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PHOSPHATE VALORIZATION BY DRY CHLORINATION ROUTE

N. Kanari,[a]*, N. Menad[b], F. Diot[a], E. Allain[a], J. Yvon[a]

[a]Université de Lorraine, GeoRessources Laboratory, France
[b]BRGM, Orléans, France

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Abstract

This work deals with the extraction of phosphorus chlorinated compounds from phosphate materials using chlorination with gaseous chlorine. An industrial sample of dicalcium phosphate dihydrate, after transformation into calcium pyrophosphate ($Ca_2P_2O_7$), is subjected to reactions with Cl_2+CO+N_2 and Cl_2+C+N_2 at temperatures ranging from 625 to 950 °C using boat experiments. Gathering results of the thermodynamic predictions and TG/DT analysis with those of SEM and XRD examinations of the chlorinated residues allowed the interpretation of phenomena and reactions mechanism occurring during the calcium pyrophosphate carbochlorination.

Reaction rate of $Ca_2P_2O_7$ by Cl_2+CO+N_2 at 950 °C is slowed down due to the formation of a $CaCl_2$ liquid layer acting as a barrier for the diffusion of the reactive gases and further reaction progress. While, the carbochlorination with Cl_2+C+N_2 led to almost full chlorination of $Ca_2P_2O_7$ at 750 °C and the process proceeds with an apparent activation energy of about 104 kJ/mol between 625 and 750 °C.

Carbochlorination technique can be considered as an alternative and selective route for the valorization of low grade phosphates and for the phosphorus extraction from its bearing materials

Keywords: *Dicalcium phosphate dihydrate; Calcium pyrophosphate; Chlorination;Valorization*

1. Introduction

Phosphorus, based in a vast variety of the phosphorus minerals, especially phosphates, is vital for flora,fauna and human life. Most of phosphate bearing materials are used in the agriculture as fertilizer and another important end use of phosphates is detergency. Further, it seems that there are no consistent substitutes for phosphorus in agriculture. According to available statistic data [1], the world production of phosphate rock (26-34 % P_2O_5) has more than tripled during the last fifty years reaching 217 million tons by 2012. With this increase production rate and by taking into account that the phosphate natural resources are limited, the depletion of the economically viable phosphorus reserves is evident within a near future. One way to overcome this difficulty should be the exploitation and upgrading of low grade phosphate ores and recycling of the phosphorus constituents contained in the wasted materials. A coherent overview of the techniques (physical and thermal routes) used for producing high-grade phosphate products suitable for fertilizers and other phosphate compounds is given elsewhere [2].

Thermal route is also used for the reduction of phosphates by carbon in presence of SiO_2 at temperatures, often, as high as 1600°C. The elemental phosphorus is produced followed by its subsequent oxidation to phosphorus pentoxide which is an important precursor for the H_3PO_4 synthesis. The research works related to the action of gaseous chlorine on the phosphates are not found in the literature or they are based on old studies. Recent few works are focused on the behaviors of phosphorus compounds during removal of heavy metals contained in the sewage sludge ash using thermochemical methods, especially, chlorination [3-5]. However, a good number of investigations are devoted to the chlorination technique for the separation and extraction of valuable metals from raw and residual materials [6-13]. Other reports concerned the reactivity and kinetics of interaction of chlorine with several rare earth elements oxides such as CeO_2 [14], Sm_2O_3 [15], Y_2O_3 [16], Nd_2O_3 [17] and La_2O_3 [18].

In this context, this study is devoted to the possibility of the phosphate valorization and extraction of phosphorus chlorinated compounds by dry chlorination route. As the first step of the investigation, the results presented here are almost related to the reaction of dicalcium phosphate dihydrate ($CaHPO_4 \cdot 2H_2O$) with Cl_2+CO+N_2 and

* *Corresponding author: ndue.kanari@univ-lorraine.fr*

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Cl_2+C+N_2 under isothermal conditions. Both thermodynamic and kinetics aspects of the carbochlorination reactions are discussed in order to achieve a selective separation process of the phosphate constituents. This work is an extension of our most important findings concerning the chlorination processes summarized earlier [19], as well as of some kinetics of the chlorination reactions of various oxides in presence of reducing and /or oxidizing atmosphere [20-24].

