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Kinetics study on the leaching of rare earth and aluminum from FCC catalyst waste slag using hydrochloric acid

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ABSTRACT

During the industrial production of FCC catalyst, a large amount of FCC catalyst waste slag (FCC waste slag) containing rare earths and aluminum was generated. Landfill was commonly used to deal with the slag, which may cause serious environmental degradation and resources depletion. A novel hydrometallurgical process consisting of hydrochloric acid leaching and subsequent neutralization is proposed to recover rare earths and aluminum from the FCC waste slag. The effect of leaching temperature, hydrochloric acid concentration and leaching time on the metal extraction are studied. The leaching kinetics of aluminum and rare earths are also investigated. It is shown that 91.0% of La, 92.2% of Ce, and 94.2% of Al are extracted under optimum leaching conditions of hydrochloric acid concentration 9.00 mol/L, solid to liquid ratio (S/L ratio) 0.05 g/mL, leaching temperature 293 K and leaching time 30 min. The leaching behaviors of aluminum and rare earths follow a shrinking core model which can be expressed as $1-(1-x)^{\frac{1}{3}}=k_{ap}t$, and the overall leaching process is controlled by the surface chemical reaction. The activation energies for the leaching of Al, La, and Ce are 6.24, 9.71, and 9.10 kJ/mol, respectively. Zeolite Na-Y and FCC catalyst presented in the FCC waste slag is leached with HCl individually. Only the FCC catalyst has a negative effect on the leaching of rare earths and aluminum. Finally, selective precipitation is employed to produce $Al(OH)_3$ and $RE(OH)_3$, which can be reused for the industrial production of FCC catalyst.

1. Introduction

Rare earths are valuable metals which are highly demanded for the application in phosphors, light emitting diode (LED) lighting, electronic communications, magnetic materials (Huang et al., 2015; Yang et al., 2013). To meet the global demand for rare earths, a number of methods for the recovery of rare earths from the secondary resources such as spent catalyst, computer monitor scraps, scrap magnet and municipal solid waste have been proposed (Alexandre et al., 1991; Behera and Parhi, 2016; Funari et al., 2016; Lin, 2014; Ober, 2016; Resende and Morais, 2010; Zhao et al., 2016).

FCC catalysts are used in a well-known process for cracking heavy gas oil into gasoline blending compounds (Velázquez et al., 2016). However, a large amount of FCC waste slag containing rare earths and aluminum is discharged during the production of FCC catalysts. In China, almost 100 thousand tons of FCC waste slag is discharged per annum. In the past decades, the FCC waste slag was mainly treated by landfilling, not only causes serious environmental pollution and land consumption, but also results in a waste of valuable metals.

Therefore, it is the urgent practical requirement for recovering valuable metals from the FCC waste slag regarding the concern of environment and resources. A variety of processes for the treatment of the FCC waste slag have been proposed. Li and Zhang (Li et al., 2013; Zhang, 2011) have reported the synthesis of Y-zeolite and ZSM zeolite using FCC waste slag. Sun (Sun et al., 1991) used the FCC waste slag to directly produce ceramic tile. However, rare earths cannot be effectively recovered in these methods, resulting in a waste of valuable metals. Hydrometallurgical method is commonly used to recover valuable metals from the secondary resources due to the relatively low energy consumption, low off-gas emission and low waste generation, and high recoveries of valuable metals (Cano et al., 2016; Kinoshita et al., 2003). In the hydrometallurgical process, valuable metals are first extracted into leaching solution, and conventional separation techniques such as solvent extraction, selective precipitation and ion-exchange are then employed to recover valuable metals from the leaching solution (Marafi and Stanislaus, 2003; Singh, 2009). For example, Qiu (Qiu and Wei, 1992) has studied the recovery of rare earths and aluminum from FCC waste slag by stepwise leaching using hydrochloric

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Table 1
Chemical composition of FCC waste slag (wt%).

Component	La_2O_3	CeO_2	Al_2O_3	Na_2O	CaO
Content	2.06	2.16	33.46	4.02	1.14

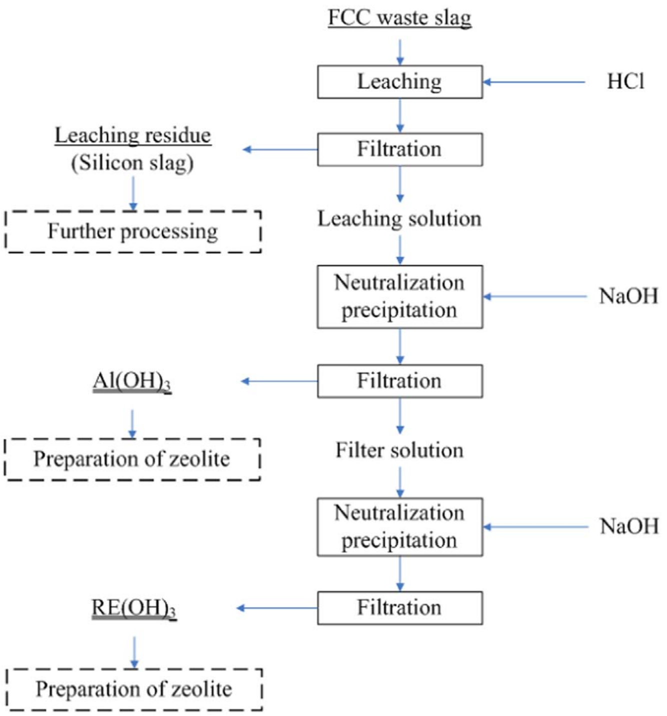

Fig. 1. Flow sheet for recovering rare earths and aluminum from the FCC waste slag.

