

MORPHOLOGICAL AND MICROSTRUCTURAL STUDIES ON CHLORINATION KINETICS OF XENOTIME WITH CHLORINE

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ABSTRACT

Reports on the chlorination of rare earth compounds have been published concerning mainly with the preparation and isolation of anhydrous lanthanides chlorides. In a previous work we focused our investigation on the reaction between xenotime (YPO_4) with chlorine in presence of carbon and we verified the formation of YOCl , corroborated by DRX data. The release of gaseous species showed up by the increase of the porosity of the pellets. In this work we report the microstructural changes in the pellets during the carbochlorination under nitrogen atmosphere and chlorine gas using SEM and BET techniques. Moreover, the surface morphology and specific surface area developed during the reaction have implications for carbochlorination kinetics.

INTRODUCTION

Chlorination process is a potential dry method of production of rare earth elements, allowing the isolation of metals from ores and concentrates, refining metals, and recovering metals from slags. Besides, it has application in advanced ceramics areas [Zongsen-1995, Gupta-1992, Ozaki-1999]. Reports on the chlorination of rare earth compounds have been published concerning mainly with the preparation and isolation of anhydrous lanthanides chlorides [Murase-1995, Ozaki-1996]. Certain advantages in relation to other decomposition processes have been arisen: phosphorous may be eliminated and the chlorides of rare earth could be obtained in a unique operation; impurities could be eliminated with the formation of volatile chlorides; this procedure makes possible the isolation of chlorides in a non-aqueous medium technique. In a previous work [Gimenes-2000] we focused our investigation on the reaction between xenotime (YPO_4) with chlorine in the presence of carbon (coal) and we verified the formation of YOCl ,

corroborated by DRX data. In addition, the results showed that the process follows the unreacted core-shrinking model with the formation of a porous product layer. Few studies have, however, been devoted to the microstructural changes occurring during the chlorination. Thus, as part of an overall investigation of the chlorination characteristics, microstructural changes in aggregates (xenotime, coal and binding agent) were examined in this work, during the carbochlorination, under nitrogen atmosphere, and chlorine gas, using SEM and BET techniques.

EXPERIMENTAL

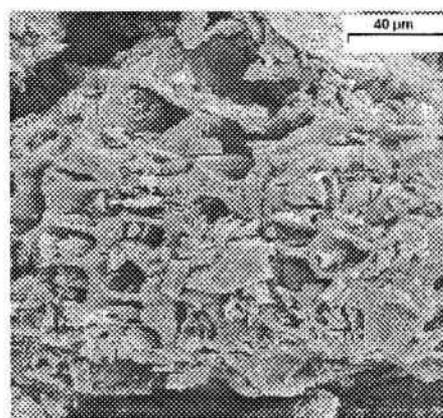
The chlorination reaction was carried out in a quartz tube (24 mm inner diameter x 850 mm length) into a horizontal tubular electric furnace (35 mm inner diameter x 500 mm length) with a programmable controller and a flow gas system. The experimental procedure was to preheat the reactor under nitrogen gas to remove the oxygen in the system with the sample inside a quartz tube (aggregates, 0.200g, placed in an alumina boat) and, when the required temperature was achieved, chlorine or the mixture N_2/Cl_2 was introduced. At the end of each experiment, the reactor was purged with nitrogen while cooling, and the quartz tube was taken out and cooled to room temperature. Finally, the residue in the alumina boat was leached with 2 mol l^{-1} HCL, filtered, rinsed with deionized water and dried at 80°C . Later, the excess carbon in the residue was burnt off in a muffle furnace at 900°C , and the unreacted xenotime ore was weighed to obtain the degree of conversion (X). Agglomerates containing xenotime (particle diameter between $62 \mu\text{m}$ and $45 \mu\text{m}$) and coal (particle diameter smaller than $75 \mu\text{m}$ and 97% of purity) used in this work were prepared by a palletizing technique. In order to prepare them it was required the utilization of a binding agent: an aqueous solution of sugar (1:1 mass/mass). The mixture was placed inside of a drum and than rotated at 100 rpm speed with a 45° angle to the horizontal. The binding