2. Materials and experimental procedures

A wet sample of dicalcium phosphate dihydrate ($CaHPO_4·2H_2O$), known also as brushite, of industrial origin, is used for this study. $CaHPO_4·2H_2O$ represents about 98.0 % of dried solid of the sample. Raw wet sample is heated at 150°C and X-ray diffraction (XRD) analysis revealed the presence of $CaHPO_4·2H_2O$ and neo-formed monetite ($CaHPO_4$) as main crystallized phases. This sample is mostly used for the carbochlorination tests and it is designated as DCPI. Both samples (wet and dried samples) are subjected to the thermogravimetric (TG) analysis under N_2 atmosphere over 20-1000°C temperature range with a linear heating rate of 5 °C/min. Results are depicted in Fig. 1 as evolution of the percent mass loss (% ML) as a function of the temperature. Solid products obtained at 200 °C, 600°C and 1000°C are examined by XRD. The % ML observed for the wet sample at temperatures lower than 100°C corresponds to the free water removing of the wet brushite sample. Transformation of brushite into monetite occurred between 100°C and 200°C, as confirmed by XRD. The next step of % ML observed at T > 400°C is attributed to the thermal conversion of the monetite into calcium pyrophosphate ($Ca_2P_2O_7$) which is stable up to at least 1000°C.

Charcoal is chosen as carbon bearing substance for the carbochlorination of DCPI. XRD analysis showed two broad diffraction peaks attributed to slightly graphitized carbon structure. Used gases (N_2, CO and Cl_2) are of a high purity (99.9 wt %). Boat chlorination experimental tests were performed in a horizontal setup described previously [22]. This setup is composed of a gas measuring unit followed by a gas purification item and a horizontal electric furnace. The chlorination residues were examined by scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) and XRD.

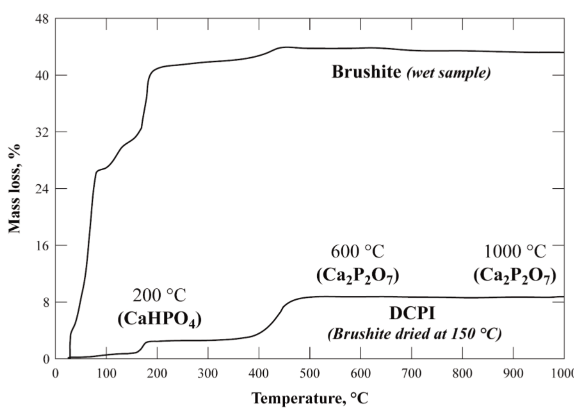

Figure 1. Behavior of the brushite samples (wet and dried sample) under nitrogen atmosphereheated for 10h

3. Results and discussion

3.1. Thermodynamic elements

As noted in the previous section, thermal treatment of $CaHPO_4·2H_2O$ and $CaHPO_4$ under nitrogen atmosphere at temperatures higher than 500°C led to the formation of the calcium pyrophosphate ($Ca_2P_2O_5$). Therefore, $Ca_2P_2O_5$ is considered as only compound for the thermodynamic calculations of chlorination (Cl_2) and carbochlorination (Cl_2+CO; Cl_2+C) reactions. The evolution of free standard energy changes (ΔG°) as a function of the temperature for the overall reactions of $Ca_2P_2O_7$ with Cl_2, Cl_2+CO and Cl_2+C (Eq.1 through 9) are calculated by using thermochemical databases [25-26] and the obtained results are traced in Fig. 2.

$$1/5\ Ca_2P_2O_7 + Cl_2 = 2/5\ CaCl_2 + 2/5\ PCl_3 + 7/10\ O_2 \qquad (1)$$

$$1/5\ Ca_2P_2O_7 + Cl_2 = 2/5\ CaCl_2 + 2/5\ POCl_3 + 1/2\ O_2 \qquad (2)$$

$$1/7\ Ca_2P_2O_7 + Cl_2 = 2/7\ CaCl_2 + 2/7\ PCl_5 + 1/2\ O_2 \qquad (3)$$

$$1/5\ Ca_2P_2O_7 + Cl_2 + 7/5\ CO = 2/5\ CaCl_2 + 2/5\ PCl_3 + 7/5\ CO_2 \qquad (4)$$

