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Recovery of manganese from silicomanganese slag by means of a hydrometallurgical process

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ABSTRACT

A hydrometallurgical process is proposed in this paper to recover manganese from silicomanganese slag. The paper reports the digestion–leaching experiments and precipitation and electrowinning assays to recover Mn from this residue. Silicomanganese slag was first treated with sulfuric acid in a furnace at 200 °C. It was then leached with water, CaO and KOH, and finally filtered to dissolve the manganese. Sulfuric liquor needs a purification step in order to remove Zn, Ni, Co and Cu. Na_2S was used to remove pollutants, a 5% excess with respect to the stoichiometric amounts of sulfide required for the reaction being employed for this purpose. The purified liquor is suitable for electrolysis. α-manganese is obtained with a purity of 99.99.

1. Introduction

Silicomanganese alloy is produced by carbothermal reduction of oxide ores in electric submerged arc furnaces. The (SiMn) slag is produced by silica and other basic oxides associated with the ores. At the end of the electric arc furnace, slag is separated from the alloy by density and poured into a pit where it is slowly air cooled to room temperature. The most common method for disposing of this slag is dumping in landfill.

Around 1.2–1.4 t of slag is normally generated for every ton of SiMn alloy produced. Significant volumes of slag are accordingly produced yearly worldwide.

Slags have often been considered as only slightly reactive materials because of the low-solubility of their solid phases. However, more recent studies have shown that slags could be reactive and may be a source of environmental pollution when sent to landfill. Thus, in areas contaminated by smelting activities, high amounts of heavy metals can often be detected in the soil and/or groundwater. Mn is present in the slag under study here and is known to be an environmental pollutant due to its potentially toxic effects (Pareuil et al., 2010a, 2010b, 2011; Navarro et al., 2008; Parsons et al., 2001).

SiMn slag consists of oxides such as SiO_2, CaO, Al_2O_3, MgO and MnO. The MnO content of industrial SiMn slag usually ranges between 6 and 10%. The slag presents a mainly amorphous structure.

Due to their chemical and mineral composition, slags have cementitious and/or pozzolanic properties; hence, the majority of research on the use of SiMn slag is in the field of cement (Frías et al., 2006, 2009; Frías and Rodríguez, 2008; Zhang et al., 2011; Kumar et al., 2013). Others researchers suggest recycling silicomanganese slag back into the silicomanganese alloy smelting furnace (Byung-Su et al., 2011; Kutsin et al., 2011).

It is important to find a possible way of recovering manganese in order to minimize its environmental impact. However, very little data is available on the use of silicomanganese slag as a source of manganese.

The aim of the present research is thus to propose a hydrometallurgical method to recover the manganese present in slag in order to obtain a liquor suitable for manufacturing manganese electrolytic. The experimental parameters affecting the leaching and purification processes were studied and optimized.

The proposed hydrometallurgical process avoids high temperature reduction roasting (800–1000 °C), which is conventionally used in processing high-grade material to convert it into acid-leachable manganese using sulfuric acid.

The sulfate process is used in hydrometallurgy due to the lower cost of H_2SO_4 compared to other acids and because the sulfate solution is less corrosive. Extensive research has been carried out on the dissolution of manganese ores in acidic media (Elsherief, 2000; Hariprasad et al., 2007, 2013; Sahoo et al., 2001; Ayala and Fernandez, 2013; Nayl et al., 2011; Beolchini et al., 2001; Senanayake, 2004; Jiang et al., 2003, 2004; Zhang and Cheng, 2007a; Zhang et al., 2013; Vafaeian et al., 2011; Ghafarizadeh et al., 2011; Pakarinen and Paatero, 2011; Senanayake, 2011).

Furthermore, electrodeposition of manganese has been widely studied in sulfate solutions (Wei et al., 2007, 2010; Kemetco Research Inc., 2010; Mendonça de Araujo et al., 2006; Duan et al., 2011; Xu et al., 2014).

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2. Experimental procedures

2.1. Characterization of the silicomanganese slag

The silicomanganese slag was crushed and thoroughly homogenized. Representative samples were then taken for characterization and the subsequent leaching test.

The chemical analysis of the slag was determined by atomic absorption spectroscopy (Perkin Elmer A Analyst 200) after acid digestion, while a gravimetric technique was used to analyze sulfate content.

The mineralogical composition was examined by XRD analysis (Philips X'Pert Pro system with CuKα radiation). Particle size distribution was determined by screening, the results of which are given in Table 1.

2.2. Manganese dissolution experiments

Leach solutions were prepared by adding a suitable amount of sulfuric acid to distilled water to obtain the required acid concentration.

