KINETICS STUDY OF CARBOTHERMIC REDUCTION OF IRON OXIDES CONTAINED IN MONAZITE CONCENTRATE FOR RARE EARTH EXTRACTION*

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Abstract

Kinetics of iron reduction process contained in Brazilian monazitic concentrate has been investigated in this study using charcoal and petroleum coke as reducing agents under isothermal condition. The reduction experiments of monazite concentrate-coal mixture have been performed twice at varying temperatures ranging between 973-1273K for 180 minutes. The materials are characterized by representative techniques like, XRF, XRD and SEM, in order to evaluate the particles morphology, ore composition and identify the main phase of iron oxide present. The isothermal kinetic study has been performed considering the loss of oxygen fraction from the monazite iron oxides calculated from the thermogravimetric analysis mass loss results; which showed the charcoal as better reducer and that the reaction follows the Ginstling-Brounshtein model for both reducing agents. The corresponding activation energies using Arrhenius equation are evaluated as 157.68 and 266.95 kJ/mole, for mixtures with charcoal and petroleum coke respectively assuming a mixed controlling process.

Keywords: Monazite concentrate; Iron oxides; Reduction process; Charcoal; Coke petroleum.

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1 INTRODUCTION

Nowadays, monazite has a great technological importance for nuclear, electric, ceramic and chemical industries by the presence of rare earths in its composition [1-3]. The largest deposits have been found in India, Brazil, the USA, Australia and Madagascar [2-5]. After due concentration processes, monazite-based rare earth ores can be digested or chemically attacked using essentially two routes [1-6]: an acid with H_2SO_4, and a basic one with NaOH or Na_2CO_3. The main reaction as shown in Equation 1 of the acid digestion process is carried out at two temperature levels, one below and one above 573K [4-6].

$$2TRPO_4 + 3H_2SO_4 = TR_2(SO_4)_3 + 2H_3PO_4 \tag{1}$$

It is worth noting that stoichiometrically 0.5 kg of H_2SO_4 is required per kg of processed $TRPO_4$ to be dissolved. If an ordinary monazite concentrate contains, for example, 30% of Fe_2O_3 it would require at least 0.65 kg of H_2SO_4 per kg of $TRPO_4$ only to solubilize Fe as shown in Equation 2 [7].

$$Fe_2O_3 + 3H_2SO_4 = Fe_2(SO_4)_3 + 3H_2O \tag{2}$$

Reagent expenditure and environmental liability and risk therefore increase with the presence of Fe in the concentrate [3]. Consequently, the removal of Fe by carbothermic reduction prior to digestion is an interesting alternative in monazite processing.

2 EXPERIMENTAL PROCEDURE

A monazite concentrate, received from the Brazilian Company of Metallurgy and Mining (CBMM), was used as the main material in this study and its chemical composition, analyzed by XRF, is listed in table 1. LOI (loss on ignition) was measured by heating the concentrate at 1293 K in air and resulted of 10.0 wt. %. The particle size distribution of the concentrate determined by Laser Diffraction Granulometry showed a D10, D50 and D90 of 0.624 µm, 3.119 µm and 11.402 µm respectively. The charcoal and petroleum coke used as reductants consisted of 73.45% and 81.16% fixed carbon, 19.23% and 6.17% volatiles and 2.02% and 11.21% ash, respectively. The particle sizes of both were between 63 µm and 104 µm.

Table 1. Chemical composition of monazite concentrate (mass percent, wt. %).

Fe_2O_3	P_2O_5	CeO_2	La_2O_3	Nd_2O_3	Al_2O_3	SiO_2	TiO_2	MnO
50,6	12,2	4,21	2,77	2,48	3,33	3,05	2,98	2,56
BaO	Nb_2O_5	MgO	SO_3	Pr_2O_3	SrO	CaO	ThO_2	ZnO
1,32	1,08	0,79	0,66	0,56	0,38	0,31	0,16	0,12
PbO	Cl	K_2O	Y_2O_3	ZrO_2	MoO_3	LOI		
0,12	0,09	0,08	0,07	0,06	0,04	10,0		

