Jarosite Precipitation of Iron From Leach Solutions of Waste Printed Circuit Boards (WPCBs)

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JAROSITE PRECIPITATION OF IRON FROM LEACH SOLUTIONS OF WASTE PRINTED CIRCUIT BOARDS (WPCBs)

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ABSTRACT: Waste of printed circuit boards (WPCBs) with its significant content of base and precious metals is of particular interest for the recovery of metals. Sulphate/chloride leaching of WPCBs produces leach solutions in high concentration of copper as well as impurities such as iron. These impurities can adversely affect downstream processes. In this study, removal of iron as ammonium- or sodium-jarosite from leach solutions of WPCBs was investigated. Precipitation tests were carried out using synthetic (30 g/L Cu2+ and 1 M SO42-) and real leach solutions. The effects of initial concentration of iron (1-4.5 g/L Fe3+), [Fe3+]/[NH4+] ratio (1.5-2.4), pH (1.4-1.8), temperature (80-90°C) and seeding (23.3 g/L) were examined. The results showed that precipitation efficiency was high at low iron concentrations and high [NH4+]/[Fe3+] ratios favoured the iron removal. Seeding and temperature also positively influenced the precipitation process. About 68-69% of iron was found to be removed as sodium-jarosite from sulphate/chloride solutions ([Na+]/[Fe3+]: 16.3-40.8). Precipitation of iron from real leach solutions produced by sulphate (H2SO4-H2O2) and sulphate/chloride leaching (H2SO4-CuSO4-NaCl) of WPCBs were found to be 76% and 89%, respectively. SEM-EDS analysis detected 3.0-5.7% copper in the precipitates.

1. INTRODUCTION
The rapid and evolutionary development of technology leads to the decline in the life span of electrical and electronic equipments and hence, the amount of their waste rapidly increases [Culver, 2005; Modesitt and Gilbert, 2005] In EU, the quantity of waste of electrical and electronic equipments (WEEE) between 2008 and 2014 is expected to increase by ~11% [Beck, 2012]. In view of the environmental concerns associated with the hazardous components present in WEEE and its potential as a secondary resource for many valuable metals, proper management of WEEE is required [McPherson, 2005; Lincoln et al., 2007; Yazıcı et al., 2010; Yazıcı and Deveci, 2011].

Industrial treatment of WEEE for recovery of the contained metals is carried out via pyrometallurgical processes [Cui and Zhang, 2008; Yazıcı and Deveci, 2009]. In recent years, hydrometallurgical processes have attracted particular interest particularly due to their inherent potential for small scale operations and treatment of low grade WEEE [Bas et al., 2014; Deveci et al., 2010; Tuncuk et al., 2012]. WEEE contains a wide variety of metals, which may dissolve during leaching and present as impurities in leach solutions [Ehsani et al., 2012; Yazıcı, 2012; Yazıcı and Deveci, 2013]. Ehsani et al. [2012] reported that the impurities present (e.g. iron, in particular) in the leach solution adversely influence the electrowinning of copper leading to low current efficiency and poor cathode quality. Therefore, the development of suitable downstream purification processes or refining existing ones prior to metal recovery is prerequisite for the removal of these impurities from loaded leach solutions.
Solvent extraction (SX) is effectively used to purify and enrich copper loaded leach solutions where iron is the main impurity [Habashi, 1999; Jha et al., 2014]. The leaching of waste of printed circuit boards (WPCBs) generates highly concentrated solutions of copper, which are not particularly suitable for purification by SX [Yazici, 2012; Yazici et al., 2013]. Industrially, iron is often removed by precipitation as oxy/hydroxy compounds (i.e. ferric hydroxide, jarosite, goethite and hematite) (Figure 1) [Arslan and Arslan, 2003; Dutrizac and Jambor, 2000; Ismael and Carvalho, 2003]. Yazici et al. [2014] investigated the removal of iron from the leach solutions produced by the leaching of WPCBs in sulphate (H$_2$O$_2$-H$_2$SO$_4$) and sulphate/chloride (H$_2$SO$_4$-CuSO$_4$-NaCl) media. They found that iron could be effectively removed as goethite from the leach solutions; but, significant co-precipitation of copper also occurs particularly at high pHs. In the electrolytic process (RLE) for zinc, jarosite process (1) is extensively used to remove iron from pregnant leach solutions by adding monovalent ions (e.g. Na$^+$, K$^+$, NH$_4^+$) under suitable conditions of pH (1.5-1.8) and temperature (95-100°C) [Dutrizac and Jambor, 2000].

$$X^++3Fe^{3+}+2SO_4^{2-}+6H_2O \rightarrow$$
$$XFe_3(\text{SO}_4)_2(\text{OH})_6^{n+}6H^+$$

(1)

(X: H$_3$O$^+$, Na$^+$, K$^+$, NH$_4^+$)

In this study, removal/precipitation of iron by precipitation as ammonium- or sodium-jarosite from synthetic and real (sulfate/chloride) leach solutions of WPCBs was investigated. The influences of various operating conditions i.e. iron concentration, [Fe$^{3+}$]/[NH$_4^+$] ratio, pH, temperature and seeding on iron removal were examined. SEM-EDS analysis of the iron precipitates was also undertaken.

