# Kinetics of Chlorination and Microstructural Changes of Xenotime by Carbon Tetrachloride

EVANDRO B. AUGUSTO and HERENILTON P. OLIVEIRA

Among the rare earth minerals, fluorides, phosphates, and oxides have received attention from the rare earth industry. Traditional methods of decomposition of these minerals, usually alkaline or acid processes, involve several operations. Another possibility to obtain lanthanide chlorides or oxychlorides is reacting the mineral with chlorinating agents, such as gaseous chlorine, hydrogen chloride, thionyl chloride, and carbon tetrachloride, reducing the operation costs and making the process less complicated. In this context, we investigated the decomposition of xenotime using carbon tetrachloride at temperatures from 873 to 1173 K and kinetic and mechanistic studies have been performed. Powder X-ray diffraction, scanning electronic microscopy, energy dispersive X-ray spectrometry, ultra-violet/visible spectroscopy, and thermal analysis techniques were used in this study. The results showed that the reaction follows the shrinking-unreacted-core model with formation of a product layer (lanthanide oxychloride), confirmed by powder X-ray diffraction. Moreover, microstructural changes of xenotime grains during the chlorination reaction were verified.

## I. INTRODUCTION

RARE earths elements are more abundant in the earth's crust than their name suggests, occurring in many mineral deposits. However, rare earths do not occur in minerals as individual compounds; therefore, among 200 minerals, only three minerals are commercially available (bastnasite, monazite, and xenotime).[1] Whereas bastnasite and monazite have a higher proportion of the cerium subgroup of the lanthanide elements, xenotime contains approximately 60 pct of the yttrium subgroup. The search for high purity individual elements provides the possibility of synthesis of new materials suitable for many fields such as optics, electronics, alloys, and catalysis.[1,2] Traditional methods of decomposition of rare earth minerals (alkaline or acid processes) into soluble forms in water or acid solutions involve several operations that can introduce impurities and, thus, result in a more laborious separation/purification operations. The use of chlorination in extractive metallurgy is an alternative route for obtaining intermediate compounds such as metallic chlorides, considered basic feedstock in developing new processes and materials.[3] A number of investigations on the chlorination of rare earth compounds have been reported concerned mainly with the preparation and isolation of anhydrous lanthanide chlorides. In addition, direct chlorination makes it possible to realize the mutual separation of rare earths using chemical vapor transport (CVT) by forming volatile complexes with KCl and AlCl₃.[4] Despite these investigations, few studies have been devoted to the investigation of kinetic, mechanism, and structural changes between rare earths minerals and gaseous chlorinating agents. In this work, we investigated the reaction between xenotime (REPO₄) and carbon tetrachloride as well as the microstructural changes occurring during the chlorination. The overall chlorination reaction can be expressed as

$$2REPO_4 + 2CCl_4 \rightarrow 2RECl_3 + P_2O_5 + COCl_2 + CO_2 \quad [1]$$
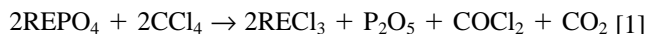
Experiments were performed in order to determine the effects of chlorination temperature, particle size of ore, and chlorine partial pressure. Moreover, analytical techniques such as scanning electronic microscopy (SEM), energy dispersive X-ray spectrometry (EDX), and powder X-ray diffraction (PXRD) were used.

## II. EXPERIMENTAL SECTION

### A. Materials and Sample Preparation

The xenotime ore (specific surface area = 0.84 m²/g) used in this work was grounded and classified into various size fractions from 60 to 325 mesh, and with no more any previous treatment. The composition of the xenotime obtained by EDX (at. pct) is Y 26.0 pct, P 30.8 pct, Dy 24.6 pct, Er 7.6 pct, and Yb 11.0 pct. The powder X-ray diffractogram of the ore revealed mainly the presence of yttrium orthophosphate phase (Figure 1(a)). The chlorinating agent (carbon tetrachloride (CCl₄) was reagent grade, which was introduced from a bubbler. Nitrogen of 99.9 pct purity (carrier gas) was dried by passing through a CaCl₂ column before their mixture with CCl₄ in the bubbler.

### B. Apparatus and Procedure

The experimental apparatus included a quartz tube (24-mm i.d. × 700-mm length) into a horizontal tubular electric furnace (35-mm i.d. × 500-mm length) with a programmable controller and a flow gas system. The temperature of the furnace was controlled within ±2 °C. The sample (0.100 g) was put in an alumina boat, and then placed in the quartz tube. The product stream issuing from the reactional system was scrubbed by passing it through a sodium hydroxide solution (10 pct m/v) and water. The flask containing CCl₄ was heated by a water bath at the desired temperature with a controller in the ±1 °C range. In order to obtain the required partial pressures in the gas mixtures, the flow rate