agent was introduced by spraying the sugar solution until nearly spherical particles were formed. In addition, the pellets with different specific surface area were prepared by addition of different amounts of binding agent before drying at 80° C. Pellets were prepared in a Pelletizing machine from Tecnal Industry. Scanning electron microscopy (SEM) studies were done on a ZEISS - DSM 940 microscope, operating at 20 kV. Specific surface area (BET) data were obtained from a Quantachrome equipment model NOVA 1200 Gas Sorption Analyser.

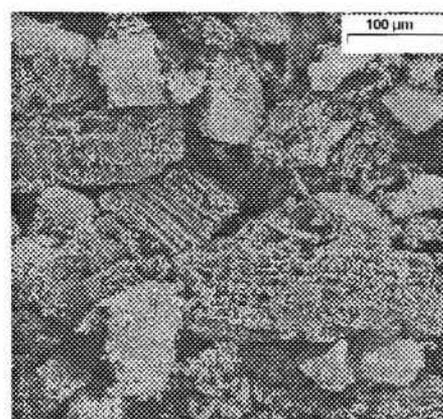
RESULTS AND DISCUSSION

Changes in the particles morphology during the chlorination of pellets are shown in Figure 1. Figure 1a shows the surface of the pellets before the reaction in which their morphology is coherent with the formation of particles clung together. In addition, we observed that the agglomerates were not homogeneous in shape and size, also presenting some cavities that, presumably, extended into the interior of the agglomerate. A comparison with the pellets before reaction indicates that the samples after the chlorination (Figure 1b) have diminished their size, became more irregular and presented cracks. Moreover, along the reaction we note that the surface is covered with small crystallites and the presence of holes related to evolution of gaseous products (Figure 1c). We also performed some experiments in which the carbon: ore ratio (*mass/mass*) was kept constant (0.6) and the amount of binder agent was varied, in such a way that we obtained samples with different values of specific surface area. Figure 2 indicates that high values of fraction of ore chlorinated were found for samples with high specific surface area. In addition, we also verified almost the same microstructural changes during the reaction, even for samples with different surface area ($0.52 \text{ m}^2\text{g}^{-1}$ and $1.1 \text{ m}^2\text{g}^{-1}$), as shown in Figure 3.

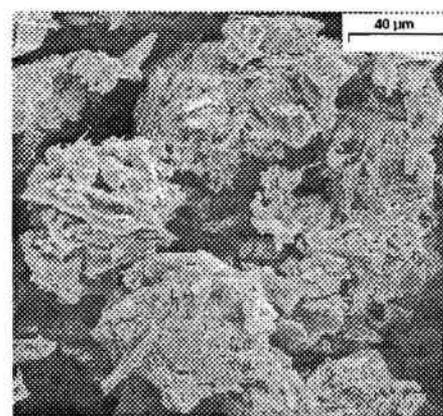
These results are coherent with the chlorination process involving porous solids, allowing diffusion and chemical reaction to occur simultaneously throughout the solid [Szekely-1976].



(a)



(b)



(c)

Figure 1 - Micrographs of surface structure of pellets before (a) and after chlorination (b) and (c). Conditions: 1173 K, 1.0 L/min, PCl_2 of 50 kPa, 1.3 carbon:ore ratio, 40 min.

The overall reaction of xenotime ore with chlorine ($\text{YPO}_4 + 3\text{C} + 3\text{Cl}_2 \rightarrow \text{YCl}_3 + \text{POCl}_3 + 3\text{CO}$) includes diffusion of the reactant gases and the gaseous products that play an important role. At a first glance,

we may suppose that the reaction occurs in a zone closed to the outer surface of the particle, producing crystallites of $YOCl$, an intermediate step ($YPO_4 + Cl_2 \rightarrow YOCl + 1/2P_2O_5 + 1/2COCl_2$), as demonstrated by powder X-ray diffraction [Gimenes-2000] and SEM (Figure 1b). Then, the chlorination proceeds toward the center. Topochemically and gradually, numerous pores are formed that, probably, extends deeply into the interior of the particles (Figure 1c).