$$1/5\ Ca_2P_2O_7 + Cl_2 + CO = 2/5\ CaCl_2 + 2/5\ POCl_3 + CO_2 \qquad (5)$$

$$1/7\ Ca_2P_2O_7 + Cl_2 + CO = 2/7\ CaCl_2 + 2/7\ PCl_5 + CO_2 \qquad (6)$$

$$1/5\ Ca_2P_2O_7 + Cl_2 + 7/10\ C = 2/5\ CaCl_2 + 2/5\ PCl_3 + 7/10\ CO_2 \qquad (7)$$

$$1/5\ Ca_2P_2O_7 + Cl_2 + 1/2\ C = 2/5\ CaCl_2 + 2/5\ POCl_3 + 1/2\ CO_2 \qquad (8)$$

$$1/7\ Ca_2P_2O_7 + Cl_2 + 1/2\ C = 2/7\ CaCl_2 + 2/7\ PCl_5 + 1/2\ CO_2 \qquad (9)$$

Chlorination of $Ca_2P_2O_5$ by chlorine in absence of reducing atmosphere seems to be not feasible since the value of ΔG° are higher than 100 kJ/mol Cl_2 in whole temperature interval studied and whichever is the phosphorus chlorinated species (Fig.2a).

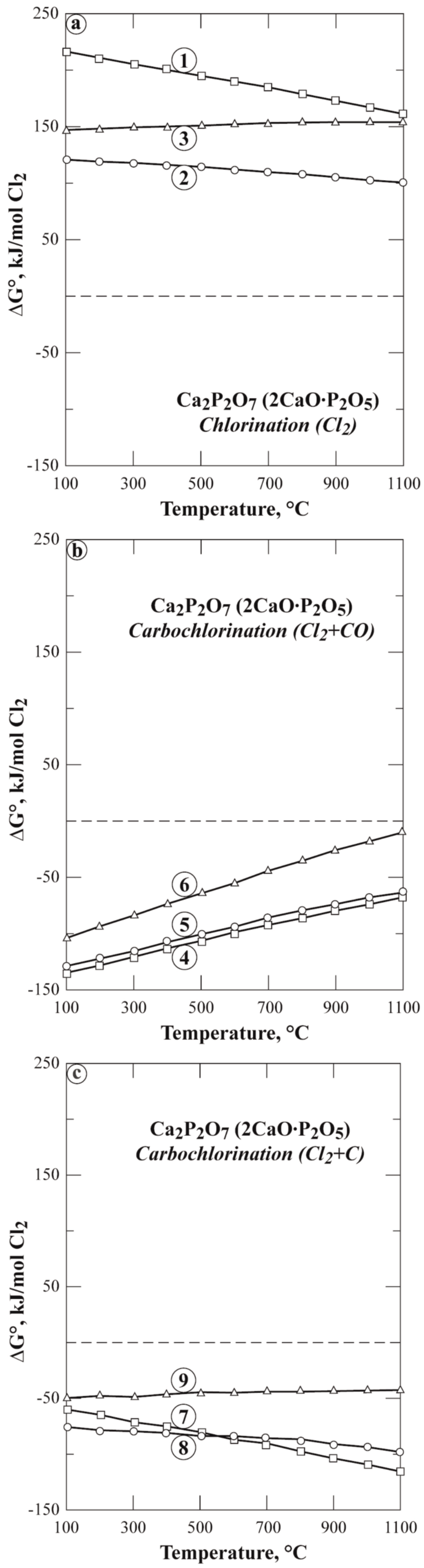

Figure 2. Standard free energy change of the chlorination reactions of the $Ca_2P_2O_7$ with: (a): Cl_2; (b): Cl_2+CO; (c): Cl_2+C

Carbochlorination reactions of the calcium pyrophosphate with Cl_2+CO and Cl_2+C (Fig. 2b and 2c, respectively) are characterized by negative values of the ($\Delta G°$) resulting to a favorable process from thermodynamic point of view.

The phase predominance area diagrams (Fig. 3) for the system Ca-O-Cl and P-O-Cl as a function of temperature and partial pressure of chlorine at two fixed partial pressures of oxygen (pO_2) are established by using HSC Chemistry thermochemical database [26].