Figure 1: Stability of hematite, goethite, ferric hydroxide and hydroxyl salts (e.g. jarosites) depending on temperature and pH [Babcan, 1971].

2. MATERIALS AND METHODS

Leaching tests (H$_2$SO$_4$-H$_2$O$_2$) have shown that pregnant leach solutions contain typically >1 g/L iron, which adversely affects downstream electrowinning of copper [Ehsani et al., 2013]. Therefore, the removal of iron from sulphate as well as chloride leaching solutions as ammonium- or sodium-jarosite was examined. In these tests, synthetic and real leach solutions were used.

Precipitation tests were carried out in Erlenmeyer flasks (100 ml). A 50-ml synthetic or leach solution was prepared in each flask. Effect of initial concentration of iron in the range of 1-4.5 g/L Fe$^{3+}$, [Fe$^{3+}$]/[NH$_4^+$] ratio (1.5-2.4), pH (2.5-4.0), temperature (80-90°C) and seeding (23.3 g/L) on the precipitation of iron was studied. A synthetic copper solution of 0.5 M CuSO$_4$ was prepared. MgSO$_4$ was used to fix the total concentration of sulfate. Real pregnant leach solutions obtained from sulfuric acid-hydrogen peroxide (H$_2$SO$_4$-H$_2$O$_2$) leaching and sulfuric acid leaching in the presence of copper and chloride (H$_2$SO$_4$-CuSO$_4$-NaCl) were also used in the precipitation tests. Initial pH was adjusted using diluted H$_2$SO$_4$ or Li$_2$CO$_3$, but, it
was not controlled during the tests. A reciprocal shaker operating at 140 rpm was used to agitate the flasks. On termination of the experiments after 6 h, the precipitate was recovered by centrifugation for 5 min at 4100 rpm. Clear supernatant was analysed for iron using Perkin Elmer AAnalyst 400 atomic absorption spectrometer. SEM-EDS (Zeiss EVO LS10 Scanning Electron Microscope) and XRD (Rikagu D/max-IIIC) were used to identify and characterise iron precipitates.

3. RESULTS AND DISCUSSION
Table 1 shows the result of jarosite precipitation tests under different conditions of initial iron concentration, ammonia concentration (as \([\text{Fe}^{3+}] / [\text{NH}_4^+]\) ratio), temperature, pH and seeding. It was found that pH (1.6-1.8) and temperature (80-90°C) exert no significant effect on the removal of iron. In these tests, no pH control was exercised and, on the completion of the tests, pH was determined to decrease to pH 1.0-1.4. This decrease in pH could have adversely affected the precipitation of iron. Dutrizac and Jambor [2000] reported that the formation of Na-jarosite remarkably decreased with increasing acidity at <pH 1.5 and it completely ceased at pH 0.5. These investigators also noted that temperature was an important parameter affecting the rate and extent of formation of jarosite, which increased particularly at high temperatures (>90°C).

Removal of iron (%) was observed to increase with decreasing the initial concentration of iron. At the lowest level of iron tested (1 g/L Fe\(^{3+}\)), 73% of iron was removed over 6 h (Table 1). This mode of effect for initial concentration of iron appeared to be essentially linked with pH. That is, the amount of acid that forms as a result of precipitation would increase with increasing the concentration of iron, leading to the decrease in pH
everting a suppressing effect on the precipitation of iron. The results also revealed that the presence of copper tended to adversely affect the precipitation of iron (Table 1). On the other hand, seeding slightly improved the removal of iron. Increasing the concentration of NH\(_4^+\) i.e. \([\text{NH}_4^+] / [\text{Fe}^{3+}]\) ratio, produced an enhancing effect on the iron removal (Table 1).

In the precipitation tests from chloride containing solutions (Exp. 6 and 7 in Table 1), no NH\(_4^+\) was added due to the presence of copious amount of Na\(^+\) in the solution (i.e. \([\text{Na}^+] / [\text{Fe}^{3+}]\): 16.3-40.8). This suggested that the precipitation of iron was independent of Na\(^+\) concentration in these tests. The chloride level appeared to produce no significant effect on the final removal of iron, which was determined to be 68-69% at 47-117 g/L Cl\(^-\) (Figure 2). Notwithstanding this, the precipitation of iron was faster at 47 g/L Cl\(^-\) than at 117 g/L Cl\(^-\). Relatively low levels of iron removal observed despite excessively high \([\text{Na}^+] / [\text{Fe}^{3+}]\) ratio could be attributed to increasing acidity (~pH 1) and slow kinetics of precipitation. Dutrizac and Jambor [2000] reported that the formation of jarosite continued for 15 h; thereafter, it became independent of reaction time. They also noted that NH\(_4^+\)-jarosite is more stable than Na-jarosite.
Table 1: Removal of iron as jarosite from synthetic and real leach solution under different conditions in 6 h.

