	3.06	Fluorapatite carbonate	89.2
				Quartz low	9.2
				Calcite	1.6
M14	4.76	5.14	4.05	Fluorapatite carbonate	82.0
				Quartz low	10.3
				Calcite	6.1
				Hatrurite	1.5
M15	4.43	5.29	3.33	Fluorapatite carbonate	87.7
				Quartz low	9.3
				Calcite	3.0
M16	4.44	5.64	3.51	Fluorapatite carbonate	88.0
				Quartz low	9.2
				Calcite	3.7

type of thermophosphate is (30 A, 40 s, 70 wt.% of PRIZA).

The above is due to decomposition of adsorbed water and the burning of organic matter, largely due to the combination of carbon dioxide there by increasing the degree of phosphate in the calcined product [15]. According to [4] achieved high conversions of P_2O_5 through heat treatment of Syria phosphoric rock and without using additives, as shown in this work.

The samples M13 to M16 reported the higher conversion among the TPPT–PC ones, due to the nature of the raw material and the intensity of current applied.

The calcite phase is present in all the samples and is typical of original source, which, according to [17], define it as phosphate quartz sands with the presence of carbonates. Regarding silicon oxides and silicates, they are first presented as low quartz and coesite, and subsequently as hatrurite in M10.

3.2 Chemical composition analyses by XRF.

The results of the elemental analysis carried out by XRF to samples obtained from PRIZA and TPPT–IZA are shown as most probable oxides in Table 4 and their quality indexes are presented in Table 5.

Table 4. *Chemical composition of thermophosphates obtained by plasma torch TPPT–IZA (30 A – 45 A).*

	Chemical composition of samples (wt.%)								
Oxide	PRIZA	M1	M2	M3	M4	M5	M6	M7	M8
Na_2O	0.32	0.00	0.00	0.00	0.24	0.35	0.00	0.00	0.19
MgO	0.14	0.19	0.18	0.19	0.17	0.18	0.19	0.19	0.21
Al_2O_3	3.29	3.25	3.27	3.19	3.36	3.33	3.22	3.31	3.14
SiO_2	29.93	30.26	30.42	31.06	31.21	30.62	29.67	29.87	29.46
P_20_5	27.05	27.00	26.62	26.44	26.67	26.59	26.31	26.46	26.24
SO_3	0.16	0.24	0.20	0.19	0.18	0.21	0.25	0.21	0.20
K_2O	0.30	0.45	0.45	0.42	0.41	0.43	0.47	0.45	0.48
CaO	37.05	36.80	37.08	36.65	35.96	36.48	37.97	37.51	38.03
TiO_2	0.14	0.14	0.14	0.14	0.14	0.14	0.16	0.15	0.14
Fe_2O_3	1.28	1.41	1.40	1.46	1.39	1.41	1.50	1.42	1.49
Others	0.34	0.26	0.26	0.26	0.26	0.27	0.27	0.43	0.43
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Table 5. *Quality indexes of thermophosphates TPPT – IZA.*

Sample	CaO/P_2O_5	MgO/P_2O_5	$R_2O_3(Al_2O_3+Fe_2O_3)/P_2O_5$
M1	1.360	0.007	0.170
M2	1.390	0.007	0.180
M3	1.390	0.007	0.180
M4	1.350	0.006	0.180
M5	1.370	0.007	0.180
M6	1.440	0.007	0.180
M7	1.420	0.007	0.180
M8	1.450	0.008	0.180

According to the Table 4, the PRIZA used as raw material for TPPT-IZA samples is constituted by 27.05 wt.% of P_2O_5, while in the thermophosphates M1 until M8 lower concentrations (≤ 27.00 wt.%) were detected, which is due to a loss on ignition (LOI) during the thermal treatment [18].

An established method to determine the quality indexes of phosphate rock and phosphate fertilizers was reported by [19] and [20] as following: $CaO/P_2O_5 \leq 1.6$, $MgO/P_2O_5 \leq 0.022$, R_2O_3 $(Al_2O_3+Fe_2O_3)$ $/P_2O_5 \leq 0.1$, and the results are displayed in Table 5 for the thermophosphates of Table 4.

