Hydrometallurgy 169 (2017) 201–206

Contents lists available at ScienceDirect

Hydrometallurgy

journal homepage: www.elsevier.com/locate/hydromet

Potential-controlled selective recovery of manganese and cobalt from cobalt slag leaching solution

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ARTICLE INFO

Article history:
Received 3 June 2016
Received in revised form 22 November 2016
Accepted 29 January 2017
Available online 01 February 2017

Keywords:
Ozone
Leaching solution of cobalt slag
Potential-controlled
Selective recovery of manganese and cobalt
Zinc

ABSTRACT

In this study, manganese and cobalt were selectively separated and recovered from zinc in a leaching solution of cobalt slag by potential-controlled oxidation with ozone. The separation mechanism was discussed. When ozone was pumped into the solution, the manganese (II) was first oxidized and precipitated. After the precipitated manganese is removed from the solution, the cobalt (II) in the solution was oxidized and separated in the same way. Partial zinc was also lost in the precipitates in the form of encapsulated inclusions. The effects of dilution ratio, solution pH values, system temperatures on the manganese and cobalt recoveries were investigated. High recovery rates of cobalt and manganese were achieved, high-grade cobalt precipitate and highly purified liquid were obtained at optimized conditions.

1. Introduction

In the hydrometallurgical process of zinc extraction, impurity cobalt is harmful to cathode plate (Mei, 2001; Krause and Sandenbergh, 2015; Yang et al., 2006), and plate-burning easily take places when the concentration of cobalt is higher than certain levels. Therefore, removing cobalt from zinc solution before zinc electrowinning is necessary. One method to remove cobalt from zinc solution is to use activated zinc powder to replace the cobalt in solution, which is widely used in industry (Ma and Yang, 2005; Fattahi et al., 2016). In order to effectively purify the solution, excessive activated zinc powder is usually be added. The precipitate is called as cobalt slag. The cobalt slag contains lots of valuable metal elements (Zeng and Xie, 2008), such as zinc, cobalt and so on. For the sake of financial, social and environmental benefits, recovering the valuable metals from the cobalt slag is needed. Currently, the cobalt slag is processed by an oxidation-leaching process in which a multi-metal solution is obtained. Then the cobalt in the leaching solution is recovered and replaced by adding zinc powder once again (Xu et al., 2006), or is oxidized by strong oxidants (Li et al., 2011). After these processes the cobalt would be enriched in precipitate once again.

At present, processes widely used to purify cobalt or separate cobalt from its slag are solvent extraction and ion exchange methods (Wang et al., 2012; Jha et al., 2013). However, the recovering process of these methods is quiet long as complex multi-metal solutions are treated. On the contrary, the oxidation-precipitation method works well and is widely used in cobalt removal. However, this method has also some disadvantages: it usually brings secondary pollution to the solution when traditional oxidants (such as $KMnO_4$, NaClO and Cl_2) are used, which is also harmful to the subsequent procedures. So an adaptable, clean and short recovering process is required to treat cobalt-bearing multi-metal solutions. Ozone is considered as a cleaner oxidant compared with $KMnO_4$, NaClO and Cl_2. Due to its strong-oxidation capability, ozone is widely used in the fields of environmental protection, sterilization and disinfection, etc. (Beltrán, 2004; Gottschalk et al., 2004).

In this study, the ozone, generated from oxygen and finally turned into oxygen/oxides, is selected as a clean oxidant for the oxidation-precipitation process of cobalt (Tian et al., 2010), where cobalt is effectively separated without secondary pollution. The raw material we used in our experiments is a leaching solution of cobalt slag. The cobalt slag is yielded. Besides zinc and cobalt, some manganese is also in the solution. So it is necessary and meaningful to recover these valuable metals from the solution. In order to obtain high-grade manganese precipitate, cobalt precipitate as well as purer zinc sulfate solution, we analyzed the mechanism of separating manganese and cobalt by controlling the potential and investigated the influence of dilution ratio, pH values and operating temperatures on the process in this paper.