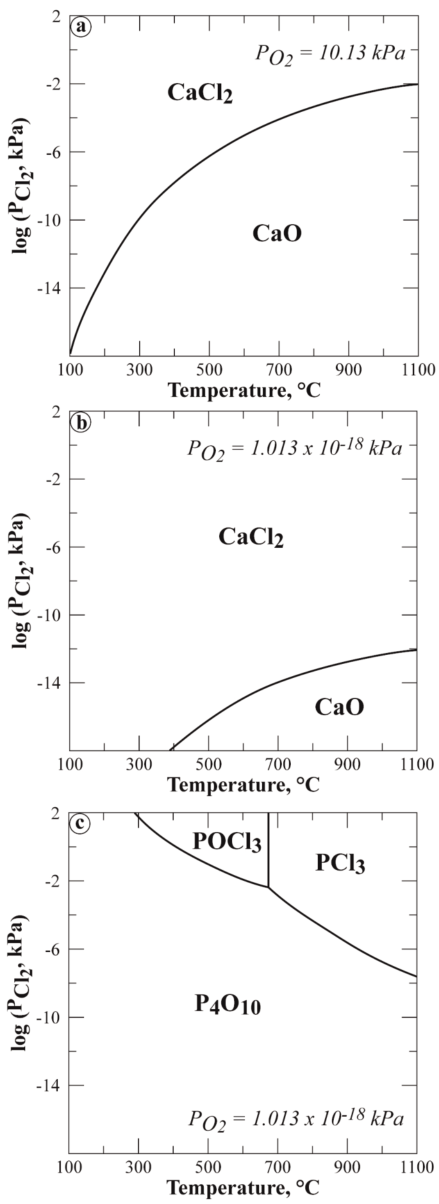

Figure 3. Evolution of the phase stability area as a function of the temperature of: (a): Ca-O-Cl for pO_2 = 10.13 kPa; (b): Ca-O-Cl for pO_2 = 1.013 x 10^{-18} kPa; (c): P-O-Cl for pO_2 = 1.013 x 10^{-18} kPa

Calcium chloride is the predominant phase in Ca-O-Cl system at high partial pressure of chlorine at two chosen values of pO_2 (Fig. 3a and 3b). As could be expected, its predominance area is extended at low oxygen potential (pO_2 = 1.013x10^{-18} kPa). Phosphorus pentoxide (with molecular formula P_4O_{10}) is the only stable phase in the P-O-Cl system for pO_2 = 10.13 kPa at whole temperature range studied (it is not shown in the Fig.3). However, phosphorus oxychloride ($POCl_3$) and trichloride (PCl_3) are the most stable phases for temperatures higher than 300°C and 600°C, respectively for low oxygen potential (pO_2 = 1.013x 10^{-18} kPa) and for high partial pressure of chlorine (Fig. 3c). Decreasing the oxygen partial pressure at values lower than (pO_2 = 1.013x10^{-18} kPa) leads to the formation of phosphorus trichloride as the main phase in equilibrium with P_4O_{10}. In summary, these thermodynamic data indicate that $Ca_2P_2O_7$ can be chlorinated by chlorine only in presence of a reducing agent leading to the formation of the phosphorus chlorinated compounds.

Another interesting thermodynamic knowledge of the above mentioned systems is the vapor pressure of the synthetized chlorides. Fig. 4 gives the vapor pressure of phosphorus, iron and calcium chlorides as a function of reciprocal temperature. It is clear from this figure that the large difference between the vapor pressure of phosphorus chlorides (PCl_3, $POCl_3$, PCl_5) and that of $CaCl_2$ will allow their separation. Similarly, these phosphorus chlorides can also be separated from iron chloride by fractional distillation and/or by controlled cooling of the gas phase. Oxidation of these phosphorus chlorides leads to the synthesis of phosphorus pentoxide.

This thermodynamic study summarizes the basic elements for a selective extraction the phosphorus chlorinated compounds from calcium phosphate during its chlorination, while the kinetics parameters of the process will be revealed through the experimental results described in the following sections.