In Table 5 it can be observed that all the samples comply with the quality parameters (CaO/P_2O_5; MgO/P_2O_5) and therefore are suitable for acidification processes and the production of phosphoric acid, however, the results of the R_2O_3/P_2O_5 ratio exceed the threshold and affect the solubility of fertilizers as a final product according to [20].

The PRPC raw material reported a concentration of 32.07 wt.% P_2O_5, while the thermophosphates M9, M10, M11, M13, M14, M15 and M16 reported concentrations less than this due to a loss on ignition (LOI) and high temperatures generated for plasma torch reactor, promote the speed of heat transfer and in turn the speed of chemical reactions [20]. On another hand, the M12 sample obtained a concentration of 33.12 wt.% P_2O_5, considered the highest and surpassing the raw material PRPC, which justifies the use of plasma for the calcination of PR, as reported by [21-22], when obtaining concentrations > 35.00 wt.% P_2O_5 by subjecting the minerals from the Karantau Basin (Russia) to heat treatment. As a result of the previous analysis, the sample M12 show the optimal conditions for heat treating the PRPC in the plasma torch reactor: 30 A, 40 s, 70 wt.% of PRPC.

In the Table 6 is reported the content of most probable oxides calculated from results obtained by elemental XRF analysis for TPPT–PC, in which the samples M13 to M16 had concentrations ≤ 31.8 wt.% of P_2O_5, showing that the higher the current intensity decreases the yield and generates greater energy consumption in the production of fertilizers.

Table 6. *Chemical composition of thermophosphates obtained by plasma torch TPPT–PC (30 A – 45 A).*

	Chemical composition of samples (wt.%)								
Oxide	PRPC	M9	M10	M11	M12	M13	M14	M15	M16
Na_2O	0.52	0.74	0.00	0.39	0.91	0.53	0.70	0.45	0.50
MgO	0.10	0.16	0.15	0.15	0.16	0.17	0.18	0.14	0.15
Al_2O_3	1.22	1.10	1.23	1.32	1.18	1.29	1.37	1.18	1.18
SiO_2	9.76	9.57	9.91	10.51	10.27	10.18	10.19	9.74	9.50
P_20_5	32.07	31.78	30.96	31.86	33.12	31.29	31.84	30.90	31.65
SO_3	0.38	0.49	0.44	0.42	0.41	0.43	0.42	0.43	0.45
K_2O	0.13	0.27	0.29	0.25	0.23	0.27	0.27	0.29	0.29
CaO	54.43	54.48	55.66	53.86	52.49	54.30	53.30	55.27	54.64
Fe_2O_3	0.85	1.04	0.98	0.91	0.89	0.91	0.87	0.97	1.02
Others	0.54	0.39	0.38	0.34	0.34	0.63	0.85	1.81	0.63
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Table 7. *Quality indexes of thermophosphates TPPT – PC.*

Sample	CaO/P_2O_5	MgO/P_2O_5	$R_2O_3(Al_2O_3+Fe_2O_3)/P_2O_5$
M9	1.710	0.005	0.070
M10	1.790	0.005	0.070
M11	1.690	0.005	0.070
M12	1.580	0.005	0.060
M13	1.740	0.005	0.070
M14	1.700	0.005	0.070
M15	1.780	0.005	0.070
M16	1.730	0.005	0.070

Another parameter to consider is SiO_2, which, according to the Government of Huila, should be in a range of 5-10 wt.%, to avoid the excessive formation of sediments inside the kiln during calcination; in the case of samples M9 to M16, they all comply by avoiding losses of thermally processed materials.

On the contrary, the TPPT–IZA samples present concentrations means of $SiO_2 \geq 29$ wt.%, and this is due to the chemical characteristics of the original mineral.

The quality indexes were calculated for TPPT–PC and are shown in Table 7, in which is evident that the sample M12 is the only one that complies the quality parameter CaO/P_2O_5. The other samples would require higher amounts of acid for the production of fertilizers [22]. The parameters MgO/P_2O_5 and R_2O_3/P_2O_5 ratio are within the ranges established by [19] and therefore would not affect the solubility of the thermophosphates produced.