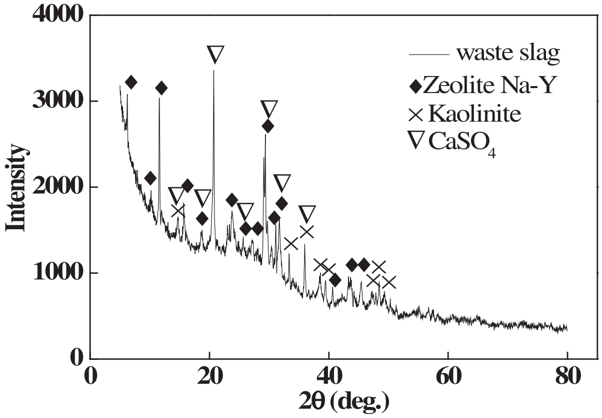

Fig. 3. XRD pattern of FCC waste slag.

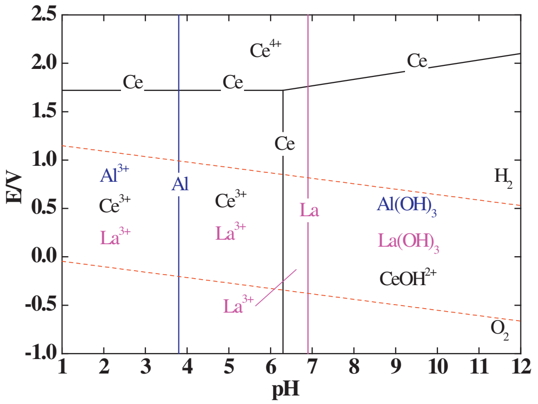

Fig. 4. Eh-pH diagram of Al-La-Ce-H_2O system.

acid (HCl) and sulfuric acid (H_2SO_4), followed by oxalic acid precipitation. The recoveries of rare earths and aluminum were 37.9% and 90.0%, respectively.

A novel hydrometallurgical process has been proposed to recover rare earths and aluminum from the FCC waste slag in this paper. The process consists of hydrochloric acid leaching and selective precipitation. Firstly, rare earths and aluminum are simultaneously extracted into the leaching solution using HCl. Thereafter, according to the different hydrolysis pH values of rare earths and aluminum, a selective precipitation process is employed to produce $RE(OH)_3$ and $Al(OH)_3$, respectively. Finally, the hydroxides are dissolved by HCl and H_2SO_4, respectively, to prepare $RECl_3$ and $Al_2(SO_4)_3$ solutions for the preparation of REY zeolite.

The reaction kinetic is essential for the design of a chemical process (Liu et al., 2012). To interpret the non-catalytic liquid-solid leaching process, kinetic models of shrinking, homogeneous, grain, uniform pore and random pore have been developed (Gbor and Jia, 2004). Among them, the shrinking core model is suitable for the reaction between an initially non-porous particle and a reagent, where the unreacted core gradually shrinks (Hong and Wadsworth, 1979). In many investigations for recovering valuable metals from the secondary resources, the dissolution of different rare earth elements were regarded as a whole unit (Yang et al., 2014a, 2014b). Regarding the dissolution of rare earths, the approach of considering the universal model for the leaching kinetics of all the constituent metals as one entity in media is a complete approximation. In particular the chemical reaction of each rare earth element in any acid would vary depending on their particle size and the mineral phases (Meshram et al., 2015b). In order to obtain accurate

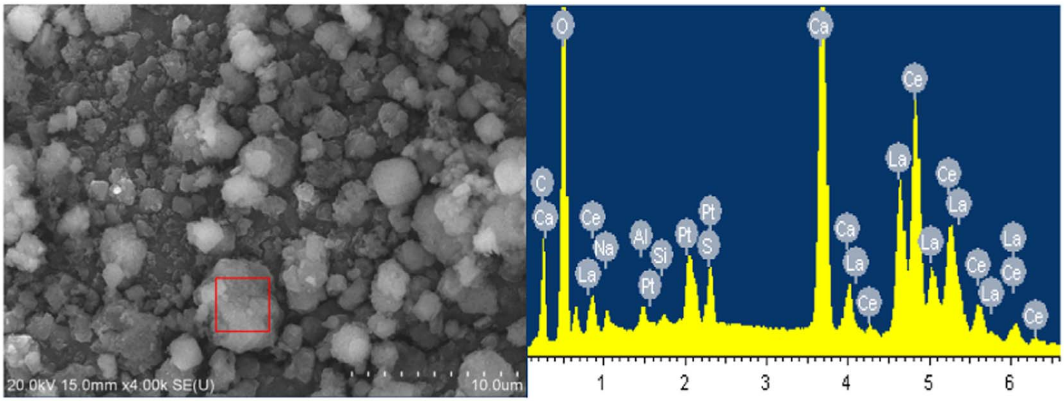

Fig. 2. SEM-EDX analysis of FCC waste slag.