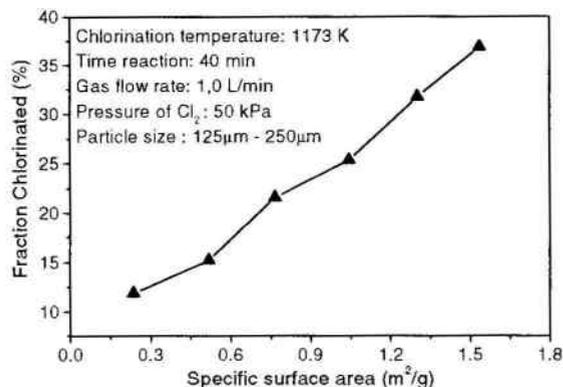
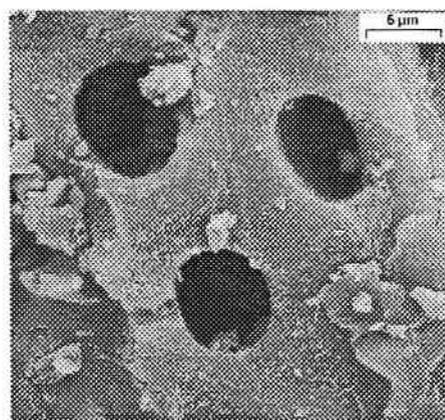
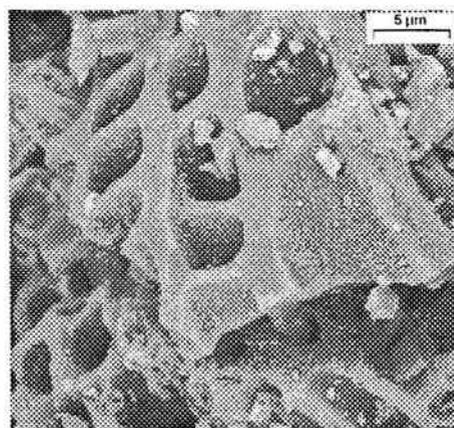


Figure 2 - Influence of specific surface area on the fraction of chlorinated xenotime ore.

The specific surface area is a critical factor on the chlorination process (Figure 2). Structural changes may occur due to the sintering of solids under high temperatures, increasing the diffusional resistance, or lead to an open pore structure, which increases the effective diffusivity in the pores [Szekely-1976, Zhou-1996]. In our study, we verified an increase in the degree of conversion of the solid reactant with the decrease of specific surface area before the reaction. At a first approximation, after drying the pellets, the binding agent clogged the intergranular spacing and may be interfered with the chlorination, by forming a kind of film between the coal and the ore agglomerate, avoiding the contact between the particles. Another point is the fact that even for different values of surface area it was observed the presence of pores in all samples after reaction, keeping the same reactional conditions (Figure 3), despite of the increase of resistance towards the intergranular diffusion.



(a)



(b)

Figure 3 - Micrographs of surface of pellets chlorinated (1173 K, 1.0 L/min, PCl_2 of 50 kPa, 1.3 carbon:ore ratio, 40 min) with specific surface area of $0.52 m^2g^{-1}$ (a) and $1.5 m^2g^{-1}$ (b).

CONCLUSION

The microstructural changes of aggregates (xenotime ore, coal and binding agent) during the chlorination must be taken into account in the analysis of reaction kinetics. For instance, with the decrease of the specific surface area of the samples occurred an increase of chlorinated fraction, probably by the increase of the rate of diffusional process of reagents and products gases, since other parameters were kept constant. Even for samples with different surface area, we verified microstructural changes with the presence of holes. Thus, the results confirm the importance of the control of variables on the preparation of pellets, since this could have implications for carbochlorination kinetics affecting the rates of conversion.

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