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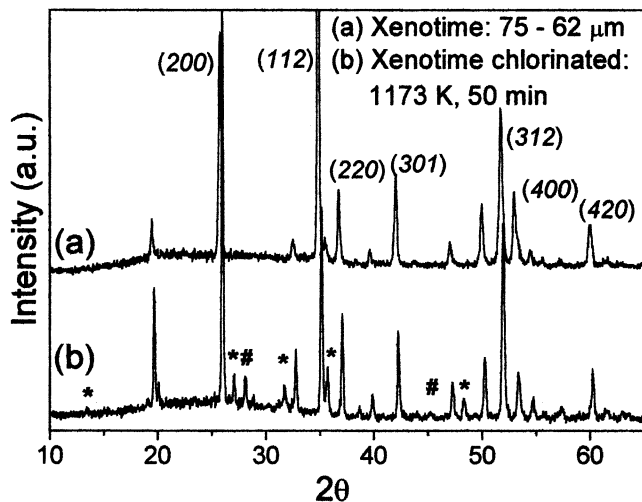
Fig. 1—Powder X-ray diffraction patterns of (*a*) xenotime ore and (*b*) xenotime after chlorination.

of nitrogen and the bath temperature were adjusted.[5] The heating of the furnace was carried out with flowing nitrogen to remove the oxygen in the system with the sample inside the quartz tube, and when the required temperature was achieved, the mixture $N_2/CCl_4$ was introduced. After the reaction, the system was purged with nitrogen until the sample reached room temperature. Finally, the residue in the alumina boat was leached with HCl 4 mol/$dm^3$, filtered, rinsed with deionized water, dried at 80 °C, and the unreacted xenotime ore was weighed. Powder X-ray data were recorded on a Siemens D5005 diffractometer (Siemens, AG, Munich, Germany) using a graphite monochromador and Cu $K_\alpha$ emission lines (1.541 Å, 40 kV, and 40 mA). The samples were placed on a glass plate and the data were collected at room temperature over the range 2 deg $\leq 2\theta \leq 65$ deg with a step of 0.020 deg. Scanning electronic microscopy (SEM) studies were done on a Zeiss-DSM 940 microscope (Carl Zeiss, Göttingen), operating at 20 kV. The transmission electronic spectra (ultraviolet/visible) were recorded on a Varian Cary 50 spectrophotometer using a 10-mm quartz cell. Energy dispersive X-ray spectrometry (EDX) data were obtained from ZAF 4FLF Link Analytical equipment (Oxford Instruments, Concord, Massachusetts). The thermogravimetric data were registered on a Thermal Analyst equipment model 2100-TA (TA Instruments, New Castle, Delaware) in air atmosphere and at a heating rate of 10 °C $min^{-1}$. Specific surface area (BET) data were obtained from a Quantachrome equipment model NOVA 1200 Gas Sorption Analyser (Quantachrome Corp., Boynton Beach, Florida).

## III. RESULTS AND DISCUSSION

### A. *Chlorination of Xenotime with $CCl_4 + N_2$*

Preliminary studies were performed in order to evaluate the microstructural changes in xenotime ore during the chlorination reaction using scanning electron microscopy and powder X-ray diffraction. Figure 1(a) shows a typical powder X-ray diffraction pattern for the xenotime ore (yttrium phosphate-tetragonal, I41/amd), where the main reflections

are indicated. Figure 1(b) shows the powder X-ray diffraction pattern for the xenotime as soon as it was reacted with carbon tetrachloride at 1173 K during 50 minutes, with a gas flow rate of 3.5 L/min and without any later treatment. This diffractogram showed a polycrystalline structure with a predominant xenotime phase and with new reflections suggesting the presence of another crystalline phase in a minor quantity. Some of these reflections (marked with an asterisk) could be attributed to the yttrium oxychloride (YOCl) phase: 13.4 deg/001, 26.9 deg/101, 31.7 deg/110, 35.7 deg/102, and 48.4 deg/201, ($2\theta/hkl$). Unfortunately, the reflections at 28.1 and 45.3 deg (marked with the # symbol) we were not able to identify.

Changes in the surface structure during the chlorination of xenotime are shown in Figure 2. Figure 2(a) shows the surface of xenotime before the reaction in which we did not observe any apparent porosity, despite the fact that the surface of grains is covered with small particles of ore. After the reaction at 1173 K for 50 minutes we observed the formation of small crystallites onto the surface of the original ore (Figure 2(b)). These results are in agreement with the diffraction data, suggesting that these crystallites consisted of yttrium oxychloride. Another interesting feature is shown in Figure 2(c), in which we can observe the xenotime surface after the reaction and leaching with HCl 4 mol/$dm^3$ at room temperature (24 °C). The remaining xenotime ore was free of small particles in comparison with the original one and, moreover, the surface presents pores that, presumably, extended into the interior of the ore. In addition, the starting material was composed by particles with sharp edges in relation with the reacted ore, an indication that it has undergone a strong chemical attack by $CCl_4$. Based on structural and morphological changes, we assume that the reaction follows a topochemical process with the formation of a solid porous product.[6,7] Comparing the results of rare earth contents by EDX analyses (Table I) of xenotime before and after the chlorination as well after leaching with HCl 4 mol/$dm^3$, we verified that the composition remained constant, indicating that there was not a selective reaction with a certain element, as expected in the function of their similar chemical properties.

