Transforming the Recycling of E-Wastes with Thiosulfate

Young Hong
PhD Student
University of Sydney
Australia

Marjorie Valix
Associate Professor
University of Sydney
Australia
An Introduction to
ATINER's Conference Paper Series

ATINER started to publish this conference papers series in 2012. It includes only the papers submitted for publication after they were presented at one of the conferences organized by our Institute every year. This paper has been peer reviewed by at least two academic members of ATINER.

Dr. Gregory T. Papanikos
President
Athens Institute for Education and Research

This paper should be cited as follows:

Transforming the Recycling of E-Wastes with Thiosulfate

Young Hong

Marjorie Valix

Abstract

This study compares the leaching of copper from copper-rich electronic waste in sulfuric acid and ammonium thiosulfate lixiviants. The efficiency of thiosulfate media was manifested by the rapid dissolution of copper resulting in a 99% Cu recovery in 15 hours at 30°C leached with 0.14M thiosulfate with a pulp density of 10g/L. Whilst under the same conditions, sulfuric acid only dissolved 2% of copper. Increasing the temperature of leaching to 40°C, 60°C and 90°C in sulfuric acid, increased the recovery. Optimal copper recovery of 99% was achieved at 90°C in 8 hours with 0.1M of acid. Furthermore the copper selectivity (mole/mole) in thiosulfate was 54.16 whereas in sulfuric acid it is only 26.44. The assessment of the leaching behavior of copper in sulfuric acid showed it was influenced by the precipitation of copper hydroxide. Sulfuric acid depolymerized the epoxy in e-waste to form bisphenol – a precursor for precipitation. The formation of the copper precipitate robbed the leachate of the dissolved copper. The epoxy induced secondary reaction found in sulphuric acid had no effect on copper recovery in thiosulfate because epoxy is inert in thiosulfate. It appears, however that the low reduction potential in thiosulfate removed dissolved iron as magnetite. The removal of iron effectively improved the selectivity of copper leaching. These results demonstrate the greater efficiency of thiosulfate lixiviant in leaching copper from electronic waste.

Keywords: Copper, E-waste, Selectivity, Sulfuric Acid, Thiosulfate

Acknowledgments: This research was supported under Australian Research Council Discovery Project Scheme (DP1096342).
Introduction

In this modern day and age, society is heavily dependent on electronic devices to perform daily tasks. Driven by consumer demand, technology has experienced a technological boom, an exponential advancement that resulted in electronic devices that are superior and cheaper. In this process, superseded electric and electronics are discarded as electronic waste (e-wastes). An ever growing problem, as described by the United Nations Environment Program (UNEP), the volume of the e-waste generated was estimated to reach 65.4 million tons by 2017 and to increase by 33% relative to figures in 2012 (Miller et al., 2012; Schluep et al., 2009). Unlike municipal waste, e-waste comprise of both toxic and valued resources, such as metals, which are lost when discarded. In order to put a stop to this material wastage, there is demand for a robust and sustainable technological management system that is able to handle the sheer volume and the intricate nature of these wastes.

Extensive effort has been put into reviewing metallurgical methods to recovery metals from electronic wastes with hydrometallurgical processing receiving significant interest because of its ease of use, predictability and low capital investment and operating cost relative to pyrometallurgical methods (Oishi et al., 2007). The hydrometallurgical method involves the use of reagents, either acidic or alkali in nature depending on targeted metals, to dissolve metallic fractions of e-waste (Cui and Zhang, 2008b). An example of reagents used to recover precious metals includes cyanide, thiourea, thiosulfate and halide solutions (Cui and Zhang, 2008b; Tuncuk et al., 2012; Zhang et al., 2012). On the other hand, both organic and inorganic acids are used to recover base metals from e-waste (Saidan et al., 2012). Precious metals from leachates are recovered through various methods such as precipitation, solvent extraction, adsorption and ion-exchange and electro wining (Coman et al., 2013; Cui and Zhang, 2008b; Rimaszeki et al., 2012; Robotin et al., 2012).