3.3 UV visible spectrophotometry analysis.

The results of assimilable phosphorus quantification, as well as, the solubility index for TPPT–IZA and TPPT–PC are shown in Table 8.

The results shown in this table indicate that for TPPT–IZA the sample M3 obtained the highest concentrations of both assimilable phosphorus (3.07 %) and solubility index (11.60 %), under conditions of 30 A, 30 s, 70 wt.% of PRIZA. On the other hand, for TPPT–PC the sample M10 obtained the highest concentrations of both assimilable phosphorus (4.83 %) and solubility index (15.59 %), under conditions of 30 A, 30 s, 65 wt.% of PRPC, demonstrating that this current intensity improves the performance of the mentioned variables.

Higher values of the solubility index and the assimilable phosphorus were not obtained, perhaps by the nature of the origin mineral and the physicochemical properties of the phosphates as indicated by [23], the non-use of additives to improve the yield, and the characteristics of the plasma torch method, all of which greatly influence the results.

Table 8. *Assimilable phosphorus quantification and solubility index TPPT–IZA and TPPT–PC.*

Sample	P_2O_5 Total [wt.%]	P_2O_5 Assimilable [%]	Solubility Index [%]
M1	27	2.45	9.09
M2	26.62	2.70	10.14
M3	26.44	3.07	11.60
M4	26.67	2.98	11.17
M5	26.59	2.96	11.12
M6	26.31	2.89	10.99
M7	26.46	2.66	10.05
M8	26.24	2.48	9.46
M9	31.78	4.03	12.69
M10	30.96	4.83	15.59
M11	31.86	2.64	8.28
M12	33.12	3.47	10.49
M13	31.29	3.14	10.04
M14	31.84	3.09	9.72
M15	30.9	3.03	9.80
M16	31.65	3.41	10.78
PRIZA	27.05	3.62	13.38
PRPC	32.07	4.02	12.54

3.4. Energy consumption analysis.

A study carried out by [24], on obtaining thermophosphates by means of an electric furnace using the same mineral sources, made it possible to compare energy consumption and show the economic benefits of plasma torch, which are observed in Table 9.

Table 9. *Energetic consumption for thermophosphates produced by electric furnace and plasma torch.*

Source	Electric oven (KW)	Plasma torch (KW)	Calcination time (h)	(KW-h)	(KW-h/Kg)
IZA	2.40	-	3.00	7.20	514.30
PC	2.40	-	3.00	7.20	514.30
IZA	2.40	-	5.00	12.00	857.14
PC	2.40	-	5.00	12.00	857.14
IZA	-	3.24	0.0083	0.027	0.64
PC	-	3.24	0.0083	0.027	0.64
IZA	-	4.86	0.0111	0.054	1.28
PC	-	4.86	0.0111	0.054	1.28

According to Table 9, the amount of energy consumed in the electric oven is 7.2 kW-h and 12.0 kW-h respectively. These data that show energy consumption is quite high related to [25] who indicate that the energy consumption for an industrial electric oven is around 12.0 kW-h/Kg-14.0 kW-h/Kg, while [26] report 12.0 kW-h/Kg for phosphorus produced in the electric oven. The samples treated by plasma torch had a low energy consumption of 0.64 kW-h/Kg and 1.28 kW-h/Kg in comparison with the results obtained by means of an electric oven; according to [27], corroborates plasma energy consumption as 1.1 kW-h/Kg and [28] of 0.8-1 kW-h/Kg, values very close to those used in this research. Therefore, the plasma torch method represents a viable alternative for obtaining thermophosphate fertilizers and improving the characteristics and performance of the process in future research.

4. CONCLUSIONS

The most representative results of the total phosphorus, assimilable phosphorus and solubility indexes of the TPPT–IZA, correspond to 27.00 wt.% P_2O_5 (M1), 3.07 % P_2O_5 (M3) and 11.60 % (M3), while for the TPPT–PC are reported as 33.12 wt.% P_2O_5 (M12), 4.83 % P_2O_5 (M10) and 15.59 % (M10), demonstrating that under current intensity 30 A and calcination times of 30 s, improve the performance of the mentioned variables.