### B. *Influence of Gas Flow Rate*

Figure 3 summarizes the results of the effect of gas flow on the reaction between xenotime and carbon tetrachloride. At low flow rate (below 2.5 L/min), the reaction rate increased with the flow rate because the reaction was controlled by external gas mass transport, and the influence of gas flow rate for values higher than 3.0 L/min could be considered negligible. The previous examination of microstructural and morphological changes in xenotime ore during the chlorination indicated the formation of an interface. So, the mechanism involved will depend on the properties of that particular layer.[7] Thus, performing experiments at 3.5 L/min in order to determine kinetics parameters, the reactant-gas starvation and boundary layer mass transfer effects had minimal influence on the rate of reaction. An attempt was made to correlate the experimental weight loss (fraction reacted) data. Considering that the diffusional process is negligible and the process is controlled by chemical reaction at the interface, the following equation for spherical particles was found to give a satisfactory correlation:[7,8]
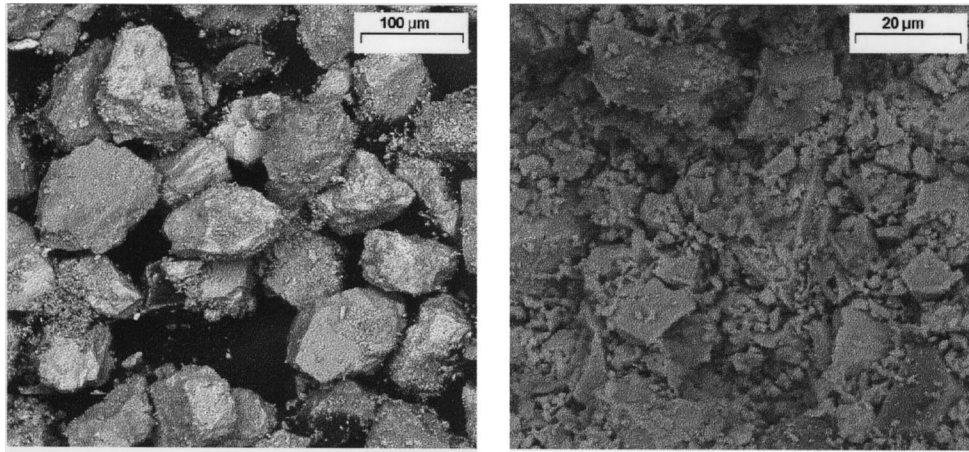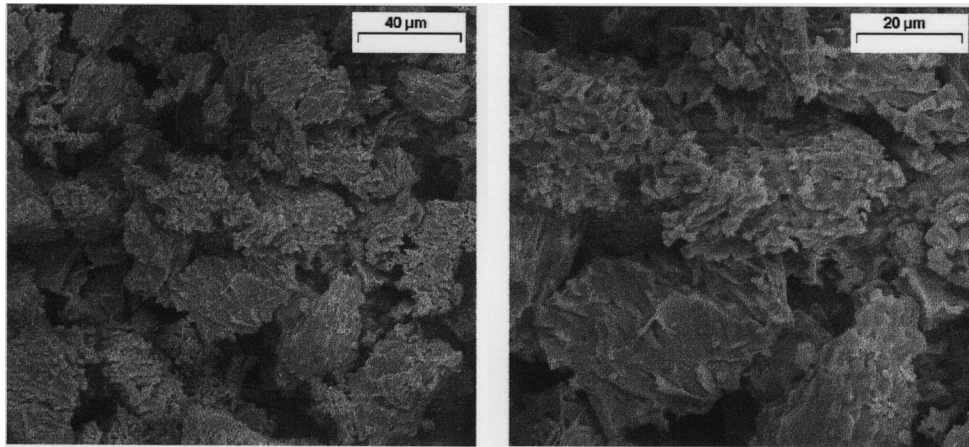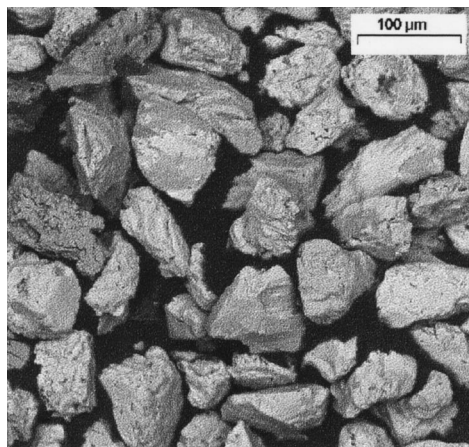
Fig. 2—Micrographs of surface structure of (*a*) original xenotime ore, (*b*) chlorinated for 50 min at 1173 K and (*c*) after leaching with HCl 4 mol/dm³.

$$1 - (1 - X)^{1/3} = K_{app}t \qquad [2]$$

where

> $X$ = fractional conversion (ratio of weight of the reacted fraction to initial weight);
> $t$ = chlorination time (minute); and
> $k_{app}$ = overall rate constant.