The first leaching tests were carried out in a 100 mL glass reactor equipped with a magnetic stirring system. The slag sample was charged and sulfuric acid was added, the mixture was stirred for a specified time interval and the pulp thus obtained was filtered and washed several times. The amount of manganese in the filtrate was determined by atomic absorption spectroscopy (AAS). The percentage extraction of Mn was calculated based on that amount.

Time (15 to 60 min) and temperature (20 to 100 °C) were varied to study the effect of these parameters on manganese leaching. Assays were carried out varying the acid concentration (10–30% by mass), in some case using the stoichiometric amount of acid needed to dissolve one gram of slag and, in others, an excess of acid (10–30%).

Several experiments were carried out under more drastic conditions: an amount of H_2SO_4 solution was mixed with 10 g slag in a porcelain dish and placed in a Carbolite OWF 1100 furnace at the required temperature (200–300 °C) using different acid concentrations (10–30% by mass). At the end of the predetermined heating period (30–120 min), the sample was removed from the furnace. The solid residue was then leached with distilled water and stirred to dissolve the sulfates. The slurry was washed several times and then filtered. The leach liquor was analyzed for Mn using AAS, subsequently calculating the percentage extraction.

The next step was to prepare several liters of a solution with a high concentration of manganese in order to carry out electrolysis.

Several tests using 50 g of silicomanganese slag with excesses of 10% sulfuric acid (10% by mass) were performed at 200 °C for 1 h. The samples were then leached with 250 mL water with the addition of CaO and KOH to reach pH = 6 so as to prevent the silicon, aluminum and iron from being released into the liquor, and were finally filtered (Biswal et al., 2013; Sun et al., 2013). Table 2 shows the chemical composition of the liquor thus obtained. The washwaters were not added in either case, as the aim was to obtain a concentrated manganese dissolution. Washwaters with a low manganese concentration could be reused in this process during the leaching stage.

The solid residue obtained after filtration was dried and characterized by X-ray diffraction.

Table 1
Silicomanganese slag particle size distribution after milling.

Fraction (μm)	%
>300	15.02
300–150	15.90
150–100	9.67
100–75	25.68
75–32	12.47
<32	21.26

2.3. Purification of the leach solution

Besides other impurities, the leach liquors contain manganese, zinc, cobalt, copper, calcium and potassium. As manganese has a high negative value in the electromotive series, the levels of other metals with a less negative potential should be very strictly controlled.

The separation of impurities such as Zn, Ni, Co and Cu from manganese can be carried out via sulfide precipitation. The precipitation and separation of metal sulfides are based on the different sulfide solubility of metals at a specific pH and temperature. Gaseous hydrogen sulfide (H_2S), sodium sulfide (Na_2S) or ammonium sulfide $(NH_4)_2S$ is usually employed in the precipitation of metal sulfides (Jackson, 1986; Hayes, 1985; Veeken et al., 2003; Jakuszewski et al., 1972; Zhang and Cheng, 2007b; Lewis, 2010, Biswal et al., 2015).

The zinc and other impurities in the solution were precipitated using a Na_2S solution at pH 5–7, leaving manganese in solution for subsequent recovery:

$$Na_2S + Zn^{2+} \text{ – – – – – – – – – } ZnS(s) + 2\,Na^{+} \quad (1)$$

Precipitation assays were carried out at room temperature in a 250 mL covered glass reactor under constant stirring, monitoring the pH of the solution during 60 min. Different tests were carried out using the stoichiometric amount and others with an excess of Na_2S concentrated solution. The sulfide precipitate was likewise separated by filtration. The overflow solution containing mainly $MnSO_4$ was then ready for electrowinning of Mn, Tables 3 and 4.

2.4. Electrodeposition

The predominant electrochemical reactions at the electrodes are as follows:

Cathodic reactions:

$$Mn^{2+} + 2e^{-} \rightarrow Mn \quad (2)$$

$$2H_2O + 2e^{-} \rightarrow H_2 + 2OH^{-} \quad (3)$$

$$2H^{+} + 2e^{-} \rightarrow H_2 \quad (4)$$

Anodic reactions:

$$2H_2O \rightarrow O_2 + 4H^{+} + 4e^{-} \quad (5)$$

$$2H^{+} + SO_4^{2-} \rightarrow H_2SO_4 \quad (6)$$

Table 2
Composition of leach solution.

Mn (g/L)	Zn (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Ca (ppm)	Mg (ppm)	K (ppm)	Na (ppm)	Fe (ppm)	Al (ppm)
31.2	2.63	0.23	1.0	0.57	258	2792	1202	326	0	0