The results of Rietveld analysis show that the predominant crystalline phase in thermophosphates obtained by the plasma torch method is fluorapatite carbonate, but also report new structures as apatite–(CaF) and apatite–(CaOH), product of the thermal treatment, experimental conditions and structural substitutions. The used method to determine the quality indexes in this paper, allowed to verify that the calculated variables for thermophosphates TPPT–IZA and TPPT–PC, meet the quality standards for the fertilizers.

The design of the plasma torch reactor allowed the obtaining of thermophosphates with low energy consumption, corresponding to 0.64 kW-h/Kg-1.28 kW-h/Kg, in comparison with the results obtained by the electric furnace, which are higher and do not meet the expectation of reducing production costs. Additionally, it could be experimentally verified that the current intensity of 30 A allows an energy saving of 50.0 %, compared to the intensity of 45 A.

5. ACKNOWLEDGMENT

Mayra Mojica, MSc. In Digital Technologies Applied to Education, National Learning Service Sena, Mining Center, Sogamoso, Colombia; Enterprise Phosphate Boyacá, Pesca, Colombia; National Learning Service Sena, Mining Center, Sogamoso, Colombia and Sennova, Pedagogical and Technological University of Colombia Irme, Sogamoso, Colombia

6. REFERENCES

[1] CRU Consulting. "Roca Fósfórica Caracterización y análisis de mercado internacional de minerales en el corto, mediano, y largo plazo con vigencia al año 2035", CRU Consulting, Santiago de Chile, Chile, Tech. Rep. C-378359-003, 2018.

[2] Ministerio de Minas y Energía República de Colombia. "Plan Nacional de Desarrollo Minero con Horizonte a 2025. Minería responsable con el territorio", Ministerio de Minas y Energía República de Colombia, Bogotá, Colombia, Tech Rep UPME, 2017.

[3] CRU Strategies. "Estudio para caracterizar el mercado nacional e internacional de los minerales estratégicos", CRU Strategies, Santiago de Chile, Chile, Tech. Rep. ST420686-

13, 2013.

[4] A. Watti, M. Alnjjar, A. Hammal," Improving the specifications of Syrian raw phosphate by thermal treatment", *Arab J Chem*, vol. 9, no. 6, pp. S637-S642, September 2016.

[5] A. Z. M. Abouzeid, "Physical and thermal treatment of phosphate ores - An overview", *Int J Miner Process*, vol. 85, no. 4, pp. 59–84, January 2008.

[6] E. Gomez, D. A. Rani, C. R. Cheeseman, D. Deegan, M. Wise, A.R. Boccaccini, "Thermal plasma technology for the treatment of wastes: A critical review", *J Hazard Mater*, vol. 161, no. 2-3, pp. 614–626, May 2009.

[7] F. Correa-Méndez, A. Carrillo-Parra, J. G. Rutiaga-Quiñones, F. Márquez-Montesino, H. González-Rodríguez, E. Jurado Ybarra, *et al*. "Distribución granulométrica en subproductos de aserrío para su posible uso en pellets y briquetas", *Rev Mex Cienc. Forestales*, vol. 5, no. 25, pp. 52–63, september 2014

[8] C. Morales, A. Nieto, L. Quiroga, M. Quicazan, "Method Validation and Determination of Soluble and Insoluble Dietary Fiber in Wheat Flour and Bread", *Vitae*, vol. 19, no. 1, pp. 340–342, 2012.

[9] J. S. Echeverry, "Diseño de maquina prensadora para hacer briquetas de biomasa", B. Eng. Thesis, Universidad de los Andes, Cundinamarca, Colombia, 2006.

[10] AOAC, Official Methods of Analysis., 15th Ed, Virginia, Association Official of Analitycal Chemists, 1990.

[11] K. Tõnsuaadu, K.A. Gross, L. Pluduma, M. A. Veiderma, "Review on the thermal stability of calcium apatites", *J Therm Anal Calorim*, vol. 110, no. 2, pp. 647–659, November 2012.