The apparent rate constant, $k_{app}$ can be expressed as

$$k_{app} = kf(d_0, P_{CCl_4}) \qquad [3]$$

where $k$ is the rate constant and $f(d_0, P)$ is a function of the partial pressure of $CCl_4$ and initial particle size.[9,10] In addition, if we assume that $f(d_0, P)$ takes the form of $d_0^b P_{CCl_4}^c$, we can obtain $b$ and $c$ constants from slops in plots for different partials pressures and initial particle size. The rate constant, $k$, can be obtained from the Arrhenius plots.[9,10]

**Table I.  EDX Analysis of Original and Chlorinated Xenotime**

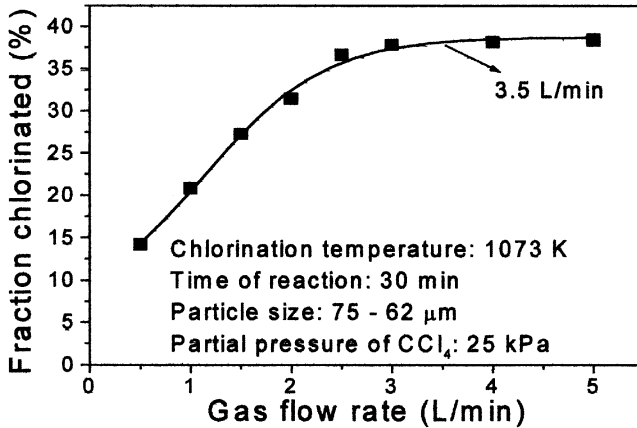| Element | Original Xenotime (At. Pct) | Chlorinated Xenotime (At. Pct) | Leached Xenotime (At. Pct) |
|---|---|---|---|
| Y | 26.0 | 28.3 | 28.8 |
| P | 30.8 | 28.7 | 27.7 |
| Dy | 24.6 | 20.8 | 20.4 |
| Er | 7.6 | 8.7 | 8.4 |
| Yb | 11.0 | 13.5 | 14.7 |



Fig. 3—Effect of gas flow on the chlorination of xenotime.

In this case, we can consider that $k_{app}$ is composed of the following parameters: initial particle diameter ($d_0$), partial pressure of carbon tetrachloride ($P_{CCl_4}$), and activation energy ($Ea$). Thus, a general form of the rate expression for $k_{app}$ can be written as

$$k_{app} = k_0 \, d_0^b \, P_{CCl_4}^c \exp\left(-\frac{Ea}{RT}\right) \qquad [4]$$

where $k_0$, $b$, and $c$ are experimental constants.[9,10,11] It should be noted that an approximate analytical solution for the rate of gas-solid reaction involving some parameters was developed. Although there is an error arisen from this approximation in relation with an exact numerical solution, we believe that the impact of this error could be neglected and does not affect the qualitative discussions and conclusions.[9,10]

### C. *Effect of Particle Size*

The chlorination of xenotime curves of different initial particle sizes varied from 62 to 45 $\mu$m to 300 to 250 $\mu$m are shown in Figure 4(a). A significant increasing of the conversion was observed with a decrease of the particle size from 300 to 250 $\mu$m to 62 to 45 $\mu$m. The plot of the apparent rate constant (In $k_{app}$) obtained from the graphic $1 - (1 - X)^{1/3}$ *vs* $t$ against the initial particle size (In $d_0$), shown in Figure 4(b), gave a slope of $-0.7$ ($b$ constant), suggesting a strong dependence of the particle grain size on reaction rate.