The morphology of the monazite concentrate was observed by a scanning electron microscope (SEM) using secondary and backscattered electron images. The concentrate phase's constitution was determined by XRD with Cu Kα radiation. In the carbothermic reduction, the hematite in the concentrate would be reduced to metallic iron as shown in Equation 3 below. Whit this reaction was calculated the theoretical amount of carbon used in the process considering the loss of carbon in the gaseous phase in the form of CO.

$$Fe_2O_3 + 3\mathrm{C} = 2\mathrm{Fe} + 3\mathrm{CO} \qquad (3)$$

The reduction process was carried out in a thermogravimetric analyzer (TGA) with accuracy of 0.1 mg. Alumina crucibles with 9 mm of inner diameter were used for holding the samples. The temperature is controlled by a thermocouple type S. The heating was 50K/min to the selected reduction temperatures (973, 1073, 1173 and 1273K) during 180 minutes. The relatively fast heating rate (50 K/min) is used in an attempt to minimize the reduction that would occur during the heating stage. A dynamic pure argon atmosphere was used.

3 RESULTS AND DISCUSSION

As shown in the figure 1, the diffraction peaks indicate that iron is present in two phases, hematite and goethite. For stoichiometric calculations the total iron in the concentrate was assumed as hematite. Based on the XFR analysis, phosphorus was considered as a pentoxide (P_2O_5) and the rare earth oxides were considered as Ce_2O_3, La_2O_3 and Nd_2O_3 in monazite. Furthermore were observed secondary phases as bariopyroclhore, Gorceixite and Baryta, minerals rich in niobium and barium.

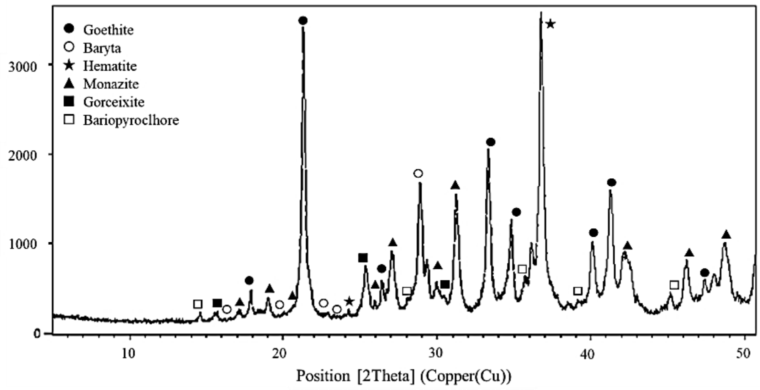
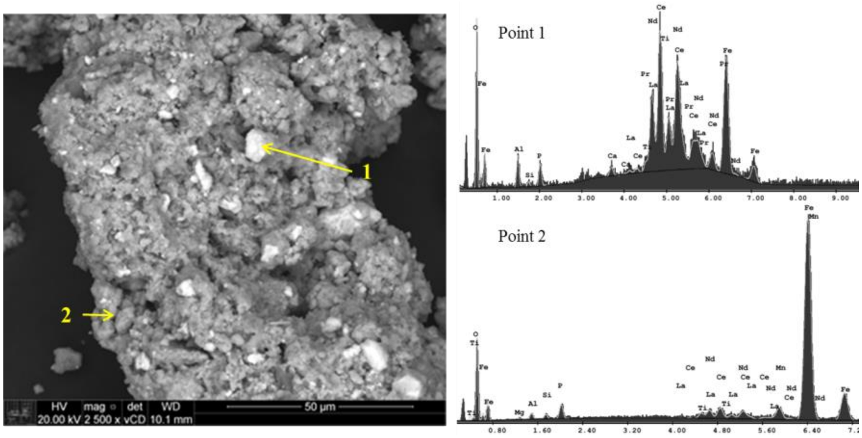


Figure 1. XRD pattern of monazitic concentrate.

Figure 2 shows the morphology of the concentrate indicating a high agglomeration degree. The EDX chemical analysis is present in figure 2 (b). It shows that the lighter particles (point 1) correspond to the monazite and the darker particles (point 2), most in the figure, correspond to the Fe-rich particles.