2. Experimental

2.1. Material and apparatus

The concentration of manganese & cobalt were detected by inductive coupled plasma and atomic emission spectrometer (ICP-AES, PS-6,

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http://dx.doi.org/10.1016/j.hydromet.2017.01.011
0304-386X/© 2017 Published by Elsevier B.V.

Baird, USA), and the potential was measured by potential-pH meter (PHS-3C, INESA, China). The main material is leaching solution of cobalt slag from some smelt plant, the composition is listed in Table 1.

Reagents used in our experiment were NaOH (AR, Sinopharm Chemical Reagent Co., Ltd.), O_2 (TECH, CSGaoke Co., Ltd.), H_2SO_4 (AR, Sinopharm Chemical Reagent Co., Ltd.), CoSO4(AR, Sinopharm Chemical Reagent Co., Ltd.), $MnSO_4$ (AR, Sinopharm Chemical Reagent Co., Ltd.).

Equipments used in the experiment were ozone generator (OZOMJB-10B, ANQIU OZOMAX EQUIPMENT, China), thermostat water bath (DF-101B, YUHUA, China), constant speed stirrer (JJ-1B-200w, Jintan Xunsheng Instrument, China) and some other auxiliary equipment. Oxygen was used to produce ozone for the leaching process and the mass flow of the ozone controlled by an ozonizer (OZOMJB-10B, ANQIU OZOMAX EQUIPMENT, China) at 120 mg/L.

2.2. Procedure

2.2.1. Feasibility of oxidation-precipitation of manganese & cobalt by ozone

In a multi-metal solution, besides the cobalt ion, the manganese ion could also be oxidized. The Mn(II) and Co(II) could be oxidized to unstable status by strong oxidant and the Mn(III)&Mn(IV) and Co(III) are unstable in the solution, because they react with hydroxyl and yield MnO_2, Mn_2O_3 and CoOOH which are separated from the solution (Tian et al., 2013; Hem et al., 1985). The reactions of manganese and cobalt with ozone in the oxidation-precipitation process are listed below.

$$\begin{aligned} &Mn^{2+} + 1/2O_3 + H_2O = 1/2Mn_2O_3 + 2H^+ + 1/2O_2 \\ &\qquad \Delta_rG^{\Theta}{}_m = -96.97\ \mathrm{kJ\ mol^{-1}} \\ &E_{(1)} = E_{(1)}{}^{\Theta} - 2 * 0.0591 * pH - 0.0591 *\ \lg\left[Mn^{2+}\right] \\ &\qquad \Delta E^{\Theta} = \Delta_rG^{\Theta}{}_m/(zF) \quad F = 96,485C/mol \end{aligned} \tag{1}$$

$$\begin{aligned} &Mn^{2+} + O_3 + H_2O = MnO_2 + 2H^+ + O_2 \qquad \Delta_rG^{\Theta}{}_m = -143.77\ \mathrm{kJ\ mol^{-1}} \\ &E_{(2)} = E_{(2)}{}^{\Theta} - 0.0591 * pH - 1/2 * 0.0591 *\ \lg\left[Mn^{2+}\right] \end{aligned} \tag{2}$$

$$\begin{aligned} &Co^{2+} + 1/2O_3 + 3/2H_2O = CoOOH + 2H^+ + 1/2O_2 \qquad \Delta_rG^{\Theta}{}_m = -150.54\ \mathrm{kJ\ mol^{-1}} \\ &E_{(3)} = E_{(3)}{}^{\Theta} - 2 * 0.0591 * pH - 0.0591 *\ \lg\left[Co^{2+}\right] \end{aligned} \tag{3}$$

The standard Gibbs free energy ($\Delta_rG^{\Theta}{}_m(1)$, $\Delta_rG^{\Theta}{}_m(2)$ and $\Delta_rG^{\Theta}{}_m(3)$) of these reactions calculated are negative, which means the oxidation-precipitation reactions of manganese and cobalt could happen spontaneously in theory. It is easily seen that the E has relationship with the pH and concentration, in order to controlling the potential of system, the H^+ produced in hydrolysis process was neutralized by adding NaOH slurry.