### D. *Effect of Temperature*

In order to study the effect of temperature on the chlorination rate, experiments were performed in isothermal conditions in the temperature range from 873 to 1173 K, working
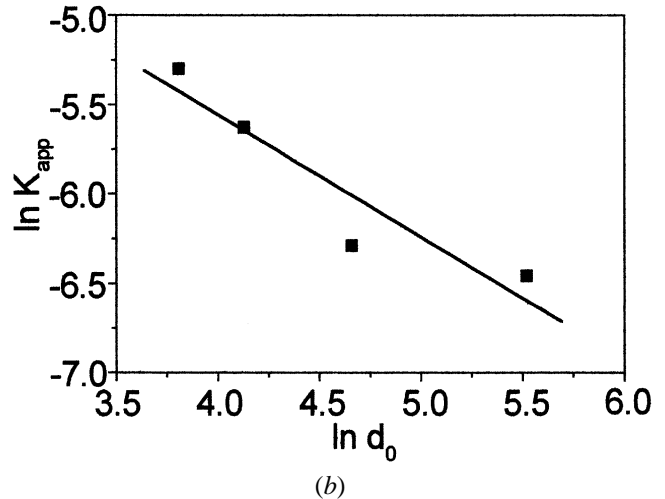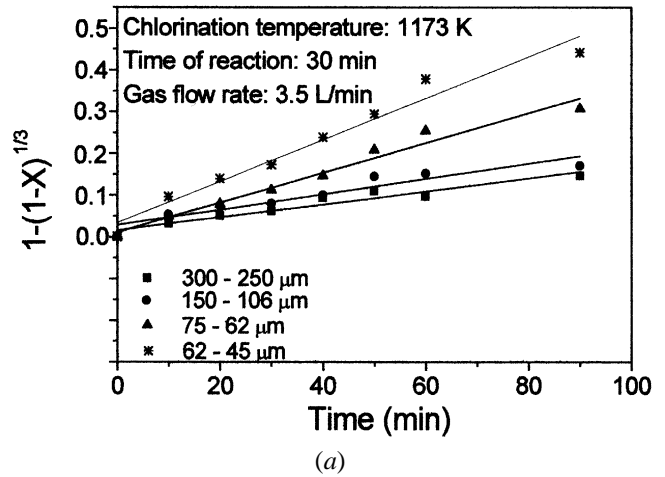


(a)



(b)

Fig. 4—Effect of particle size on the chlorination of (a) xenotime ore and (b) the dependence of the rate on initial particle size.

with carbon tetrachloride partial pressure of 25 kPa, particle size range of 75 to 62 $\mu$m, and gas flow rate of 3.5 L/min. The fractions of xenotime *vs* time curves obtained at different temperatures are shown in Figure 5(a). The Arrhenius plot of chlorination of xenotime ore, shown in Figure 5(b), suggested that the process did not change its mechanism with the increase of temperature and that there was a formation of a porous reaction product. The determined apparent activation energy ($Ea$) of 47 kJ/mol is coherent with a chemically controlled process.[7,11]

### E. *Effect of Partial Pressure of Reagent*

Experiments at four different partial pressures of $CCl_4$ in $N_2$ were carried out in order to study the effect of reagent concentration on the rate, as shown in Figure 6(a). The temperature (1173 K), gas flow rate (3.5 L/min), and particle size (75 to 62 $\mu$m) were kept constant in all experiments. It was found that the partial pressure of the reagent has a significant effect on the chlorination rate and the amount of xenotime ore reacted is proportional to the time of reaction. By plotting ln $k_{app}$ (from the data of Figure 6) *vs* ln $P_{CCl_4}$, we determined the reaction order with respect to $CCl_4$ ($n = 0.6$), as shown in Figure 6(c).

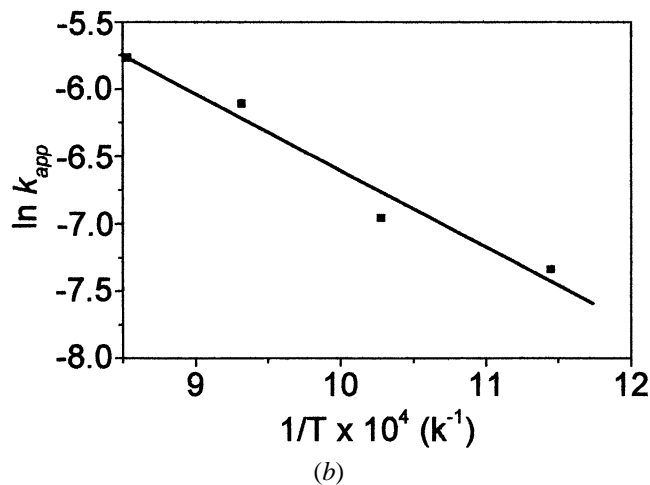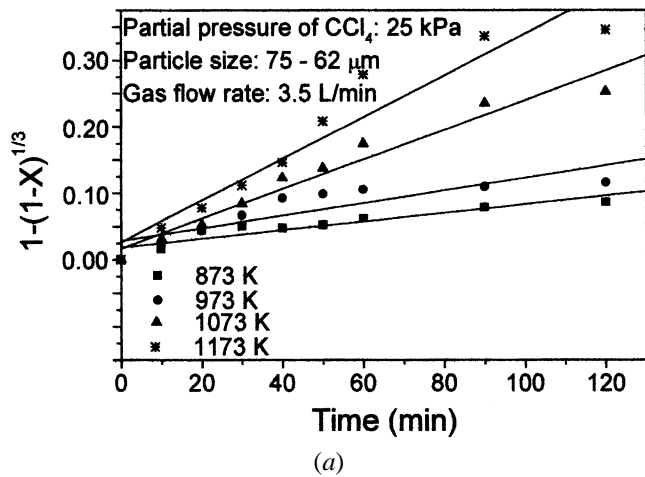In the present set of experiments, considering the factors

