Comparing iron phosphate and hematite precipitation processes for iron removal from chloride leach solutions

Saviour Masambi, Christie Dorfling *, Steven Bradshaw

Department of Process Engineering, University of Stellenbosch, Private Bag X1, Matieland 7602, South Africa

ARTICLE INFO

ABSTRACT

The presence of iron in pregnant leach solutions presents significant processing challenges. The removal of iron impurities from leach solutions by means of iron phosphate precipitation may be a feasible alternative to more conventional iron oxide/iron hydroxide precipitation processes. This study compares the performance of the iron phosphate precipitation process with that of the hematite process at different operating temperatures (40 °C–90 °C), pH conditions (pH 1–pH 3) and seeding measures for the removal of iron from a chloride leach solution. The extent of iron removal, co-precipitation of nickel and copper, and solid-liquid separation were used as performance criteria for the comparison.

Seeded iron phosphate precipitation at pH 1 and 40 °C resulted in 98.8% iron removal with 0.5% nickel and 2.8% copper losses. 99.8% iron removal was achieved with the iron phosphate precipitation process at pH 1 and 80 °C, but the nickel and copper losses increased to 8.7% and 20.8%, respectively, with the increase in temperature. Seeded hematite precipitation at pH 1 and 80 °C yielded 99.6% iron removal with 3.5% nickel and 1.7% copper losses. For the hematite process, nickel and copper losses decreased with an increase in temperature. Increasing the pH yielded higher nickel and copper losses for both processes.

All seeded precipitation experiments produced easily filterable precipitates. Unseeded iron phosphate precipitates produced at 40 °C and pH 1 were filterable, but increased nickel and copper losses were observed. Unseeded hematite precipitation resulted in high nickel and copper losses, with the precipitates practically impossible to filter. Iron phosphate precipitates exhibited more favourable settling characteristics than the precipitate produced with the hematite process.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

In hydrometallurgical processes, iron is commonly removed from pregnant leach solutions by precipitation as jarosite, goethite or hematite. The jarosite process is extensively used during iron removal in zinc hydrometallurgy. The co-precipitation of metal ions (Zn, Cu, Ni, Mn, Al, Ga and Ge) has been cited as one of the major weaknesses of the jarosite process (Claassen et al., 2002; Wang et al., 2011). Furthermore, jarosite compounds are universally classified as hazardous wastes because of the adverse effects to the environment and human health (Asokan et al., 2006). The essential feature of goethite precipitation is that the ferric concentration of the solution should be maintained at approximately 1 g/L. Goethite is said to be precipitated as either α-goethite in sulphate systems or β-goethite (akaganeite) in chloride systems. Akaganeite has been reported to sustain co-precipitation of cations and its filtration is practically impossible (Cohen et al., 2005; Dutrizac

and Riveros, 1999). Controlled precipitation of α-goethite in sulphate systems ensures lesser impurities in the precipitates and its filtration is easily achievable (Ismael and Carvalho, 2003). Production of large volumes of goethite has been reported to be an environmental concern (Dutrizac and Riveros, 1999). Hematite (Fe_2O_3) is the preferred iron precipitate because it is a stable, high density and more pure form of iron. These properties of hematite make it easier for disposal and offer the potential for it to qualify as a by-product; it is used as starting material in the production of iron and steel, pigments and ferrites (Riveros and Dutrizac, 1997).

Twidwell et al. (1987) reported the invention of a method for recovering metal values from mixed aqueous solutions by selective phosphate precipitation. It was reported that the precipitate produced was easily separated by conventional solid-liquid filtration techniques, and that the process was applicable in most systems (sulphates, chlorides and mixtures of these lixiviants). Because of its distinctive selectivity towards trivalent metal precipitation over divalent metal precipitation, phosphate precipitation was suggested to be a suitable iron removal method during the purification of solutions containing divalent metals such as nickel and copper

---

* Corresponding author.
    E-mail address: dorfling@sun.ac.za (C. Dorfling).

(Twidwell et al., 1987). Garole et al. (2012) furthermore reported that the iron phosphate precipitation process is more efficient and economical than high temperature hydroxide precipitation processes characterised by precipitates that are difficult to separate.

To date, very little information about the phosphate precipitation process for iron removal has been published, and no quantitative comparison of the technical performance of this process and conventional iron oxide/iron hydroxide processes has been done. The objective of this study was hence to investigate the iron phosphate precipitation process as an alternative iron removal process for purification of a nickel-copper chloride leach solution. More specifically, this study compares the performance of the iron phosphate precipitation process with that of the commonly used hematite precipitation process in terms of iron removal, the extent of nickel and copper co-precipitation, and solid-liquid separation.

The work formed part of a project aimed at the development of a process for copper and nickel recovery from a pregnant leach solution, with iron removal by precipitation envisaged to be the first processing step. The pregnant leach solution originates from a metal production facility that utilises hydrochloric acid leaching for the dissolution of base metals from a specific feed material. Given the operational requirements of the upstream leaching process, the leach solution produced contains approximately 4.6 M HCl, 45 g/L Fe, 3 g/L Cu and 3 g/L Ni.

1.1. Iron phosphate precipitation

Jenkins et al. (1971) presented an overview of research work performed to develop a process for phosphate removal from wastewater by means of precipitation with iron added as iron chloride salts. The same principle has been applied in hydrometallurgy for iron removal from leach solutions by means of precipitation with phosphate addition (Cruz et al., 1980; Garole et al., 2012; Twidwell et al., 1987).

