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Kinetic models based on analysis of the dissolution of copper, zinc and brass from WEEE in a sodium persulfate environment

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ABSTRACT

The purpose of this study is to provide an accurate kinetic description for the dissolution process of metals found in WEEE, such copper, zinc, and brass, using persulfate as a leaching oxidant. The factors affecting the performance and efficiency of the leaching process, such as stirring speed, persulfate concentration and temperature were separately investigated. It was observed that the leaching rate of the metals increased with the increase of temperature and persulfate concentration. We propose three models which accurately describe the variation in the surface of the solid for two kinds of geometries, a rectangular block, in the case of pure zinc dissolution, and a cylindrical rod for pure copper and brass dissolution. The apparent activation energy for the leaching of pure copper and zinc has been evaluated using Arrhenius expression and has been determined to be 5.2×10^4 J mol^{-1} for copper and 3.5×10^4 J mol^{-1} for zinc, in the range between 30 and 60 °C. The third model which describes the dissolution of brass has provided the best results.

1. Introduction

Due to rapid improvements in electrical and electronic manufacturing technologies, the electrical and electronic equipment (EEE) can be regarded as a short-life-cycle product (Tian et al., 2014). This phenomenon results in large quantity of obsolete EEE, generating a significant amount of waste electrical and electronic equipment (WEEE) in the last couple of years (Kumar et al., 2014). Hazardous components or substances (polychlorinated biphenyls, ozone-depleting substances, asbestos, fluorescent tubes, nickel cadmium batteries, cathode ray tubes, etc.) contained in WEEE may seriously pollute the environment if they are not properly disposed of (Khaliq et al., 2014). Therefore, many countries and organizations have drafted national legislation which aims to prevent the generation of WEEE and to promote reuse, recycling and other forms of recovery in order to reduce the quantity of such waste (Bereketli et al., 2011). In addition to other hazardous materials, the quantity of valuable materials, especially gold and copper, turns the waste in a potential source for new raw materials (Barbieri et al., 2010). While the remaining waste after recycling valuable materials, can be used as fuel instead of landfill (Niziolek et al., 2015).

WEEE is non-homogenous and complex in terms of different materials and components. Generally, WEEE is composed of metal (40%), plastic (30%) and refractory oxides (30%). The amount of metal contains 20% copper and 1% zinc (Gramatyka et al., 2007). Copper, zinc and brass are widely used in the production of electrical wire and cable, electrical contact, and various other parts (Ninan et al., 2014). Consequently, with the earth copper and zinc resources increasingly depleted, the development of copper and zinc recycling processes from waste has become important not only to reduce the amount of waste and minimize the effect of hazardous materials, but also to promote recovery of valuable metals from alternative sources and to preserve our natural resources (Bonnin et al., 2013).

Several methods have been investigated and applied for metal recovery from WEEE, based on mechanical/physical, pyrometallurgical and hydrometallurgical processes. Mechanical/physical processes are based on the different physical characteristics of the materials which can be found in the waste composition (Habib et al., 2013). Unfortunately, this method does not ensure a high quality for recovered metals and presents disadvantages such as high energy consumption (Muniyandi et al., 2013). Although treatments by pyrometallurgical processes are not attractive on account

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Table 1
Material description.

Material	Weight (g)	Length (cm)	Diameter (cm)	Surface (cm^2)
Copper	2	3	0.3	–
Zinc	3.2-5	–	–	1.62-1.98
Brass	3.6-5.6	1.4-2	0.6	–

of large amounts of SO_2 produced and high energy consumption, approximately 80% of the total metallic copper and zinc is produced pyrometallurgically (Liu et al., 2012). Due to stringent requirements of environmental protection, the traditional metal recovery processes based on roasting have become less desirable. For high separation of metals from WEEE, the hydrometallurgical method ensures high recovery rate and high purity metals (Fogarasi et al., 2014). In addition to some other operational advantages hydrometallurgical processes are more environmentally friendly and economically feasible.