| Exp. No | Fe$^{3+}$ (g/L) | [Fe$^{3+}$/NH$_4^+$] | pH  | T (°C) | Solution Composition | Fe Removal (%)
|---------|-----------------|----------------------|-----|--------|----------------------|----------------
| 1       | 4.5             | 2.4*                 | 1.4 | 90     | CuSO$_4$ (M) MgSO$_4$ (M) Cl (g/L) | 37.6 |
| 2       | 1.0             | 2.4                  | 1.6 | 90     | 0.5 0.5 - | 72.6 |
| 3       | 2.5             | 2.4                  | 1.6 | 90     | 0.5 0.5 - | 46.1 |
| 4       | 4.5             | 2.4                  | 1.6 | 80     | 0.5 0.5 - | 37.9 |
| 5       | 4.5             | 2.4                  | 1.6 | 90     | - 1 - | 42.4 |
| 6       | 4.5             | -                   | 1.6 | 90     | 0.5 0.5 47 | 68.1 |
| 7       | 4.5             | -                   | 1.6 | 90     | 0.5 0.5 117 69.0 |
| 8       | 4.5             | 2.4                  | 1.6 | 90     | 0.5 0.5 - | 40.0 |
| 9       | 4.5             | 0.75*               | 1.6 | 90     | PLS (H$_2$SO$_4$-H$_2$O$_2$) Cu$^{2+}$: 19.3 g/L; [H$_2$SO$_4$]: 1.2 M | 75.5 |
| 10      | 2.1             | 1.5*                | 1.8 | 90     | PLS-CuSO$_4$-NaCl Cu$^{2+}$:15.2 g/L; Cl$^-$:47 g/L; [SO$_4^{2-}$]:0.5M | 88.7 |
| 11      | 2.1             | -                   | 1.8 | 90     | PL$^*$ |

Seeding: 23.3 g/L

*1,25; 4,5; 2 times the stoichiometric (molar) ratio of [NH$_4^+$] to [Fe$^{3+}$]

Figure 2: Precipitation of Na-jarosite from chloride containing synthetic copper solutions (pH 1.6, 4.5 g/L Fe$^{3+}$, 90°C)

More extensive removal of iron from pregnant leach solutions (76-89%) than synthetic solutions (<73%) was observed (Exp. 10 and 11 in Table 1). High iron removal from chloride containing solutions (Figure 3) can be attributed to high [Na$^+$/Fe$^{3+}$] ratio. SEM-EDS analysis of the precipitates indicated the presence of %3.0-5.7 Cu due to the co-precipitation of copper. In this regard, the main detractor to jarosite process is the co-precipitation of cations present in the leaching solutions.

Figure 3: Removal of iron from pregnant leach solutions obtained from H$_2$SO$_4$-H$_2$O$_2$ (PLS) and H$_2$SO$_4$-CuSO$_4$-NaCl (PLS-CI) leaching of WPCBs.

Silver (Ag$^+$) and lead ($\frac{1}{2}$Pb$^{2+}$) is known to substitute monovalent ions such as H$_3$O$^+$, Na$^+$, K$^+$, NH$_4^+$ in jarosite. Other metal cations (Cu$^{2+}$, Zn$^{2+}$, Cd$^{2+}$ etc.) can be incorporated into the jarosite lattice substituting for iron [Dutrizac, 1984]. Dutrizac [1984] also reported that high
concentration of metals such as copper, low concentration of ferric iron and high pH promote the incorporation of these metals into the jarosite.

The characterisation of the precipitates was carried out by SEM and XRD analysis. Figure 4 shows the SEM photo of ammonium-jarosite precipitate obtained from the Exp. 9 (Table 1). XRD data corroborated the formation of ammonium-jarosites (Figure 5).

4. CONCLUSIONS
In this study, the removal of iron from synthetic copper solutions and pregnant leach solutions obtained from sulfuric acid-hydrogen peroxide (H$_2$SO$_4$-$\text{H}_2$O$_2$) leaching and sulfuric acid leaching in the presence of copper and chloride (H$_2$SO$_4$-CuSO$_4$-NaCl) of WPCBs was examined. Increasing the concentration of monovalent ion, pH and temperature, and seeding appear to facilitate the formation of jarosite. Increasing the concentration of initial ferric iron was found to adversely affect the removal of iron. This was attributed to the increasing acidity as the precipitation of iron progressed. The removal of iron was higher from chloride bearing pregnant leach solutions due to their excessively high Na$^+$ content i.e. high [Na$^+$]/[Fe$^{3+}$] ratio. SEM-EDS analysis of the precipitates has shown the incorporation of copper into the jarosite precipitate.
Acknowledgements: The authors would like to acknowledge the financial support from The Scientific and Technological Research Council of Turkey (TUBITAK) with a grant number of 109M111. They also thank Mr. Ridvan Yazici for his help during the preparation of WPCB samples.

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PROCEEDINGS OF 14th INTERNATIONAL MINERAL PROCESSING SYMPOSIUM

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