(a) (b)

Figure 2. SEM-EDX analysis of the monazitic concentrate. (a) Backscatter electron image. (b) EDX patterns from punctual analysis in point 1 and point 2

In TGA experiments, the curves for each temperate and reductant agent are shown in figure 3. At 973K the reduction process is naturally very slow and limited because of it is at the beginning of iron oxide reduction temperature. The mass loss of the charcoal and petroleum coke experiments were from 7.4 to 21.7% and 6.2 to 17.7% of initial mass, respectively, between 973 and 1173K.

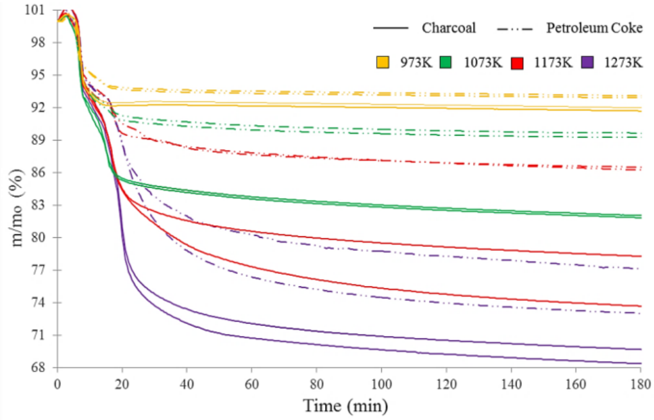


Figure 3. TG curves of carbothermic reduction of monazitic concentrate at different temperatures.

The monazite concentrate has hydrated phases that will result in mass loss during heating. The same will occur with the reductants due to volatilization of volatile matter. Theses mass losses sum up 11.47% in the case of mixture of concentrate and charcoal and 9.43% for the mixture with petroleum coke.

The reduction degree (α) was determined as shown in Equation 4, where Δm *exp* is the experimental mass loss subtracted of the amounts of volatiles in the reductants and LOI of monazite concentrate. Δm *max* is the maximum possible mass loss, calculated from reaction (3) as follows in Equation 5; where *Xc* is the ratio of concentrate in the mixture and $\%Fe_2O_3$ the percentage of hematite. *Xc* is calculated from equation 6, where *Mc* is the concentrate mass and *Mr* is the reductant mass. The average molecular mass of hematite and CO used in the calculation is 160 and 28 g/mole, respectively.

$$\propto = \frac{\Delta m\ exp}{\Delta m\ max} \tag{4}$$

$$\Delta m\ max\ = \frac{Xc * \%Fe_2O_3 * 84}{160} \tag{5}$$

$$Xc\ = \frac{Mc}{Mc + Mr} \tag{6}$$

Figure 4 shows the reduction degree against time at different temperatures and with both reductants. Calculated reduction degree (α) at 973 K is negative, since mass loss is lower than the sum of volatiles in the reductants and LOI of the concentrate. The iron oxides reduction rate reaches 31.0% and 6.2% at 1073K for charcoal and petroleum coke experiments, respectively, suggesting that the reduction process starts at this temperature even though the reduction rate is relatively low. The reduction ratio increases with the increase of temperature. Especially, at temperatures between 1173K and 1273K with charcoal experiments, the reduction degrees reached 75.23% and 96.09%, respectively. In the other hand, the reduction degree reached 79.65% at 1273K for petroleum coke experiments, indicating that charcoal presents better results.

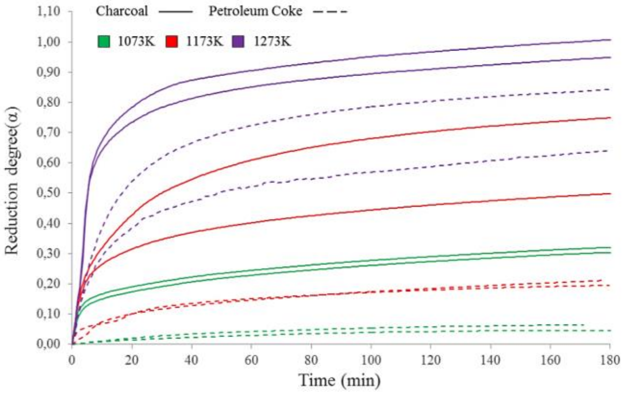


Figure 4. Reduction degree of iron oxides present in monazitic concentrate at different temperatures.