2.2.2. Potential-pH analysis of redox reactions in Mn-Co-H_2O system

Mn and Co substances in the liquid-solid phase could be seen in the potential-pH diagram the Mn-Co-H_2O system (Fig. 1) (Pourbaix, 1963; Zhang et al., 2002).

There are four key regions (A, B, C and D) in the diagram. The manganese and cobalt are in different phases, which mean that the cobalt and manganese could be separated from each other:

Region A: when the system potential is between $-0.277 \sim -1.2$ V, the cobalt ion is could be reduced to cobalt metal, while the manganese ion is stable in this potential range.

Table 1
Composition of leaching solution of cobalt slag mg/L.

Element	Co	Mn	Fe	Cu	Zn (g/L)
Concentration	1807.5	692.5	3.5	8.5	115.3

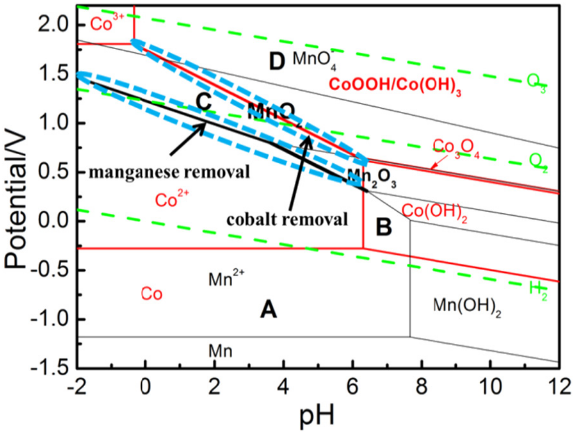

Fig. 1. Potential-pH curve of Mn-Co-H_2O.

Region B: By adding alkali materials to the solution with pHs in the range of 6 and 7, the cobalt ion will firstly be separated from the solution by hydrolysis, but the manganese ion still stay in the solution.

Region C: In an acid system, the manganese could be oxidized by oxidants and separated from the solution in the form of MnO_2 or Mn_2O_3, but the cobalt still stays in the solution.

Region D: In a high potential system with potentials higher than the potential value of MnO_4^-/MnO_2 redox reaction, the manganese ion is excessively oxidized to MnO_4^- and stays in the solution, but the cobalt ion is oxidized and separated from the solution.

In order to recover manganese and cobalt separately from the solution, it is necessary to control the potential and pH of the system in certain scope, in which the cobalt and manganese are in different phase. In this study, we selected region C as reference to recover manganese and cobalt respectively. As shown in Fig. 1, the potential value of redox reaction of $Mn^{2+}/Mn^{4+}\&Mn^{3+}$ is lower than that of Co^{2+}/Co^{3+}, so that manganese ion could be oxidized prior to cobalt ion. The high potential value of Co^{2+}/Co^{3+} could makes the Co^{3+} acting as a strong oxidant. If the Co^{2+} is oxidized to Co^{3+}, the Mn^{2+} will be oxidized and transformed into Mn_2O_3/MnO_2 by Co^{3+}, as showed below:

$$2Co^{3+} + 2Mn^{2+} + 3H_2O = 2Co^{2+} + Mn_2O_3 + 6H^+ \tag{4}$$

$$2Co^{3+} + Mn^{2+} + 2H_2O = 2Co^{2+} + MnO_2 + 4H^+ \tag{5}$$

In theory, when ozone is pumped into the solution, the manganese is firstly separated, with decreasing of the manganese ion concentrations in the solution, polarization phenomenon may happen and at the same time the system potential rises slowly. When the concentration of manganese is less than certain degree, the cobalt would start to be oxidized and separated after, which also cause the system potential rise. The manganese and cobalt were separated in two-stage in our experiment (seen in Fig. 2).

3. Results and discussion

In order to obtain high-grade precipitate and high-purity purified solution, we investigated the system potentials in the oxidation process, and impacts of dilution rate, pH values and temperatures on separating results.

3.1. Mn & Cobalt concentration change and solution potentials during oxidation process

This experiment was done at temperature of 25 °C, pH value of 4.0, stirring speed of 300 rpm, gas flow rate of 2.0 L/min, and dilution ratio