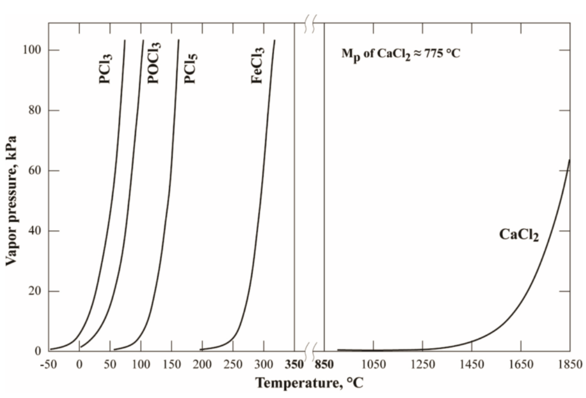

Figure 4. Evolution of the vapor pressure as a function of temperature for several chlorides generated during phosphate chlorination

3.2. Carbochlorination with Cl_2+CO+N_2

The first carbochlorination tests of the DCPI were performed at 950°C on about 3 grams of sample, when the reaction time was varied from 0.5 to 4.0 hours. A gaseous Cl_2+CO+N_2 mixture with a total gas flow rate of 100 L/h containing 30 % Cl_2+CO and having a Cl_2/CO molar ratio equal to 1 is used for the experimental tests. This high gas flow rate aims at avoiding reactive gas starvation and minimizing the mass transfer phenomena. Results are represented in Fig. 5a as an evolution of the sample %ML versus reaction time. A rough examination of these data

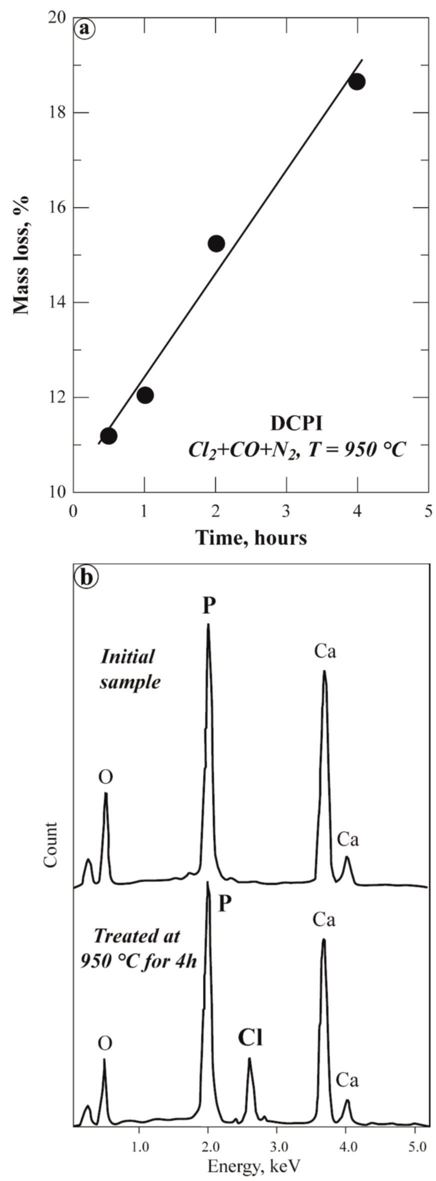

Figure 5. Evolution of the % mass loss of the sample as a function of time during carbochlorination of DCPI at 950 °C (a) and SEM-EDS analysis results (b)

indicates that %ML increased almost linearly with the reaction time. Such %ML curve shapes recall a gas-solid process with an overall rate governed by the reaction rate occurring at infinite slabs and/or the process controlled by the volatilization rate of liquid reaction products.

SEM-EDS spectra of the DCPI initial sample and that of the carbochlorination residue obtained after 4 hours are showed in Fig. 5b. These spectra are almost identical except the presence of chlorine in the chlorination residue which is attributed to $CaCl_2$. Note that all phosphorus chlorinated compounds are highly volatile at 950°C (see Fig. 4). This result suggests that the presence of the liquid calcium chloride affects the chlorination process. It probably covers the DCPI particles acting thus as a barrier for the diffusion of the reactive (Cl_2+CO) gas to the reaction zone. The progress of reaction then depends on the volatilization rate of liquid $CaCl_2$.