Economic benefits of recycling e-waste arise with the presence of a variety of valuable metals such as gold, silver and palladium with copper the most predominant metal constituting 10 to 30% by mass (Cui and Zhang, 2008a). Hydrometallurgical recovery of copper involves oxidative acidic treatments, using both inorganic and organic acids. However, in these cases, higher recovery requires leaching at 90°C or long residence periods at 30°C and is often affected by secondary reactions such as precipitation and passivation (Hong and Valix, 2014). Other researchers were able to improve the leaching rate with the addition of oxidizing agents such as H$_2$O$_2$ and ferric sulfate (Birloaga et al., 2013; Yazici and Deveci, 2014). Although the feasibility of acidic treatment has been proven; economics of processing, cost, duration and energy intensity remain issues. Alternatively, chemical leaching could also be performed using complexation, where ligands complexes with metals. Chelating agents such as EDTA, DTPA and NTA were used for the mobilization of Cr, Cu, Pb and Zn from fly ashes (Hong et al., 2000). Other complexing agents such as cyanide and thiosulfate have been widely applied in
the recovery of precious metals from e-waste (Tay et al., 2013; Tripathi et al., 2012). Environmentally, thiosulfate has been highlighted by several authors as a suitable substitute for cyanide leaching because of its low toxicity and beneficial nature as a fertilizer (Aylmore and Muir, 2001).

The presence of ammonia facilitates the dissolution of copper (Zhou et al., 1995) and other metallic fractions present in e-waste, into electrolyte as soluble ammine complexes (Lim et al., 2013). A novel alkaline leaching of copper from PCB waste has been established by Koyama et al. (2006) using Cu(I)-ammine complex under nitrogen atmosphere. The authors found evidence that Cu(II)-ammine complex significantly enhances the leaching rate, whilst the product, Cu(I)-ammine, slightly depresses the leaching rate. Oishi et al. (2007) then compared the leaching between ammoniacal ammonium sulfate and the chloride system. The authors found that copper leaching was more selective for a sulfate system than chloride. Another study demonstrated that chloride is marginally better than sulfate in leaching copper (Ha et al., 2010). Both authors reported that, Zn, Pb, Mn and some Ni were solubilized along with Cu, but Fe and Al were left in the residue.

Recovery of copper from e-waste has been traditionally dominated by acidic leaching via inorganic or organic acid whilst few have utilized an ammonia-salt system. Ammonia-thiosulfate leaching of e-waste has been primarily focused on gold; while copper received little attention. Given that copper and gold occur simultaneously in e-waste, establishing leaching ability of thiosulfate of copper could provide a single-reagent solution for the solubilization of both metals from e-waste. Based on the environmental benefits and ability of the rapid leaching rate of precious metals from electronic waste, this work examined the thiosulfate leaching copper from the e-waste and compared its efficiency to sulfuric acid leaching.

Materials and Methods

Materials

Ground electronic wastes (copper-rich) were obtained from Total Union PCB Recycle in Hong Kong. Metallic components of the PCB were separated by crushing, milling and magnetic separation. The waste from the recycling company was used as received with a minor size separation. After undergoing sieving, waste fraction with a particle size range of 40-104 µm was collected and used throughout all experiments. The elemental composition of e-waste is summarized in Table 1.

<table>
<thead>
<tr>
<th>Metals</th>
<th>Al (wt. %)</th>
<th>Cu</th>
<th>Fe</th>
<th>Mg</th>
<th>Pb</th>
<th>Sn</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.25</td>
<td>86.63</td>
<td>0.063</td>
<td>0.028</td>
<td>0.026</td>
<td>0.029</td>
<td>0.167</td>
</tr>
</tbody>
</table>

Method

Thiosulfate and sulfuric acid leaching of e-waste were carried out at temperature controlled 50ml Variomag batch reactors with a stirring speed of
1000 rpm at temperatures from 30-90°C with a pulp density of 10 to 100 g/dm³ for periods of 1-24 hours. Further experiments on thiosulfate, derived from ammonium thiosulfate, were conducted to investigate the effect of stirring speed, reagent concentration and pulp density. Metal recoveries were estimated from the ratio of dissolved metals to the original metal content of the waste. Due to the heterogeneity nature of the waste, the original content of the waste was determined through the summation of dissolved metal and the leaching residues (Eq.1). The leaching selectivity was estimated from the ratio of dissolved Cu (moles) to the sum of other metals quantities according to Eq. 2.