To study the kinetics of the carbothermic reduction process of iron oxides of the monazitic concentrate it was taken the data 20 minutes after the start of the heating. The kinetic data were analyzed by different kinetics models using the reduced time plots used by Ray [8]. The Ginstiling-Brounshtein model described by Equation 7 was adopted because it presented better statistical fit.

$$1-\frac{2}{3}\alpha-(1-\alpha)^{2/3}=k\cdot t \tag{7}$$

Figure 5 shows the kinetics curves of the carbothermic reduction of the monazite concentrate using charcoal (a) and petroleum coke (b) as reductant agents.

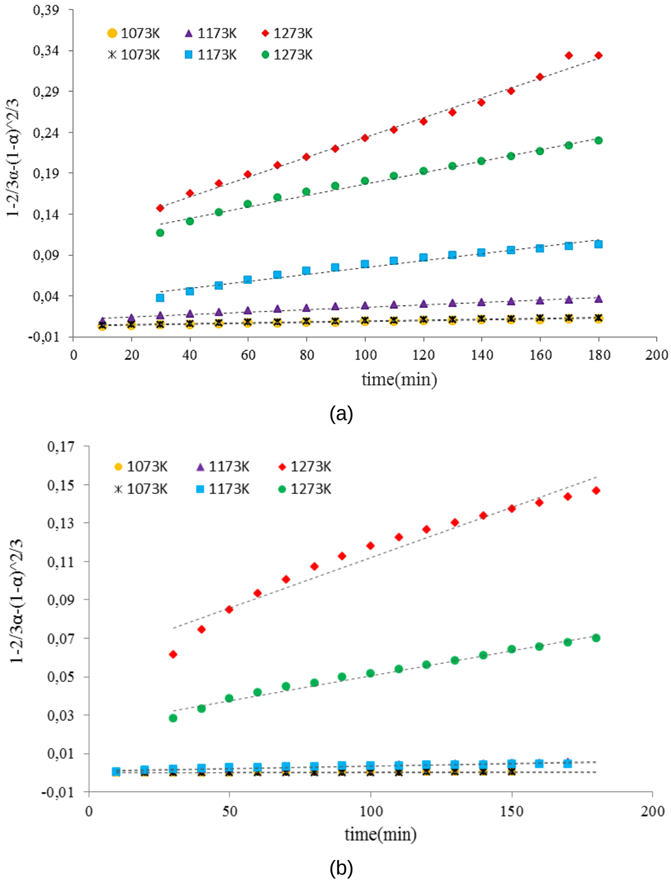


Figure 5. Kinetics curves of iron oxides of monazitic concentrate reduction at different time and temperature. (a) Charcoal as reductant agent. (b) Petroleum Coke as reductant agent.

To determine the activation energy, the kinetics constants for both reducing agents in all the temperatures were used in the Arrhenius equation (Equation 8), where k is the reaction rate constant (slope of the kinetic curve), *A* is the frequency factor, *R* is the gas constant, *T* is the temperature and *E* is the activation energy. Figure 6 shows the plot of equation 8 with experimental data of figure 5 showing in Table 2. The activation energies were 159.22 kJ/mole and 266.93 kJ/mole, respectively, for charcoal and petroleum coke which implies a mixed controlling process between 1073 and 1273K.

Table 2. Reaction rate constants (k) data and correlation coefficients (R^2) from kinetics curves of iron oxides of monazitic concentrate reduction at different time and temperature from Figures 5(a) and 5(b).