Fig. 5—Effect of temperature on the reaction rate of (a) xenotime ore with $CCl_4$ and (b) the Arrhenius plot of the rate constants.
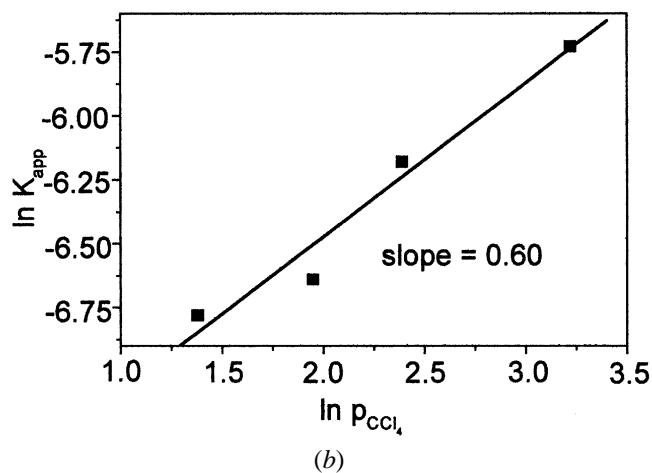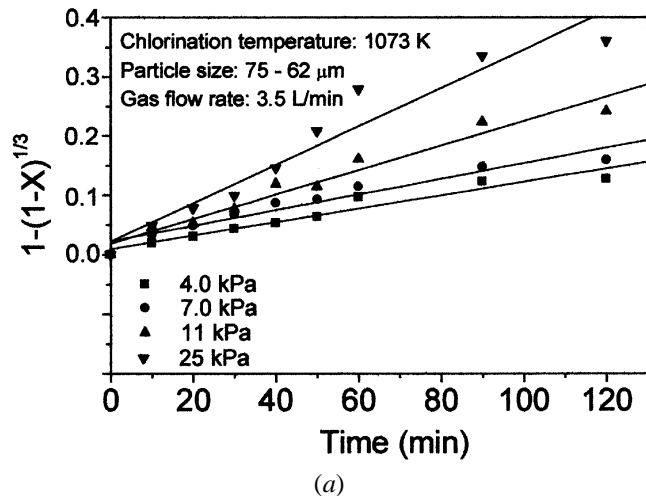


Fig. 6—Influence of partial pressure on the reaction rate of (a) xenotime ore with $CCl_4$ and (b) the dependence of the rate on partial pressure.

investigated previously and combining the parameters, we can express the global rate equation as follows:
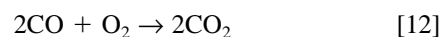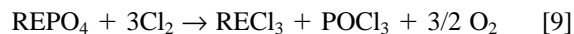
$$1 - (1 - X)^{1/3} = k_{app}t \qquad [5]$$

$$k_{app} = 1.2d_0^{-0.7} P_{CCl_4}^{0.6} \exp\left(-\frac{5680}{RT}\right) \qquad [6]$$

where $d_0$ is in $\mu$m, $P_{CCl_4}$ is in kPa, $T$ is in Kelvin, $t$ is in minutes, and the constant $k_0$ is in $min^{-1}$ $\mu m^{0.7}$ $kPa^{-0.6}$

## F. Reaction Mechanism of Xenotime with $CCl_4$ + $N_2$

Unfortunately, there are not many reports dealing with chlorination of rare earth elements, even their ores,[12–17] and most of them concern the reaction with chlorine and carbon. Moreover, as far we know, not many efforts have been done in order to study the mechanism reaction or investigate other reagents for chlorination up to the present time.[14–17] Hartley and Wylie[12] reported the preparation of lanthanide chlorides by reacting chlorine with monazite ore at temperatures above 973 K, using carbon and carbon monoxide as reducing agents. They also investigated the influence of particle size, gas flow rate, temperature, and carbon content on the reaction rate as well as proposed a mechanism for the reaction. According to the authors, two approaches

were arisen: (a) in the first one, simultaneous "trimolecular" contacts between the reactants with the reaction proceeding at the monazite-carbon interface; (b) in the second, the contact between carbon and monazite ore is not required, and reaction would proceed at the surface of the ore (see the reactions below 7 to 12).[12] However, the authors were not able to decide the actual mechanism once they had evidence for both.