Metal Recovery (\%) = \frac{\text{Dissolved metal}}{\text{Dissolved metal} + \text{Residue}} \quad (1)

Selectivity = \frac{\text{Moles of desired product}}{\sum \text{moles of undesired product}} = \frac{\text{Mols of Copper}}{\sum \text{mols of other metals}} \quad (2)

The metal content in the residues were determined by aqua regia digestion (HCl and HNO₃, ratio 3:1) of the waste (Meng and Zhang, 2012); dissolved metals were analyzed by Varian Vista AX CCD Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) using standard procedures. The pH and oxygen reduction potential of the solutions were monitored during leaching with a dedicated pH-mV-temp meter (TPS WP-80D).

Results and Discussion

Chemical Leaching with Thiosulfate and Sulfuric Acid

When comparing the recovery of metallic copper fractions from e-waste between sulfuric acid and thiosulfate, it was discovered that thiosulfate has a superior copper mobilization capacity relative to sulfuric acid (Figure 1). In fact, leaching using thiosulfate media was less energy intensive. At 30°C, rapid dissolution of copper with a recovery of 99% was achieved in 16 hours by thiosulfate media. Under similar leaching conditions, sulfuric acid achieved only a 2% recovery. To achieve a similar recovery, leaching was required to be performed at 90°C. From our previous studies, it was already established that sulfuric acid leaching is dependent on temperature (Hong and Valix, 2014). In terms of selectivity, it can be seen from Figure 2 that thiosulfate leaching is copper specific. Having established the superiority in leaching of thiosulfate over sulfuric acid, the remainder of this paper will focus on leaching optimization.
Figure 1. Comparison of Sulfuric Acid and Thiosulfate Leaching at Pulp Density 10g/dm³

![Comparison of Sulfuric Acid and Thiosulfate Leaching](image)

Figure 2. Selectivity of Thiosulfate Leaching

![Selectivity of Thiosulfate Leaching](image)
Effect of Ammonia Concentration

The concentration of ammonia had a significant effect on copper recovery. Lowering ammonia concentration to 0.05M resulted in reduced recovery due to precipitation after 24 hours of leaching. After eight hours of leaching, it is evident, from Figure 3, that the rate of leaching increased proportional to the ammonia concentration in the order of 0.3M>0.2>M>0.26M>0.1M>0.05M. It should also be noted that all concentrations except 0.05M, achieved a recovery of 95% or greater after prolonged leaching. The solubilization of copper by thiosulfate was minimal in the absence of ammonia, demonstrating the role of ammonia in the solubilization of copper.

Figure 3. Effect of Ammonia Concentration on Cu Recovery. Conditions: PD 10g/dm³, 0.14M S₂O₅²⁻, 25°C

Effect of Thiosulfate Concentration

During the leaching of copper, thiosulfate acts as a stabilizing agent. As there were no significant dissolution advantages, it was determined that 0.14M is a sufficient concentration since 99% copper recovery was achieved whilst avoiding the formation of precipitation and hence used as a baseline to compare the effects of concentration.

The absence of thiosulfate, ammonia was able to solubilize copper however pale blue precipitation had started to occur. Believed to be copper hydroxide, Cu(OH)₂, this precipitate continued to form even at lower concentrations of thiosulfate. At 0.05M and 0.1M, precipitation occurred after 5 hours and 16 hours of leaching respectively. These precipitations robbed the metal from the leachate, in turn hampering the recovery of copper.

From
Figure 4, the effect of precipitation is evident particularly for 0.05M. After 8 hours of leaching, copper recovery began to decrease. Similarly for 0.1M, recovery of copper dropped after 16 hours. It appears that precipitation occurs after the complete consumption of thiosulfate as precipitation was not observed at higher concentration when thiosulfate is in excess.

At higher concentrations of thiosulfate, there were no significant differences in terms of the leaching rate (see
Figure 5. Although 0.18M exhibited slightly faster leaching rates at shorter leaching durations, near complete recoveries were only achieved after 16 hours of leaching, uniform for all concentrations. Higher concentrations of thiosulfate appeared to hamper the dissolution rate of copper, achieving only 60% after 16 hours, similar to those observed in the leaching of gold by Ha et al. (2010). The authors suggested that variations of concentrations change the stability region of the system which in turn affects recovery.

**Figure 4.** Comparing the Lower Spectrum of $S_2O_3^{2-}$ Concentration. Conditions: PD 10g/dm$^3$, NH$_3$ 0.26M, 30°C
Figure 5. Comparing the Higher Spectrum of $S_2O_3^{2-}$ Concentration. Conditions PD 10g/dm$^3$, NH$_3$ 0.26M, 30$^\circ$C

Pulp Density

In the leaching e-waste, pulp density is an important factor to consider as it increases the available surface area per unit volume of reagent used and thus allowing a higher recovery within a specific time. It was found that the recovery decreased drastically with the increase of pulp density, as shown in
Figure 6. Although previous studies examined the effect of pulp density using different materials and reagent, the adverse effect of pulp density on recovery is consistent in this study.

