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Cleaning of high lead-bearing zinc leaching residue by recovery of lead with alkaline leaching

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ABSTRACT

In the hydrometallurgical zinc production processes, huge quantities of solid leaching residues containing different metallic compounds threat the environment are continuously generated around the world. Due to increasing demand of metals and the depletion of high grade natural resources, these types of wastes are gaining great importance in the metallurgical industries. In this study, cleaning of zinc leaching residue, containing 19% Pb in the form of anglesite, by recovering of lead with alkaline leaching was investigated. For this purpose; the effects of NaOH concentration, leaching time and temperature on the Pb recovery from the residue were studied. Under the optimum conditions using NaOH concentration of 11%, L/S ratio of 5, temperature of 100 °C, and leaching time of 60 min, the leaching ratio of Pb reached up to 99.6%. Kinetic analysis of the experimental data showed that the leaching was ash layer diffusion controlled with activation energy of 2.78 kJ/mol. Pb could be effectively separated from the pregnant leach solution with chemical precipitation by Na_2S and CO_2. TCLP and EU Directive EC/2003/33 tests applied to the remaining leach residue showed that it was environmentally stable and non-hazardous waste, respectively.

1. Introduction

Zinc is commonly produced from its ores in the combined systems consist of roasting–leaching–electrowinning processes in worldwide. In these processes, ZnO-rich calcine is first produced from the concentrates and then zinc in the calcine is leached with hot sulphuric acid solution. A pregnant leach solution and a solid leach residue are obtained after liquid–solid separation by rotary filter. The pregnant solution is purified and zinc is won by electrolysis.

Zinc leaching residues contain significant amounts of precious metals such as lead, silver, cadmium and unextractable zinc. Zinc and lead usually occur together in a variety of minerals. Therefore, zinc production residues contain important amount of lead. These residues are generally stockpiled in many plants to recover these precious metals in the future (Turan et al., 2004). The leach residue is also classified as a hazardous waste due to the presence of significant amounts of leachable heavy metals (Özverdi and Erdem, 2010). Due to increasing demand of metals and the depletion of high grade natural resources, these types of secondaries and wastes are gaining great importance in the metallurgical industries. In order to recover metallic values from these types of secondaries/wastes, a lot of researches have been made (Abdel Basir and Rabah, 1999; Banza et al., 2002; Barakat, 1999; Kinoshita et al., 2004; Kul and Topkaya, 2008; Lai et al., 2008; Li et al., 2008, 2009, 2010; Morgan and Lee, 1997; Rossini and Bernardes, 2006; Shen and Forssberg, 2003; Silva et al., 2005; Turan et al., 2004). Hydrometallurgical processes are widely used technology in today's production of base and valuable metals. Therefore, it has also received extensive attention by researchers interested in recovering metals from secondaries/wastes. In the hydrometallurgical processes, different lixiviants such as sulphuric acid (Abdel Basir and Rabah, 1999; Asadi Zeydabadi et al., 1997; Huang et al., 2007; Kul and Topkaya, 2008; Li et al., 2010; Luo et al., 2010; Nagib and Inoue, 2000; Ruşen et al., 2008), hydrochloric acid (Abdel Basir and Rabah, 1999; Nagib and Inoue, 2000), nitric acid (Ioannidis et al., 2006; Zárate-Gutiérrez et al., 2010), caustic soda (Jarupisitthorn et al., 2003; Nagib and Inoue, 2000; Santos et al., 2010; Xia and Pickles, 1999a, 1999b; Xia and Picklesi, 2000; Zhao and Stanforth, 2000), brine (Andrews et al., 2000; Guo et al., 2010; Raghavan et al., 1998, 2000; Turan et al., 2004), ammonia, ammonium carbonate, ammonium chloride, and some carboxylic acids (Jha et al., 2001) are generally used. Acidic leach solutions, caustic soda and brine solution have been found to be very effective lixiviant for the leaching of lead and zinc. Although high leaching yields can be obtained in the acidic leach solutions and brine solutions, they are not applicable due to releasing of the important amount of impurities and chloride ions, which is affected seriously the quality of zinc powder and the current efficiency in electrowinning of zinc (Zhao and Liu, 2011). Caustic soda is the most suitable lixiviant in this respect for the amphoteric lead and zinc. In the caustic soda leach process, lead and zinc are selectively dissolved in sodium hydroxide solution rejecting nonamphoterics in the residue.

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The process has been attempted for the dissolution of zinc from different sources such as iron and steel making dusts (Dutra et al., 2006; Frenay and Hissel, 1984), electric arc furnace dust (Xia and Pickles, 1999a, 1999b; Xia and Picklesi, 2000), smithsonite Zn–Pb ores (Zhao and Stanforth, 2000), and fly ash generated from municipal incineration plants (Nagib and Inoue, 2000). In these researches, atmospheric leach processes have been widely applied and readily soluble constituents have been leached out. Particularly, Nagib and Inoue (2000) have been reported that the alkaline leaching of fly ash generated from municipal incineration plants is a potentially feasible method for simultaneous detoxification and metal recovery. Santos et al. (2010) reported that 74% of zinc was extracted from zinc silicate ore by leaching with 6 M NaOH in 4 h. Zhao and Stanforth (2000) studied the production of zinc powder by alkaline treatment of smithsonite Zn–Pb ores that could obtain 85% of both Zn and Pb recovery using 5 M NaOH at over 95 °C. Xia and Picklesi (2000) found that 95% zinc recovery from zinc ferrite in the electric furnace was achieved by 8 M microwave NaOH leaching. Jarupisitthorn et al. (2003) also studied the kinetics of zinc leaching from electric arc furnace dust by NaOH. They achieved the recovery of 77% Zn with 1.5–4 M NaOH in 60 min.

