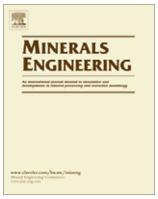
Minerals Engineering 24 (2011) 1421–1429

Contents lists available at ScienceDirect

Minerals Engineering

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



Recovery of manganese from iron containing sulfate solutions by precipitation

Jouni Pakarinen *, Erkki Paatero

Lappeenranta University of Technology, Laboratory of Industrial Chemistry, P.O. Box 20, FI-53851 Lappeenranta, Finland

ARTICLE INFO

Article history:
Received 12 April 2011
Accepted 8 June 2011
Available online 5 July 2011

Keywords:
Manganese
Iron
Carbonate
Precipitation
Selectivity
Tailings

ABSTRACT

Worldwide consumption of manganese is increasing, nevertheless huge amounts of manganese from hydrometallurgical processes still end up as waste since the recovery of manganese from multi-metal solutions at low concentrations is not considered feasible. Poor iron control typically prevents the production of high purity manganese. This work studies a number of precipitants in manganese recovery and iron separation from sulfate solutions. The precipitation reagents were compared from the point of view of selectivity and economy. Carbonate precipitation is a fast and effective method for the recovery of manganese from bulk solutions. Subsequent leaching of metal carbonate is also easier and consumes less acid than, for example, hydroxide or sulfide precipitates. In order to avoid gypsum formation, soda ash should be used instead of limestone. It was found that efficient selective iron removal from $MnSO_4$ solutions is achieved with combined O_2 or air oxidation and $CaCO_3$ precipitation at pH >5.8 and at a redox potential of >200 mV. Effective mixing and sufficient retention time are essential to make the method technically efficient and economically feasible.

1. Introduction

Iron control plays a significant role in the processing of hydrometallurgical solutions of metal refineries. Iron is one of the most abundant elements in the Earth's crust and it is present in several sulfide and oxide ore minerals. Iron is also involved in several natural redox processes. In hydrometallurgy, control of iron is difficult due to the rather low oxidation potential of Fe^{2+} to Fe^{3+} (-770 mV, compared to 1.5415 mV for Mn^{2+} to Mn^{3+}) Haynes and Lide, 2011. In acidic solutions, where oxygen (O_2) is present, iron is more or less at oxidation state 3+. The presence of Fe^{3+} in metal recovery with solvent extraction (SX) with commonly used liquid cation exchangers demands special attention in the pH and redox control since Fe^{3+} has a strong affinity to the formation of coordination compounds with the organic extractants (Ritcey, 2006). An extra SX step for iron separation is possibly needed. Iron treatment from metal solutions with solvent extraction has been studied widely (Biswas and Begum, 1998; Demopoulos and Gefvert, 1984; Hoh et al., 1983; Preston, 1985; Ritcey, 2006; Saji et al., 1998; Sato and Nakamura, 1971; Sato et al., 1985; Vazarlis and Neou-Syngoyna, 1984; Zhou et al., 1989), and different reactants have been utilized in SX plants (Cole et al., 2006; Dutrizac and Monhemius, 1986). The main problem in iron solvent extraction is stripping, which requires strong acids and reduction (Demopoulos and Gefvert, 1984; Lupi and Pilone, 2000; Vazarlis and Neou-Syngoyna, 1984). The use of strong acids entails a risk of reagent decomposition. Moreover, if iron concentration is high, the economic viability of the SX may decrease through large solvent inventory.

In sulfide precipitation, Fe^{3+} ions reduce to Fe^{2+}, since the sulfide ion (S^-) tends to act as a reductant (Wei and Osseo-Asare, 1996; Habashi, 1999). Reductive conditions give the possibility of selective recovery of some metals using precipitation without iron pre-treatment. The iron selectivity is, however, significant only for Ag, Bi, Cd, Cu, Pb, and Zn and at low pH (<3) and cannot be used for Fe–Mn separation (Monhemius, 1977). Moreover, due to environmental concerns and the closed circuits in hydrometallurgy, iron separation is necessary.