[12] J. X. Chao, J. P. Xia, C. Q. Yang, Z. S. Zhang, X. J. Ren, "Research on the thermal decomposition process of K-feldspar-$CaSO_4$-CaO system", *Adv Mater Res*, vol. 734–737, pp. 916–920, August 2013.

[13] M. C. M. Toledo, "Os fosfatos aluminosos da série da crandallita - uma revisão" *Rev do Inst Geológico*. vol. 20, no. 1-2, pp. 49–63, 1999.

[14] E. A. B. Francisco, L. I. Prochnow, M. C. M. De Toledo, V. C. Ferrari, S. L. De Jesus, "Thermal treatment of aluminous phosphates of the crandallite group and its effect on phosphorus solubility", *Sci Agric*, vol. 64, no. 3, pp. 269–274, June 2007.

[15] F. Jaballi, M. Felhi, M. Khelifi, N. Fattah, K. Zayani, N. Abbes, *et al*, "Mineralogical and geochemical behavior of heated natural carbonate-apatite of the Ypresian series, Maknassy-Mezzouna basin, central Tunisia", *Carbonates and Evaporites*, vol. 34, no. 4, pp. 1689–1702, July 2019.

[16] S. Elgharbi , K. Horchani-Naifer, M. Férid, "Investigation of the structural and mineralogical changes of Tunisian phosphorite during calcinations", *J*

Therm Anal Calorim, vol 119, no. 1, pp. 265–271, January 2014.

[17] H. L. Cuy, A. L. Girón, "Correlación estratigráfica y caracterización petrográfica de algunos niveles fosfáticos de la formación hermitaño (Kse) aflorantes en los municipios de Iza (vereda centro) y Sogamoso (vereda Pilar y Ceibita)", B. Eng. thesis, Universidad Pedagógica y Tecnológica de Colombia, Boyacá, Colombia, 2016.

[18] A. Ziv, A. Tamlr, "Part I . Development , Theory and Modeling". *Can J Chem Eng*, vol. 71, no. 5, pp. 771–783, October 1993.

[19] FAO, *Utilización de las rocas fosfóricas para una agricultura sostenible*, 13th Ed, Roma, Editorial FAO, 2017.

[20] Unión Temporal G.I. Georecursos, "Analisis de la estructura productiva y mercados de la roca fosforica" Union Temporal G.I. Georecursos, Bogotá, Colombia, Tech. Rep 1517-08-2005.

[21] N. Venkatramani, "Industrial plasma torches and applications", *Curr Sci*, vol. 83, no. 3, pp. 254–262, 2002.

[22] A. L. Mosse, V. V. Pechkovsky, E. D. Dzyuba, L. I. Krasovskaya, "Production of condensed phosphate by plasma chemical treatment of phosphate raw material", *Plasma Chem Plasma Process*, vol. 5, no. 3, pp. 275–282, September 1985.

[23] R. Guilmour, *Phosphoric Acid*, 1st Ed, CRC Press, Florida, 2014.

[24] E. M. El Ouardi, "Effect of temperature and residence time of calcination phosphate on the chemical reactivity: Application to the case of Bouchane phosphate (Morocco)", *Int J Innov Appl Stud*, vol. 4, no. 2, pp. 387–407, October 2013.

[25] N. M. Espinel Pérez, "Aprovechamiento de roca fosfórica, por vía térmica, para la obtención de termofosfatos", *Rev Invest*, vol. 12, no. 2, pp. 113–133, August 2020.

[26] M. B. Hocking, *Handbook of Chemical Technology and Pollution Control*, 3rd Ed. British Columbia, Academic Press, 2006.

[27] E. R. Riegel, J. A. Kent, *Riegel's Handbook of Industrial Chemistry*, 9st Ed. New York,Van Nostrand Reinhold, 1992.

[28] P. Taboada-gonzález, "La tecnología de plasma y residuos sólidos", *La Tecnol plasma y residuos sólidos*, vol. 13, no. 2, pp. 51–56, August 2009.