$$REPO_4 + 3C + 3Cl_2 \rightarrow RECl_3 + POCl_3 + 3CO \qquad [7]$$

$$REPO_4 + 3/2C + 3Cl_2 \rightarrow RECl_3 + POCl_3 + 3/2CO \qquad [8]$$

$$REPO_4 + 3Cl_2 \rightarrow RECl_3 + POCl_3 + 3/2 O_2 \qquad [9]$$

$$2C + O_2 \rightarrow 2CO \qquad [10]$$

$$C + O_2 \rightarrow CO_2 \qquad [11]$$

$$2CO + O_2 \rightarrow 2CO_2 \qquad [12]$$

In a later work, Hartley,[13] continuing their investigation on chlorination of rare earths, suggested that the process involves three possible stages (Eqs. [13] through [15]):
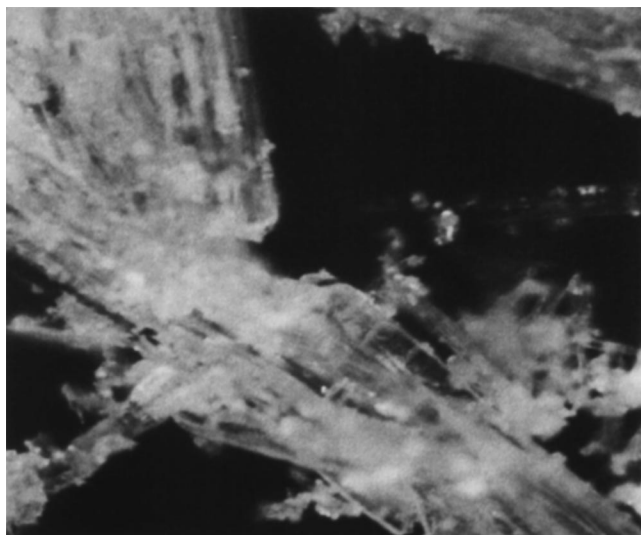
Fig. 7—Photography of a pale yellow crystalline (needle-shape) byproduct produced at the end of the quartz tube.



Fig. 8—Powder X-ray diffraction patterns of (*a*) xenotime ore and (*b*) the byproduct produced during the chlorination.

$$REPO_4 + 3C + 3Cl_2 \rightarrow RECl_3 + POCl_3 + 3CO \quad [13]$$

$$REPO_4 + 4C + 3Cl_2 \rightarrow RECl_3 + PCl_3 + 4CO \quad [14]$$

$$REPO_4 + 3C + 3/2Cl_2 \rightarrow RECl_3 + 1/4P_4 + 4CO \quad [15]$$

Ozaki *et al.*[17] studied the chlorination of monazite with carbon tetrachloride and concluded that the reaction follows a topochemical process and obeys the relationship $1 - (1 - X)^{1/3} = kt$. Moreover, the authors suggested that the kinetic control step was the reaction at the interface. Our results are coherent with the formation of an intermediate step, as shown by PXRD data and SEM micrographs indicating the presence of YOCl (Figures 1 and 2). In addition, we performed an assay in which we leached the xenotime ore after the chlorination with HCl 4 mol/dm$^3$. The ultraviolet/visible spectra of the supernatant showed bands at 216, 254 and 334 nm, attributed to $Y^{3+}$ e $Tb^{3+}$ ions. Furthermore, during the performance of the experiments was observed the formation of pale yellow crystalline (needle shape, as shown in Figure 7) byproduct at the end of the quartz tube for reaction temperatures above 973 K. Another point is the fact that it was produced only in the presence of xenotime ore and that there was no reaction between the alumina boat and the chlorinating agent at the temperature range of this study. Thermal analysis of the byproduct, from 25 °C to 1000 °C, indicated that the material was decomposed into three steps (25 °C to 330 °C, 330 °C to 520 °C, and 520 °C to 600 °C) with a mass loss of 50 pct. The powder X-ray diffraction pattern of the byproduct, shown in Figure 8, has several peaks and indicates that the material presents a polycrystalline structure, which becomes difficult to identify. However, at first glance, we could ascribe some reflections as belonging to $P_2O_5$ and $YCl_3$ polycrystalline phases. Another feature is the thermal dissociation of $CCl_4$ at high temperatures.[18,19] What probably occurs is the generation of radicals at high temperatures that react with lanthanide oxychlorides producing volatile complexes, which are transported by $N_2$ to a lower temperature zone in the quartz tube.[4,20] Despite
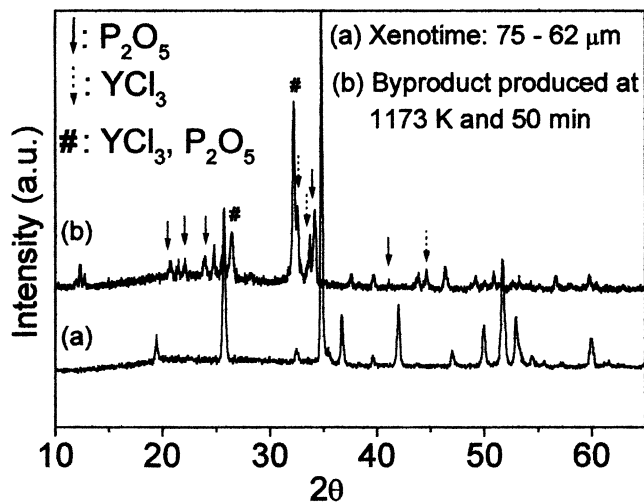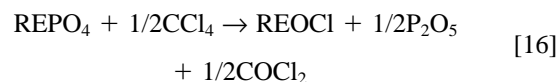
several and complicated reactions including thermal dissociation of $CCl_4$, the overall process can be presented as follows:

$$REPO_4 + 1/2CCl_4 \rightarrow REOCl + 1/2P_2O_5 + 1/2COCl_2 \quad [16]$$

and then, as the reaction was carried out, we had the production of the following products:

$$REOCl + 1/2CCl_4 \rightarrow RECl_3 + 1/2CO_2 \quad [17]$$

## IV. CONCLUSIONS

From this set of experiments, it can be concluded that the chlorination between xenotime ore and carbon tetrachloride follows a topochemical process, in which the controlling step was the surface reaction producing lanthanide oxychloride. The influence of several parameters on the reaction such as particle size, gas flow rate, and temperature were studied as well as global rate expression has been formulated:

$$1 - (1 - X)^{1/3} = k_{app}t = 1.2d_0^{-0.7} P_{CCl_4}^{0.6} \exp\left(-\frac{5680}{RT}\right)t$$

$$[18]$$

The overall process is strongly dependent on the initial particle size of the grain and, in the conditions that this study was carried out, the apparent activation energy value evidenced a chemically controlled process. Moreover, we observed morphological and structural changes during the reaction.

# REFERENCES

1. C.K. Gupta and N. Krishnamurthy: *Int. Mater. Rev.*, 1992, vol. 37 (5), pp. 197-248.
2. *Rare Earth Elements and Their Applications*, Y. Zongsen and C. Minbo, eds., Metallurgical. Industry Press, Beijing, 1995, pp. 138-273.
3. F. Habashi: *Principles of Extractive Metallurgy*, Science Publishers, Paris, 1980, vol. 3, pp. 218-39.
4. T. Ozaki, J. Jiang, K. Murase, Ken-ichi Machida, and Gin-ya Adachi: *J. Alloys Compounds*, 1998, vol. 265, pp. 125-31.
5. P.K. Jena, E.A. Brocchi, and T.F. Villela: *Metall. Mater. Trans. B*, 1995, vol. 26B, pp. 235-40.
6. L. Zhou, H.Y. Sohn, G.K. Whiting, and K.J. Leary: *Ind. Eng. Chem. Res.*, 1996, vol. 35, pp. 954-62.
7. F. Habashi: *Principles of Extractive Metallurgy*, Science Publishers, Paris, 1980, vol. 1, pp. 111-222.
8. M. Djona, E. Allain, and I. Gaballah: *Metall. Mater. Trans. B*, 1995, vol. 26B, pp. 703-10.
9. K.I. Rhee and H.Y. Sohn: *Metall. Mater. Trans. B*, 1990, vol. 21B, pp. 321-30.
10. H.Y. Sohn, L. Zhou, and K. Cho: *Ind. Eng. Chem. Res.*, 1998, vol. 37, pp. 3800-05.
11. J. Szekely, J.W. Evans, and H.Y. Sohn: *Gas-Solid Reactions*, Academic Press, New York, NY, 1976, pp. 65-107.
12. F.R. Hartley and A.W. Wylie: *J. Soc. Chem. Ind.*, 1950, vol. 69 (1), pp. 1-7.
13. F.R. Hartley: *J. Appl. Chem.*, 1952, vol. 2, pp. 24-30.
14. J.B. Zimmerman and J.C. Ingles: *Anal. Chem.*, 1960, vol. 32 (2), pp. 241-46.
15. A.W. Henderson, S.L. May, and K.B. Higbie: *Ind. Eng. Chem.*, 1958, vol. 50 (4), pp. 611-12.
16. N. Iordanov and Khr. Daiev: *J. Anal. Chem. USSR*, 1962, vol. 17, pp. 431-33.
17. T. Ozaki, K. Murase, Ken-ichi Machida, and Gin-ya Adachi: *Trans. Inst. Min. Metall Sect. C: Mineral Processing Extr. Metall.*, 1996, vol. 105, pp. C141-C145.
18. J.V. Michael, K.P. Lim, S.S. Kumaran, and J.H. Kiefer: *J. Phys. Chem.*, 1993, vol. 97, pp. 1914-19.
19. O.B. Koper, E.A. Wovchko, J.A. Glass, J.T. Yates, and K.J. Klabunde: *Langmuir*, 1995, vol. 11, pp. 2054-59.
20. T. Ozaki, Ken-ichi Machida, and Gin-ya Adachi: *Metall. Mater. Trans. B*, 1999, vol. 30B, pp. 45-51.