To have an idea about the thermal behavior of the calcium chloride, a TG analysis coupled with differential thermal (DT) measurement is performed under nitrogen and the obtained results are shown in Fig. 6.

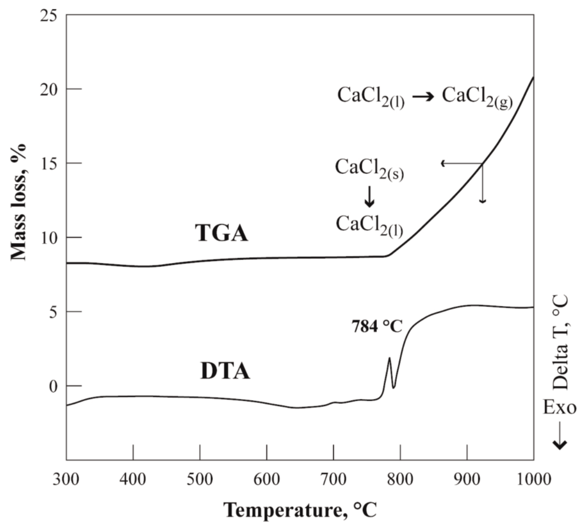

Figure 6. *Results of the TG-DT analysis for the calcium chloride in nitrogen atmosphere*

Data recorded above 750°C are the most important for this study. The endothermic peak at 784°C is attributed to the melting of $CaCl_2$ and it is close to the fusion point (775°C) of the calcium chloride found in the literature [26]. Then, the mass loss recorded beyond this temperature is due to the volatilization of the liquid calcium chloride. Comparison these results with the previous ones, indicates that the carbochlorination rate of the calcium phosphate is affected by the physical properties, i.e. melting point and volatilization rate, of the synthetized calcium chloride. For these reasons it was suggested to achieve the chlorination of DCPI at temperatures lower than the melting point of $CaCl_2$. Further, the solid carbon is used as reducing agent instead of gaseous carbon monoxide which can disperse the solid $CaCl_2$ product creating free paths for the chlorine diffusion.

3.3. Carbochlorination with Cl_2+C+N_2

Mixtures of DCPI and carbon with various C/DCPI molar ratios were prepared. The most appropriate mixture for the carbochlorination tests is chosen to be (DCPI+C) having 1.5 times more carbon than the stoichiometric amount required according to Eq. (7). A gaseous Cl_2+N_2 mixture with a total flow rate of 100 L/h containing 30 % Cl_2 is used for the chlorination. Experimental tests were carried out under isothermal conditions in the range 625 - 900°C for a reaction time of 8 h. Results are plotted in Fig. 7 as evolution of %ML of the DCPI+carbon sample vs temperature.

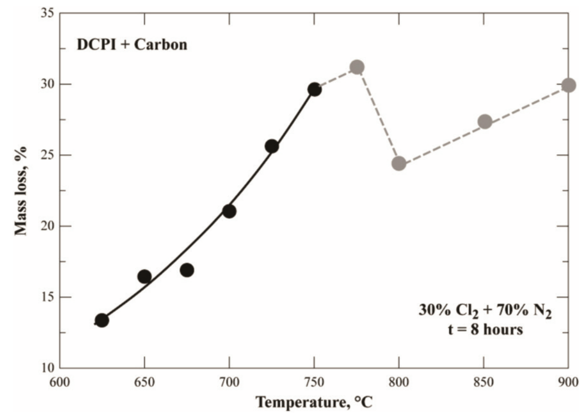

Figure 7. *Evolution of the % mass loss of the sample as a function of the temperature during carbochlorination of DCPI by C+Cl_2+N_2 for 8 hours*

As seen in Fig. 7, a regular and almost exponential function shape of %ML of the sample vs temperature is recorded for the treatment temperature up to 750°C. Afterward, the reaction extent decreased and temperatures as high as 900°C are necessary to have the similar %ML as that obtained at 750°C. Again, the complications of the DCPI carbochlorination at high temperatures are interpreted assuming that the process is affected by fusion of $CaCl_2$. Similar phenomena have been reported previously for the carbochloruration of MgO [22].