Cruz et al. (1980) investigated the removal of iron from electrowinning solutions. It was reported that iron(III) phosphate was precipitated at pH 2 and a temperature of 50 °C. The morphology of the iron phosphate was spherites and agglomerates of spherites. Redissolution of the phosphate precipitate was, however, observed at a ferric to phosphate ratio higher than 3.15. Twidwell et al. (1987) reported that the phosphate precipitation process selectively recovers trivalent metal cations as easily separable crystals, making it suitable for purification of sulphate or chloride solutions containing divalent metal cations such as nickel and copper. Twidwell et al. (1987) suggested a similar precipitation temperature (60 °C) and pH (pH 2) to those proposed by Cruz et al. (1980). The findings of Cruz et al. (1980) and Twidwell et al. (1987) were confirmed by Garole et al. (2012). Garole et al. (2012) reported that the low co-precipitation of divalent metallic cations can in part be ascribed to poor adsorption on the precipitated iron phosphate, which exhibited spherical shapes and a low specific surface area. Typical reaction times recorded ranged from 30 min to 1 h, achieving more than 99% iron removal. Iron phosphate precipitation was proposed to proceed according to Eq. (1).

$$Fe^{3+} + PO_4^{3-} + 2H_2O \leftrightarrow FePO_4 \cdot 2H_2O \tag{1}$$
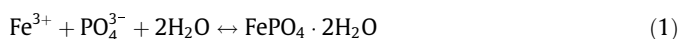
The variation in iron phosphate solubility at 50 °C with pH was determined by Huang (2001) and reported by Twidwell and Dahnke (2001). The solubility was reported to decrease linearly with increasing pH. At pH 0, the solubility is approximately 1050 mg/L; above pH 2 iron phosphate is virtually insoluble. Robins et al. (1991) reviewed literature on the solubility and speciation of iron(III) phosphate and concluded that the reported solubility constants of ferric phosphate dihydrate, which is the

more common type of iron(III) phosphate, ranged between 4.57×10^{-3} and 2.24×10^{-8}. The dimorphic nature of iron(III) phosphate (orthorhombic or monoclinic structure) was the proposed reason for the differences in solubility constants reported in literature.

Twidwell et al. (1986) reported that conversion of ferric phosphate to ferric hydroxide, and therefore regeneration of phosphate, is possible at moderate temperature (25–50 °C) and high pH (pH 11–pH 12) conditions. Complete conversion with caustic soda was achieved after two hours reaction time at pH 12 and 50 °C. Unlike the precipitates produced in a conventional hydroxide precipitation process, the ferric hydroxide precipitates produced by the conversion of ferric phosphate filter as easily as ferric phosphate and do not contain heavy metals (which presents environmental challenges) because of the purity and morphology inherited from the ferric phosphate precipitates. The conversion reaction is shown in Eq. (2).

$$FePO_4 + 3NaOH \leftrightarrow Fe(OH)_3 + Na_3PO_4 \tag{2}$$
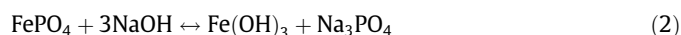
1.2. Hematite precipitation

Traditionally, hematite precipitation has been reported to be possible at a temperature greater than 100 °C and under pressure oxidation of greater than 5 bar (Dutrizac and Monhemius, 1986). Hematite precipitation proceeds according to Eq. (3).

$$2Fe^{3+} + 3H_2O \leftrightarrow Fe_2O_3 + 6H^+ \tag{3}$$

Dutrizac and Riveros (1999) investigated the precipitation of hematite from chloride solutions at temperatures below 100 °C and ambient pressure mainly by employing seeding. In the absence of seeding, a reaction time of almost 100 h was required for akaganeite to precipitate and transform to hematite. Tests conducted at 100 °C yielded hematite after only 2 h of reaction time when seeded with 15 g/L Fe₂O₃. It was reported that hematite precipitation occurred via two pathways: the precipitation of akaganeite (a metastable phase) which then gradually transforms to hematite, and the direct precipitation of hematite. A combination of both pathways was suggested to be possible, but the direct formation of hematite was identified as the more likely pathway in seeded reactions. Decreasing the temperature to 60 °C did not have an adverse effect on the iron removal achieved by hematite precipitation. More than 99% of the iron initially in solution was reported to be in the hematite precipitate.

Cohen et al. (2005) also investigated iron removal by hematite precipitation. It was reported that pH values below 1 did not significantly affect filtration rates and ensured almost complete removal of iron, provided seeding levels were between 10 and 20 g/L. Seeding had a significant impact on the rate of filtration. Typical filtration rates averaged 83 mL/min and increased with an increase in operating temperature and reaction time. Seeding beyond 20 g/L did not have any further impact on filtration rates. Unseeded experiments performed at temperatures below 100 °C did, however, produce precipitates that were not practically possible to filter; this was attributed to the formation akaganeite instead of hematite.

2. Experimental

2.1. Materials

Unless stated otherwise, all chemicals were reagent grade chemicals supplied by Sigma-Aldrich. Synthetic leach solutions containing 45 g/L iron, 3 g/L nickel and 3 g/L copper were prepared using iron(II) chloride tetrahydrate, copper chloride, nickel