From an economic point of view, the ratio of iron to manganese in tailings solutions is critical. Compared to, for example, cobalt, copper or, nickel plants, the Mn process is more cost-sensitive; a result of the less valuable end-product. On the other hand, increased demand for stainless steel and greater use of batteries in electrical devices and vehicles have lead to increased consumption of manganese. (Zhang and Cheng, 2007a). Moreover, metals are increasingly being recovered from low-grade, complex and small-body ores, since most rich ore bodies are already utilized. In this context, it is reasonable to make efforts to recover metals from low concentration solutions. According to Zhang and Cheng (2007b), in mining operations worldwide, about 122 kt Mn is annually leached from laterite ores as side metal and handled as waste. The main difference between the classical Mn processing and this study is the manganese concentrations, which are typically tenfold higher than here in impurity removal. In order to make the recovery of Mn economically possible, cheap reagents and highly optimized energy efficient techniques are needed.

---

* Corresponding author. Fax: +358 5 6212199.
E-mail address: Jouni.Pakarinen@lut.fi (J. Pakarinen).

0892-6875/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.mineng.2011.06.004

Precipitation, as jarosite, goethite, or hematite, is the most common method currently used to remove iron from leaching solutions. This process is, however, problematical because of the high temperature demands. Furthermore, the gelatinous and metastable solids produced can be difficult to process (Loan et al., 2006). Jarosite and hematite processes are preferred above 100 °C and goethite between 80 and 90 °C (Ismael and Carvalho, 2003). Claassen et al. (2002) and Loan et al. (2006) have reported the possibility of iron removal at temperatures closer to normal hydrometallurgical temperatures (about 60–80°C) using a so-called para-goethite process. The narrow operational range may, however, create practical problems. Jarosite, goethite and para-goethite do not have any further applications, but pure hematite can be utilized as a pigment or in steel making.

The aim of this work is to study manganese recovery from multi-metal sulfate solutions containing Mn, Fe, Ca, Mg, and Na at low concentrations (<5 g/L). The emphasis is on finding the technically and economically most feasible method to refine Mn and remove iron from $MnSO_4$ solutions. Selectivity and consumption of reagents in the precipitation and leaching are significant factors studied. The presence of Ca, Mg and Na in the solution is not of major importance, since these metals can be separated with SX (Pakarinen and Paatero, 2011). The research concludes with the study of iron separation in a continuous pilot process using limestone and air at parameters found in batch experiments.

2. Theory

2.1. Precipitation equilibria

Precipitation occurs when the product of the metal and its counter-ion concentrations (activities) rise over a critical value (solubility product, K_S) (Eq. (1)). The selectivity of the precipitation can be estimated by comparing the values of the solubility products of different metal salts.

$$mM^{n+} + nA^{m-} \overset{KS}{\rightarrow} M_mA_n \quad (1)$$

Here, M represents a metal cation at oxidation state *n*+ and *A* an anion at oxidation state *m*−. Precipitation diagrams for metals in different systems have been published by Monhemius (1977), where solubility trends and approximate conditions for precipitation can be found. The measured values for single metals are not, however, necessarily relevant in non-ideal multi-metal solutions, where the activity coefficients differ from unity and several side reactions may occur. Metal precipitation in sulfate media differs from precipitation in a nitrate or chloride system because of two dissociation equilibria: the sulfuric acid and hydrogen sulfate equilibrium, and the sulfate ion equilibrium. In acid solutions with high concentration (pH < 1) the second equilibrium (Eq. (2)) is negligible, but at higher pH (between 1 and 4), dissociation of the hydrogen sulfate ion should be taken into account in solution chemistry and metal coordination. Furthermore, when solution pH is higher than 4, total dissociation of HSO_4^- can be assumed.

$$HSO_4^- \rightleftarrows SO_4^{2-} + H^+ \quad pKa = 2.0 \quad (2)$$

Solution pH plays a critical role in ion exchange and precipitation reactions, and consequently, extra acidity after leaching is neutralized with an appropriate reagent. Based on the process chemistry and economic considerations, limestone ($CaCO_3$) is widely used in manganese processes (Chang and Cheng, 2007b). Eqs. (3)–(5) present the competing reactions between the bicarbonate ion, carbonic acid, and the formation of metal carbonate in acidic sulfate solutions.