Attempts were made to follow the evolution of the elemental and mineralogical composition of the treatment residues at different carbochlorination temperatures. General spectra of the SEM-EDS analysis regarding to the initial sample (DCPI+carbon) and to the carbochlorination residues are grouped in Fig. 8.

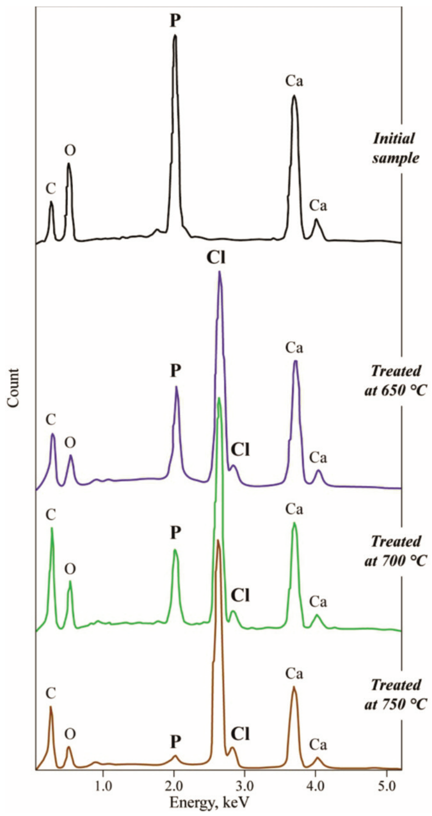

Figure 8. *SEM-EDS spectra of the (DCPI+C) initial sample and treatment residues obtained during carbochlorination by N_2+Cl_2 at different temperatures*

As expected, the initial sample is composed of Ca, P, O and C. The carbochlorination residue at 650°C displays a broad peak of chlorine which can be assigned to calcium chloride. The spectra of the residue obtained at 700°C and especially of that produced from 750°C are characterized by a significant decrease of the phosphorus peak intensity indicating its remove from the residue due to high volatility of the phosphorus chlorides already generated during reaction of Cl_2+CO with DCPI. The gas phase of the carbochlorination tests is cooled at room temperature and no substantial solid condensate is observed during treatment at T≤750°C. This observation reinforces the hypothesis that the most likely chlorinated compounds of phosphorus is PCl_3 having a sufficient vapor pressure at room temperature (see Fig. 4) to leave with exhausted gases.

The results of the XRD analysis applied to the raw sample (DCPI+carbon) and to the treatment residues are summarized in Table 1.

Table 1. *Identified phases in the carbochlorination residues of DCPI at different temperatures*

Temperature, °C	Main crystallized phases identified by XRD
Initial	$CaHPO_4$, $CaHPO_4{\cdot}2H_2O$, C*
625	$Ca_2P_2O_7$, $CaCl_2{\cdot}2H_2O$, C
650	$Ca_2P_2O_7$, $CaCl_2{\cdot}4H_2O$, $CaCl_2{\cdot}2H_2O$, C
675	$CaCl_2{\cdot}4H_2O$, $CaCl_2{\cdot}2H_2O$, $Ca_2P_2O_7$, C
700	$CaCl_2{\cdot}2H_2O$, $Ca_2P_2O_7$, C
725	$CaCl_2{\cdot}2H_2O$, $CaCl_2$, $Ca_2P_2O_7$, C
750	$CaCl_2{\cdot}2H_2O$, $CaCl_2$, C
775	$CaCl_2{\cdot}2H_2O$, $CaCl_2$, C

Main phases of the raw samples are $CaHPO_4$, $CaHPO_4{\cdot}2H_2O$ and carbon. However, as mentioned in the Section 2, $CaHPO_4$ and $CaHPO_4{\cdot}2H_2O$ are transformed into $Ca_2P_2O_7$ at temperatures higher than 400°C. The presence of the $CaCl_2{\cdot}2H_2O$ in the carbochlorination residue generated at 625°C is confirmed by XRD. One may mention that the identification of the hydrate species for $CaCl_2$ ($CaCl_2{\cdot}2H_2O$ and $CaCl_2{\cdot}4H_2O$) is due to the hygroscopic character of the $CaCl_2$ which is transformed into its hydrate forms during sample preparation and XRD measurement.