In addition, there was formation of blue precipitate similar to those observed in previous sections. Jha et al. (2012) reported that precipitation in the form of Pb(NO$_3$)$_2$ that formed at higher pulp density resulted in a reduction in Pb dissolution. The authors highlighted that a decrease in recovery at higher pulp density arises due to insufficient reagents and oxidants, such as oxygen and solubilize metals. Thus the formation of the blue precipitate could be attributed to the lack of reagent, consistent with the decrease in metal recovery.
**Figure 6.** Effect of Pulp Density (g/dm$^3$). Conditions: 0.14M $S_2O_3^{2-}$, $NH_3$ 0.26M, 25°C.

---

**Effect of Temperature**

As mentioned prior, sulfuric acid requires higher temperatures in order to achieve higher recoveries. At room temperature, oxidants such as hydrogen peroxide ($H_2O_2$) could be used to improve the rate of dissolution (Yang et al., 2011).

On the other hand, the effect of temperature on thiosulfate was not investigated due to two reasons. Firstly, near complete recovery of copper was achieved at room temperature. Hence elevated temperature is not necessary as it will constitute additional resource consumption deeming the method less sustainable. In addition, higher temperatures would promote degradation of thiosulfate, which in turn increases reagent consumption.

**Effect of Stirring Speed**

The shrinking sphere kinetic by Levenspiel (1972) is often used to describe the fluid-solid reaction particularly ammoniacal copper(II)-thiosulfate leaching (Senanayake, 2004). The model states that the rate of reaction or dissolution of the particles is determined by the diffusion of the reactant to the surface of the solid. By performing a study on the stirring speed during the leaching of copper from thiosulfate, it was determined that diffusion had a significant effect (see Figure 7), similar to those reported by Koyama et al. (2006). Thus it is apparent that agitation promotes leaching.
Figure 7. Effect of Stirring Speed. Conditions: PD 10g/dm$^3$, NH$_3$ 0.26M, 30°C, S$_2$O$_3^{2-}$ 0.2M

Secondary Reactions

Secondary reactions, such as precipitation and passivation, are commonly observed in the leaching of e-waste due to its complex makeup that facilitates these unwanted reactions. Several authors have reported these reactions which often results in lower recoveries (Brandl et al., 2001; Choi et al., 2004; Hong and Valix, 2014; Ilyas et al., 2007; Ilyas et al., 2013; Ilyas et al., 2010; Saidan et al., 2012). Similarly, in this study, the leaching of copper in sulfuric acid was influenced by precipitation in the form of copper hydroxide. Precipitation occurs due to the depolymerisation of epoxy in e-waste by sulfuric acid giving rise to bisphenol which induces the secondary reaction. The occurrence of precipitation could not be avoided due to the presence of epoxy in e-waste. Similar precipitation was also observed during the leaching using thiosulfate, it appears to be dependent on the concentration of reagent used. Manifestation of precipitation only occurs at low thiosulfate or ammonia concentration which diminishes with increasing concentration for both reagents.

Unlike sulfuric acid, precipitation could be controlled and avoided during the leaching using thiosulfate. As epoxy is inert in the alkaline mixture, bisphenol-induced precipitation does not occur. Thus it can be concluded that secondary reactions are more predictable in thiosulfate leaching compared to sulfuric acid leaching.
Conclusions

A comparison between alkaline and acidic leaching of copper from electronic scraps was performed. Ammonium thiosulfate and sulfuric acid were used as respectively leaching reagents. It was established that metallic fractions of copper from e-waste could be leached using ammoniacal thiosulfate. In comparison to sulfuric acid, thiosulfate is a satisfactory alternative to achieve good recoveries without heating or additional oxidants. Temperature had a significant effect only on sulfuric acid leaching. Thiosulfate leaching was affected by stirring speed, pulp density, ammonia and thiosulfate concentrations. Both reagents were affected by secondary reactions (precipitation) that hampered recovery. Unlike sulfuric acid, secondary reactions during thiosulfate leaching could be avoided by controlling reagent concentration.

References


