Process optimization and kinetics for leaching of cerium, lanthanum and neodymium elements from iron ore waste's apatite by nitric acid

A. FERDOWSI, H. YOOZBASHIZADEH

Department of Materials Science and Engineering, Sharif University of Technology,
Azadi Ave., Tehran, P. O. Box 11155-9466, Iran

Abstract: The leaching of rare earth elements (REEs) including cerium, lanthanum and neodymium from apatite concentrate obtained from iron ore wastes by nitric acid was studied. The effects of nitric acid concentration, solid to liquid ratio and leaching time on the recoveries of Ce, La and Nd were investigated using response surface methodology. The results showed that the acid concentration and solid to liquid ratio have significant effect on the leaching recoveries while the time has a little effect. The maximum REE leaching recoveries of 66.1%, 56.8% and 51.7% for Ce, La and Nd, respectively were achieved at the optimum leaching condition with 18% nitric acid concentration, 0.06 solid to liquid ratio and 38 min leaching time. The kinetics of cerium leaching was investigated using shrinking core model. It was observed that the leaching is composed of two stages. In the first stage a sharp increase in cerium leaching recovery was observed and at the longer time the leaching became slower. It was found that in the first stage the diffusion of reactants from ash layer is the rate controlling mechanism with an apparent activation energy of 6.54 kJ/mol, while in the second stage the mass transfer in the solution is the controlling mechanism.

Key words: rare earth elements; apatite; leaching; response surface methodology; shrinking core model

1 Introduction

The demand for rare earth (RE) metals and their compounds are increasing rapidly due to their unique magnetic, electrical, chemical, catalytic, optical and spectroscopic properties that have led to their application in many fields of advanced materials applications [1−3]. They have applications in numerous fields including electronic, metallurgy, petroleum, textiles, and agriculture, and they are also becoming uniquely indispensable and critical in many high-tech industries such as hybrid cars, wind turbines, and compact fluorescent lights, flat screen televisions, mobile phones, disc drives, and defense technologies [3]. There are a wide variety of rare earth minerals, but notably the mined minerals are bastnasite, monazite, and xenotime [3−5]. Apatite, cheralite, eudialyte, loparite, and phosphorites make up the remaining resources [3]. Apatite containing average 0.1%−0.8% rare earth oxides is the main source of phosphate fertilizers and phosphoric acid. In spite of its low rare earth content apatite could become an important source of rare earths

because it is processed in large quantities [6]. Different processes for extracting race earth elements (REEs) from apatite are investigated. Leaching with sulfuric acid is the most common method for treating apatite [5]. During the manufacture of phosphoric acid about 70% of rare earth element is lost in the gypsum. However, if leaching is conducted by nitric acid, most of the rare earths substituted in the apatite lattice for calcium ions will go into solution, and the rate of REEs recovery is essentially higher than that when using sulfuric acid [7,8]. Besides, nitrate solutions are more preferable for extraction and separation of the REEs [9]. Hydrochloric acid is also used for dissolution of apatite for extraction of rare earths [7], however, the application of this acid is very limited.

Leaching of apatite in different acid media has been extensively studied [10−16]. However, there are few works on the leaching behavior of REEs from apatite. GUMGUM [17] studied the effect of acid concentration, agitation time and solid to liquid ratio on the leaching of yttrium from apatite by sulfuric acid. KHAWASSEK et al [18] studied the effect of acid concentration, agitation time, ore particle size, acid to ore ratio, temperature and

addition of H_2O_2 as oxidant on sulfuric acid leaching of apatite. WANG et al [19] investigated the influence of phosphoric acid concentration, temperature, liquid to solid ratio and additives on the REEs leaching efficiencies in digestion of apatite by sulfuric acid. They reported that REEs leaching recoveries increased by decreasing temperature and increasing the concentration of phosphoric acid and liquid/solid ratio. KANDIL et al [20] investigated the effect of acid concentration, flow rate and the presence of additives on the column leaching of REEs from apatite by hydrochloric acid, nitric acid and sulfuric acid solutions. They studied the kinetics of leaching by shrinking core model and reported that the rate controlling step is diffusion through ash layer and the activation energy for leaching is calculated accordingly. JORJANI et al [21] studied the effect of acidity, pulp density, agitation rate and time on the leaching recoveries of REEs from apatite by nitric acid. They used laboratory data to predict mathematical models for recoveries of REEs as function of various factors.

In the present work, apatite was leached by nitric acid and the effects of main process parameters including acid concentration, solid to liquid ratio and leaching time were investigated. For this purpose, the response surface methodology (RSM) and experiment design were employed and the influence of parameters affecting the leaching process and optimum condition were obtained. The kinetics of REEs leaching from apatite was also investigated and the controlling kinetic model of the reaction process was determined.

2 Experimental

2.1 Materials and apparatus

The apatite sample was the product of processing plant of Chadormalu Iron Ore Mine of Iran. The particle size of apatite concentrate was below 50 μm and no further grinding was performed. Nitric acid of analytical grade (Merck) was applied as leaching agent. XRD experiments were carried out to determine the mineralogical analysis of apatite sample. The rare earth elements in the apatite were determined by ICP-MS and for leaching samples by ICP-AES.

2.2 Leaching experiments

Leaching tests were carried out in a 200 mL glass reactor on a magnetic heater and stirrer. It has been reported that temperature has no significant effect on REEs leaching recoveries from apatite but higher temperature has favor advantageous due to volatilization of flour and sulfur [22]. Therefore, all leaching tests for optimization were performed at 60−70 °C. The pulp was stirred at an agitation speed of 800 r/min by magnet

stirrer in all tests including optimization and kinetics studies. Samples were taken after reaction period at pre-determined intervals and were filtered using a filter paper. The filtrate solution was analyzed for REEs and the leaching recovery was determined by the following equation:

$$R = \frac{C_L}{BC_A} \times 100\% \tag{1}$$

where R is the leaching recovery, B is the solid to liquid ratio, and C_L and C_A are the concentrations of REE in the leachate and apatite sample, respectively.

2.3 Design of experiments (DOE)

Response surface methodology (RSM) is widely used for optimization of process variable in many chemical systems. RSM helps to decrease the number of experiments needed for analyzing the process, and also analyze the interaction between the parameters [23]. Central composite design (CCD) was employed for experimental design. Nitric acid concentration, solid/liquid ratio and leaching time were chosen as the independent variables with their levels and ranges shown in Table 1. The chosen independent variables used in the process optimization were coded according to

$$X_i = \frac{x_i - x_0}{\Delta x} \tag{2}$$

where X_i is the dimensionless coded value of each independent variable, x_0 is the value of x_i at the center point and Δx is the step change value.

Table 1 Independent variables and their levels used in RSM design

Variable	Symbol	Range and level		
		−1	0	+1
Nitric acid concentration/%	A	10	20	30
Solid/liquid ratio	B	0.05	0.075	0.1
Leaching time/min	C	10	35	50

The leaching recoveries of lanthanum, cerium and neodymium were the response variables of the experimental conditions in the design of experiments. The nitric acid concentration was varied from 10% to 30%, the solid/liquid ratio was varied from 0.05 to 0.10, and the leaching time was selected in the range of 10 to 60 min. A total of 18 experiments consisting of 8 factorial points, 6 axial points and 4 replicates at the central points were carried out. The experimental results obtained from the CCD model were described by a second order polynomial as a function of X_i as given

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i X_i + \sum_{i=1}^{n} \beta_{ii} X_i^2 + \sum_{i<j}^{n} \beta_{ij} X_i X_j \tag{3}$$