		Charcoal		Petroleum Coke	
Temperature		K	R^2	K	R^2
1073K	●	0,00005	0,9835	3,0E-06	0,988
	*	0,00006	0,982	3,0E-06	0,988
1173K	▲	0,0001	0,9598	0,00002	0,9371
	■	0,0004	0,962	0,00003	0,9893
1273K	●	0,0012	0,9861	0,0005	0,9834
	◆	0,0007	0,9918	0,0003	0,9499

$$\ln(k) = lnA - \frac{E}{RT} \tag{8}$$

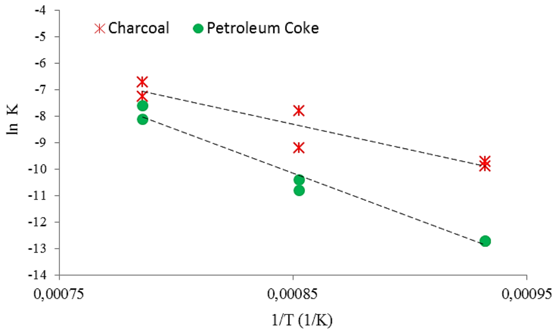
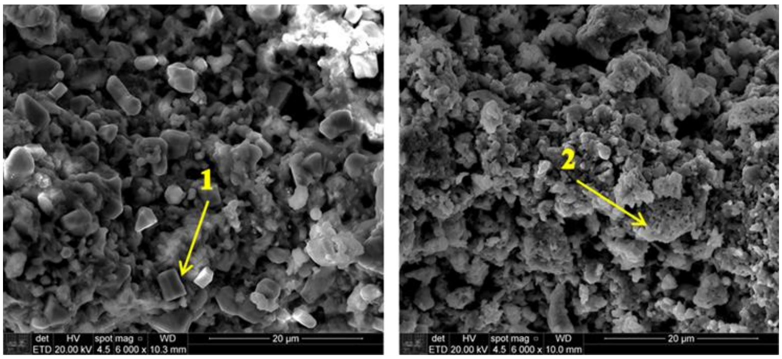


Figure 6. Ln k – 1/T of iron oxides of monazitic concentrate reduction by charcoal and petroleum coke.

Figure 7 shows the products of reduction with charcoal (a) and petroleum coke (b) at 1173K. Isolated reduced iron grains (point 1) were found in the sample reduced with charcoal and the EDX analysis of such particles is presented in figure 8 (a). In the sample reduced with petroleum coke, isolated reduced iron particles were not found (point 2). Figure 8 (b) shows the EDX analysis of a phase containing iron and other elements with oxygen. The reduction degree observed at this temperature in the reduction with petroleum coke was 21.09%. Conversion of Fe_2O_3 to Fe_3O_4 results in a reduction degree of 11.1% and to FeO in 33.3%. Therefore, iron is expected to be in the form of oxides, which agrees well with the EDX analysis showed in figure 7 and figure 8 (b). Microstructure of the concentrate reduced with charcoal shows sintering of different particles while the concentrate reduced with petroleum coke is composed of agglomerated grains but without sintering.



(a) (b)

Figure 7. SEM images of monazitic concentrate before carbothermic reduction at 1173K with (a) Charcoal. (b) Petroleum coke.

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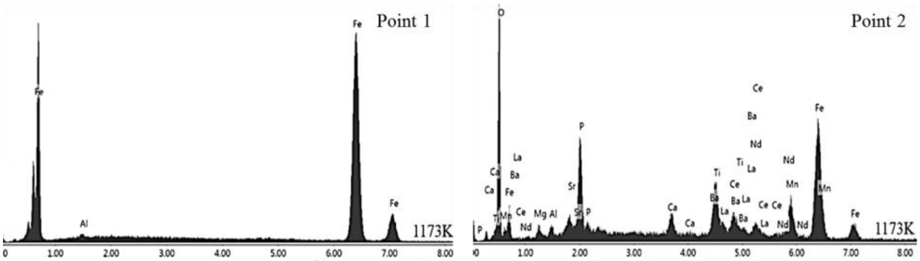

Figure 8. EDX patterns of monazitic concentrate after carbothermic reduction at 1173K. (a) Charcoal experiments. (b) Petroleum experiments.

4 CONCLUSIONS

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Monazite concentrate present a uniform morphology and an average particle size conferring a high agglomeration with the reductant agents. The main phases of iron present in the concentrate are hematite and goethite. These iron oxides carbothermic reduction follows the Ginstilin-Brounshtein kinetic model and obeys to a mixed control reaction with activation energies of 157.68 and 266.95 kJ/mole with charcoal and petroleum coke as reductant agents, respectively.

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