The hydrometallurgical process is based on dissolving the metal content into leaching solution such as acids or alkaline. There are many studies related to leaching of copper, zinc, and brass using various agents such as sulfuric acid and hydrogen peroxide (Yang et al., 2011), ammonia, hydrochloric acid, nitric acid, cyanide, and acetic acid (Le et al., 2011). These leaching agents can dissolve many types of metals from WEEE, but due to their corrosive and poisonous properties they require adequate corrosion-proof equipment as well as complicated follow-up separation procedures. A potential alternative to acid and alkaline leaching of metals and alloys is to use persulfate as an oxidizing agent. Persulfate is known as a strong oxidant and has the advantage that it can be regenerated by electrochemical oxidation (Liu et al., 2014). Considering its regeneration properties, this type of leaching agent can also address the problem of large amounts of waste solution generated by the hydrometallurgical process. The operating parameters with the greatest impact on the dissolution of metals using persulfate are leaching time, temperature, and oxidant concentration (Popescu et al., 2014). The development of detailed chemical kinetic models is necessary for the design and optimization of complex chemical systems (Perumal et al., 2013). Various methods that describe the dissolution kinetics of copper and zinc have been developed over the last years. Liu et al. (2012) developed a new shrinking core model, which is based on the interfacial transfer and diffusion through the product layer and can be used to describe the dissolution kinetics of copper in the ammonia-ammonium sulfate with sodium persulfate. The activation energy was found to be 22.91 kJ/mol. The kinetic study developed by Babu et al. (2002) indicated that the leaching of zinc in ammonium persulfate followed a diffusion-controlled model and the rate was governed by the diffusion of lixiviant through porous sulfur layer as the reaction product. The activation energy was found to be 41 ± 2 kJ/mol.

Based on literature survey, it appears that sodium persulfate has not been considered for oxidation of metal for the purpose of metal recovery from WEEE. Therefore, it is considered imperative to use an environmentally friendly oxidant for leaching of metals from WEEE, which has high extraction efficiency and seems attractive in view of its regeneration. Also, existing kinetic models can only accurately describe the dissolution process of metals at a micro scale.

The present study aims to analyze the dissolution kinetics of copper, zinc, and brass from WEEE in sodium persulfate environment in order to take the first step in the design process of a technology which can recover precious metals from waste. The first phase involves testing individually the efficiency of sodium persulfate in the dissolution process of copper, zinc, and brass, respectively. Based on experimental data, we propose three kinetic models with different complexity, which adequately describes the leaching process of the investigated materials at a macro scale. These models can be used for different purposes as we summarize in Section 3.

2. Experimental

2.1. Material

The materials used in the leaching process derived from WEEE; shape, size, weight, and composition (Table 1) were chosen to highlight specific components of the dissolution kinetics. The first set of experiments aimed at investigating the usage of $Na_2S_2O_8$ in copper dissolution. The material used in these experiments was metallic copper wire with a purity of 99.99%. For the study of zinc dissolution in persulfate environment, a rectangular block of zinc was chosen. Five facets of the block were varnished and one facet has been left untouched to interact with the persulfate solution, since the zinc block sinks to the bottom of the reactor. The material used for copper and zinc dissolution from brass is a cylindrical rod of brass. The composition of the alloy (65% copper and 35% zinc) was determined by complete dissolution of the metal in nitric acid and analysis of the components was performed using an atomic absorption spectrometer.

2.2. Experimental process

The chemical leaching experiments were carried out in a 150 mL isothermal stirred batch reactor. The reaction vessel was connected to a thermostatic circulating water bath with a controlling temperature accuracy of $\pm 0.1\,^{\circ}C$. Agitation was provided by a magnetic stirrer. One hundred milliliters of $Na_2S_2O_8$ solution was added to the reactor. When the desired stirring speed and reaction temperature were reached, the solid sample was added into the reactor. One milliliter of sample solution was withdrawn at specific time intervals and copper/zinc concentration was analyzed using an atomic absorption spectrometer (AAS). Metals (Cu and Zn) or brass samples remained after the leaching process were dried and weighed after each experiment.

3. Results and discussions

The global reactions describing the leaching process of zinc and copper using sodium persulfate as an oxidizing agent are presented in Eqs. (1) and (2). The same reactions have been proposed for kinetic analysis and parameter identification.

$$Zn + Na_2S_2O_8 \rightarrow ZnSO_4 + Na_2SO_4 \quad (1)$$

$$Cu + Na_2S_2O_8 \rightarrow CuSO_4 + Na_2SO_4 \quad (2)$$

The experiments were conducted to separately investigate the performance and efficiency of the $Na_2S_2O_8$ solution in the leaching process of copper, zinc, and brass respectively. The effect of temperature and concentrations of sodium persulfate were determined on the rate of the dissolution process. We kept the following parameters constant: leaching time (2 h) and stirring speed (350 rpm). The initial pH was low (3.8) in the reactor and it was not controlled during the dissolution process. Specific kinetic parameters were identified for each set of experimental data.

3.1. Effect of stirring

Usually, agitation of the sample solution could improve the mass transfer and accelerate the dissolution process. In order to investigate the effect of the stirring speed on the copper/zinc dissolution, experiments were carried out at different stirring rates (namely: 50,