$$CO_3^{2-} + \frac{2}{n}M^{n+} \rightleftarrows M_{\frac{2}{n}}CO_3 \quad (3)$$

$$M_{\frac{2}{n}} + H^+ \rightleftarrows \frac{2}{n}M^{n+} + HCO_3^- \quad (4)$$

$$HCO_3^- + H^+ \rightleftarrows H_2CO_3 \quad (5)$$

In this study, M is Ca^{2+}, Na^+, Fe^{2+} or Mn^{2+} and n has the values of 1 or 2, respectively. The carbonate ion is not stable in acidic solution and tends to decompose to carbon dioxide and water according to below equation:

$$CO_3^{2-} + 2H^+ \rightleftarrows H_2O + CO_2 \uparrow \quad (6)$$

Hydroxide precipitation is a commonly used separation method in hydrometallurgy. The selectivities for base metals and manganese are, however, rather poor. MgO and $Ca(OH)_2$ are widely used as hydroxide reagents. Metal precipitation with hydroxide ions and acid leaching of metal hydroxide are shown in Eqs. (7) and (8).

$$n(OH)^- + M^{n+} \rightleftarrows M(OH)_n \quad (7)$$

$$M(OH)_n + nH^+ \rightarrow M^{n+} + nH_2O \quad (8)$$

Due to its abundance and easy dissolution, iron is one of the main impurity metals in hydrometallurgical sulfate processes (Zhang and Cheng, 2007b). The precipitation efficiency of ferrous ions (Fe^{2+}) as hydroxide is poor, but is significantly increased in the ferric form. In this study, iron oxidation with molecular oxygen is assumed to follow the mechanism published by Zhang et al., 2000b and is affected by the partial pressure of oxygen. The sum reaction is shown in Eq. (9). Iron at the oxidation state 3+ precipitates selectively from manganese due to the very low value of the solubility product (2×10^{-39}). Depending on the precipitation conditions, different ferric oxo hydroxides (α-FeO·OH, β-FeO·OH or α-Fe_2O_3) (Loan et al., 2006) can be formed (as the following equation).

$$4Fe^{2+} + O_2 + 2H^+ \rightleftarrows 4Fe^{3+} + 2OH^- \quad pKa = 3.0^* \quad (9)$$

$$Fe^{3+} + 3OH^- \rightleftarrows FeO \cdot H + H_2O \quad pKa = 41.6^* \quad (10)$$

(* calculated with HSC® 6.1) Oxidation of Mn^{2+} to Mn^{3+} and to Mn^{4+} with SO_2/O_2 or with SO_2/air has been studied by some research groups (Menard and Demopoulos, 2007; Zhang et al., 2002; Zhang et al., 2010). The latter approach, in particular, is feasible from the economical point of view, but in both methods, the use of poisonous and corrosive SO_2 is disadvantageous to equipment and people. The oxidation reactions (Eqs. (11) and (12)) are, according to Zhang et al., 2002 and Zhang et al., 2010:

$$2Mn^{2+} + SO_2 + O_2 + 3H_2O \rightleftarrows 2MnO \cdot OH + SO_4^{2-} + 6H^+ \quad (11)$$

$$Mn^{2+} + SO_2 + O_2 + 3H_2O \rightleftarrows MnO_2 + SO_4^{2-} + 4H^+ \quad (12)$$

MnO_2 is a potential oxydizing reagent for iron, since the potentials (E^0) of $Mn^{4+} + 2e^- \rightarrow Mn^{2+}$ is 1.23 V and $Mn^{3+} + e^- \rightarrow Mn^{2+}$ 1.54 V, are high enough for iron oxidation in acidic conditions (Eq. (13)). Moreover, MnO_2 is often formed as a side product in manganese electrolysis and this is a reasonable way to recycle it back into the process.

$$2Fe^{2+} + MnO_2 + 4H^+ \rightleftarrows 2Fe^{3+} + Mn^{2+} + 2H_2O \quad pKa = 15.15^* \quad (13)$$

3. Experimental

3.1. Measurements and modeling

An authentic metal solution after removal of base metals (a tailings solution) was used in the experiments. One aim of the experimental work was to study metal precipitation and solution chemistry. Precipitation of metals was studied by measuring solu-