Note that these hydrated species are the predominant phases of the carbochlorination residues at temperatures higher than 675°C. The calcium pyrophosphate ($Ca_2P_2O_7$) phase is detected by XRD up to 725°C, indicating that the almost full breakdown of the $Ca_2P_2O_7$ structure is achieved beyond this temperature. The presence of carbon in the carbochlorination residues is also detected during the treatment at each temperature between 625 and 775°C. This is due to the fact that the quantity of carbon used is about 1.5 times higher than that of amount assumed for the carbochlorination reactions. Further, some isothermal tests of carbon in Cl_2+N_2 stream between 650 and 750°C (with a % ML less than 1.5 %) indicated that the carbon does not react with this chlorinating gaseous mixture.

These experimental evidences and assumptions (i.e. the phosphorus trichloride is volatilized; calcium chloride remained totally in the residue; carbon is consumed only for the carbochlorination reactions) permit using the percent mass loss for describing the reaction extent for temperatures lower than 775°C. According to the data processing of Fig. 7, the Arrhenius' diagram is established for temperature range 625-750°C and it is exhibited in Fig. 9. It depicts the evolution of the apparent carbochlorination rate (on logarithm scale) as a function of the inverse of the absolute temperature according to the kinetic equation shown early [24]. Note that the figures of the reaction rate deduced from % ML are corrected due to an apparent interaction of the silica sample boat with $C+Cl_2$. A mean value of the apparent activation energy of about 104 kJ/mol is calculated from the data plotting of this Figure. Such a value tends to indicate that the overall reaction rate of the $Ca_2P_2O_7$ chlorination with Cl_2+C is expected to be controlled by the chemical reaction.

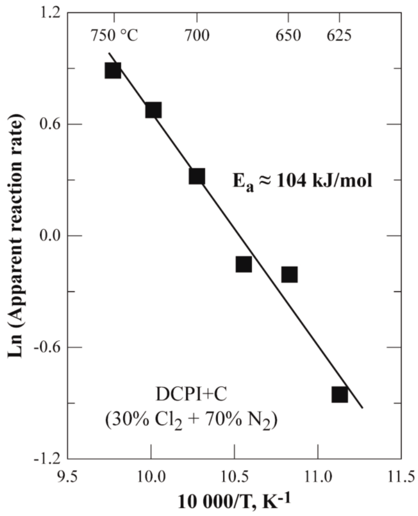

Figure 9. *Arrhenius diagram for the carbochlorination of the DCPI at 625-750 °C*

4. Conclusions

The dicalcium phosphate dihydrate ($CaHPO_4 \cdot 2H_2O$ - bruchite) is converted into calcium pyrophosphate ($Ca_2P_2O_7$) at temperatures higher than 400°C through monetite ($CaHPO_4$) as intermediate phase.

The thermodynamic predictions showed that the chlorination of the $Ca_2P_2O_7$ by only chlorine is not feasible for the temperatures up to 1100°C. The envisaged carbochlorination reactions of $Ca_2P_2O_7$ with (Cl_2+CO and Cl_2+C) are thermodynamically favorable in the whole temperature range investigated. The most stable chloride phases for phosphorus and calcium are PCl_3, $POCl_3$ and $CaCl_2$, respectively. The selectivity of the carbochlorination process is based on the wide difference on the vapor pressure of the chloride reaction products.

The reaction rate of the $Ca_2P_2O_7$ chlorination with Cl_2+CO+N_2 at 950°C is weak due to the formation and melting of $CaCl_2$ creating a compact layer which prevents the access of reactant gases to the reaction zone.

Kinetics of the $Ca_2P_2O_7$ chlorination is enhanced at low temperatures and by using carbon instead of CO as a reducing agent. Carbochlorination reaction of calcium pyrophosphate is almost fully completed at 750°C, leading to the separation of phosphorus chlorinated compounds from calcium chloride. A value of the apparent activation energy of about 104 kJ/mol characterizes the carbochlorination of $Ca_2P_2O_7$ in the temperature range from 625 to 750°C.

The developed process can be envisaged as an alternative of the known wet and thermal methods for the beneficiation of the low grade phosphorus ores. Further, it can be used for the recycling and extraction of phosphorus from various wasted materials.

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