In recent years, the hydrometallurgical processes carried out at elevated temperature/pressure have become great interest for recovery of valuable compounds with low solubility (Azimi and Papangelakis, 2010; Havlik et al., 2004; Huang et al., 2007; Jin et al., 2009; Langová and Matýsek, 2010). These processes improve the mass transfer of the leach solution into solid particle and thus, accelerate the dissolution kinetics by the effects of temperature and pressure. Particularly, cleaning of high lead-bearing zinc leaching residue by recovery of lead with alkaline leaching has not been investigated. Starting from this point, in this study, the application of pressure leaching technique in the recovery of whole lead from the zinc leaching residue by selective NaOH leaching was studied. The effects of parameters including the initial NaOH concentration, leaching time and leaching temperature on the leaching efficiency and the leaching kinetics, separation of lead from the leach solution and pollution potential of the leach residue were investigated.

2. Materials and methods

2.1. Materials

As described in our previous papers, the zinc leaching residue (ZER) used in the study was obtained from Çinkur Plant located in Kayseri, Turkey. It was dried at room temperature for ten days and then subjected to sieve analysis. Sieve analysis showed that about 76% of the ZER was smaller than 150 μm (−100 mesh). The sample was sieved to obtain particles smaller than 75 μm (−200 mesh) prior to use. The chemical and mineralogical compositions of the residue were determined. Chemical analysis shows that the ZER contains 19.02% Pb, 12.25% S, 7.98% Zn, 6.19% Ca, 6.74% Si, 5.44% Fe and 1.85% Al as major elements. The major mineralogical phases in the residue were determined to be gypsum [$CaSO_4.2H_2O$], anglesite [$PbSO_4$], massicot [PbO], quartz [SiO_2], maghemite [Fe_2O_3], hercynite [Al_2FeO_4] and franklinite [$ZnFe_2O_4$] (Özverdi and Erdem, 2010).

2.2. Experimental procedure

2.2.1. Leaching experiments

Leaching experiments were conducted in a 500 ml stainless steel SS 316Tl high pressure reactor (Berghof BR 500). The reactor is equipped with a PTFE insert, thermal sensor with immersion tube, gas and liquid sampler, manometer, vent valve and stirrer. All sides of the reactor are lined with PTFE. Agitation and heating are provided by a stirrer shaft in the reactor interior by means of a magnetic clutch and heater block mount, respectively. The temperature and agitation speed were controlled with a PID controller.

About 40 g of the ZER was mixed in 200 ml NaOH solution having desired concentration in the PTFE insert prior to each experiment and then it was placed in the reactor. The reactor content agitated continuously at a 700 rpm constant speed was heated up to predetermined temperature. After achieving the desired temperature, the required reaction time was started. The temperatures being used and the corresponding pressures are given in Table 1. After the reaction was completed, the reactor was removed from the heater mount and was rapidly water-cooled to 70 °C. The reactor content was filtered by vacuum filtration. The leach residue was then washed three times with 50 ml 50 °C distilled water and then the wash solutions were added to the main pregnant leach solution. The solutions were analyzed for dissolved metal ions, while the solid leach residues were subjected to mineralogical, chemical and particle size analyses.

2.2.2. Separation of the lead from pregnant leach solution

In order to separate lead dissolved from the pregnant leach solution, two chemical precipitation methods with sodium sulfide (in the form of PbS) and carbon dioxide (in the form of $PbCO_3$) were applied. For this purpose, while different weight ratios of sodium sulfide to the lead were tested to precipitate whole lead ions in the leach solution, carbon dioxide gas was bubbled through the pregnant leach solution diluted with 1/3 distilled water to reduce the alkalinity. Mineralogical compositions of the solid materials precipitated were determined by X-ray diffractometer.

Each experiment was performed in duplicate and arithmetic averages calculated from the values varied within ±5% were taken into account.

2.2.3. Determination of the pollution potential of the leach residue

The toxicity characteristic leaching procedure (TCLP) (USEPA, 1990) and the European Directive EC/2003/33 test methods were applied to determine the potential release of contaminants from the leach residue. For the TCLP, pH of the leach residue was first determined and the extraction solution was selected depending on the pH measured. Then, the leach residue was extracted at a liquid to solid ratio (L/S) of 20 in capped polypropylene bottles on a rotary tumbler at 30 ± 2 rpm and 23 ± 2 °C for 18 ± 2 h. For the European Directive EC/2003/33 (EC, 2003), the leach residue was treated with water at L/S of 2 and 10 l/kg in capped polypropylene bottles at 25 ± 2 °C for 24 h. After both extractions, the liquids were separated from the solid residue by filtration through a 0.45 μm glass fiber filter and the filtrates were analyzed.

2.3. Methods of analysis

Philips PW-2404 electron X-ray fluorescence spectroscopy and Shimadzu XRD-6000 X-ray diffractometer were used for the determination of chemical and mineralogical compositions of the samples, respectively. In addition, all solid samples were digested by microwave digestion unit (CEM MarsX Press) for chemical analysis. Perkin Elmer AAnalyst 800 was used to determine the metal ion concentrations in the solutions. Particle size of the samples was measured by using Malvern Master Sizer 3000.

3. Results and discussion

3.1. Leaching reactions

The ZER used in the study contains mainly of gypsum [$CaSO_4.2H_2O$], anglesite [$PbSO_4$], massicot [PbO], quartz [SiO_2], maghemite [Fe_2O_3], hercynite [Al_2FeO_4] and franklinite [$ZnFe_2O_4$]. In the hydrometallurgical recovery processes, different lixiviants such as sulphuric acid (Abdel

Table 1
Leaching temperatures and corresponding pressures being used for the experiments.

Temperature, °C	85	100	125	150	175
Pressure, bar	0.9	1.0	3.4	5.1	7.5