Characterization of Minerals, Metals, and Materials 2016

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Characterization of Minerals, Metals, and Materials 2016

Proceedings of a symposium sponsored by
the Materials Characterization Committee of
the Extraction and Processing Division of
The Minerals, Metals & Materials Society (TMS)
held during

TMS2016
145th Annual Meeting & Exhibition

FEBRUARY 14-18 DOWNTOWN NASHVILLE,
TENNESSEE MUSIC CITY CENTER

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Library of Congress Cataloging-in-Publication Data is available.

ISBN 978-1-119-26439-2

Printed in the United States of America.

10 9 8 7 6 5 4 3 2 1

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Session Chairs:
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TMS (The Minerals, Metals & Materials Society), 2016

SPECIATION AND CHARACTERIZATION OF E-WASTE, USING ANALYTICAL TECHNIQUES

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Abstract

Electronic waste (e-waste), have a high potential as a source of precious metals, since they can contain metals like silver, gold, platinum, copper, zinc, nickel, tin and others. In this paper some e-waste were characterized using several analytical techniques as Scanning Electron Microscopy (SEM), X-ray diffraction (XRD) and inductively coupled plasma (ICP) in addition to the thermodynamic study by Pourbaix diagrams of silver (Ag), gold (Au), platinum (Pt), copper (Cu), nickel (Ni), tin (Sn) and zinc (Zn); considering an average low concentration of HNO_3 (10% v/v). With results of the characterization was determined that the e-waste is an ideal source for the recovery of valuable metals. Similarly, the thermodynamic studies showed that it is possible to obtain all metallic species except Pt, in a potential window of 1.45V to 2.0V vs SCE.

Keywords: e-waste, Pourbaix, thermodynamic, x-ray diffraction, electron microscopy.

Introduction

Metals in the electronic industry are intended to be used for connecting cables, soldering, printed circuit boards, switches and touch screens. Among the most commonly used metals are copper, barium, nickel, zinc, tantalum, iridium, vanadium, silver, gold, beryllium, manganese, antimony, bismuth, mercury and selenium. This is due to its conductive and corrosion resistance characteristics. The metals contained in electronic waste (e-waste) make them a potential source for the recovery of high economic value metals such as: Ag, Au, Pt, Cu, Ni, Zn and Sn. The lack of technologies for a selective recovery in many countries, have promoted the illegal removal of these residues. In this paper, trying to contribute to the development of some alternatives, a general view is established for the electrochemical leaching of Ag, Au, Pt, Cu, Ni, Zn and Sn, derived from e-waste. First, a characterization study by SEM-EDS, XRD and ICP techniques, is performed. Then, Pourbaix diagrams of Ag, Au, Pt, Cu, Ni, Zn and Sn were constructed considering a low concentration electrolyte of HNO_3 (10% v/v).

Experimental

Sample characterization

The Characterization of the metal sample material of e-waste that was provided by the company "Corporación de Valores Reciclados SA de C.V.", was performed by the SEM-EDS, XRD and ICP techniques to determine the content values of the metals (Ag, Au, Pt, Cu, Ni, Zn and Sn).

The SEM-EDS characterization of the metal powder from the e-waste was carried out using an electronic microscope JEOL JSM-6300, with high vacuum, energy dispersive MORAN detector and using a magnification of 20X, with a 20kV acceleration voltage. In addition, the EDS analysis was made using different regions of the e-waste sample, to obtain an average concentration.
The XRD analysis of the e-waste sample was performed using a NEM Equinox 2000 diffractometer, with a cobalt Co-Kα1 source at 20 kV and 30 mA.
A spectrophotometer Perkin Elmer Optima 8300 was used for the study of e-waste sample by ICP. 1g of the sample was digested using concentrated HCl and HNO_3 2: 1 and heating for 15 min.

Thermodynamic study

For the Pourbaix diagrams construction of the Ag, Au, Pt, Cu, Ni, Zn and Sn species the free software *HSC Chemistry 5* was used. Simulation was performed considering a nitric acid concentration of 10% v/v (2.4 M), at room temperature and the Ag, Au, Pt, Cu, Ni, Zn and Sn concentrations of $9.1x10^{-5}$M, $4.2\ x10^{-5}$M, $4.1\ x10^{-6}$M, $2.88\ x10^{-}$M, $2.86\ x10^{-3}$M, $2.4\ x10^{-3}$M, $8.39\ x10^{-4}$M , obtained by ICP, respectively.

Results

Sample characterization

Figure 1 shows a micrograph from the e-waste powder sample with a 20X magnification. It can be observed a regular morphology of the metallic particles and a size nearby to 1 mm and white areas, which are due to the presence of plastic components from the electronic circuitry of the e-waste.

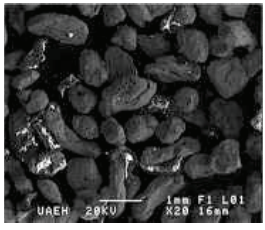


Figure 1 E-waste powder micrograph at 20X using 20 kV.

Table 1 shows the results of average weight percentages of the metals contained in the two regions under study of the sample obtained by EDS analysis.

Table 1 Percentages of the metals found in e-waste powder by SEM-EDS

Element	average weight / %
Cu	58.4 ± 2.1
Ni	25.0 ± 2.8
Zn	0
Ag	0.04 ± 0.06
Au	10.01 ± 0.1
Sn	6.6 ± 4.8
Pt	0

This table shows that the most economically valuable metals, Au and Ag, have 10.01% and 0.04% weight percentage respectively. Also it is observed that the metals with the highest concentration are Cu with a concentration of 58.4 % and Ni with 25.0%. It is noteworthy to point out that the SEM-EDS technique is semi-quantitative, so it is not possible to properly ascertain the content of Ag and Pt. Therefore it was necessary to use more precise techniques, such as XRD and ICP, for studying the e-waste sample.

Figure 2 shows the XRD pattern obtained for the contained metals in the e-waste sample. The most intense peaks correspond to the interest phases of Pt, Ag and Au, in addition to Cu, Zn, Ni and Sn. From this XRD pattern the concentrations of all metallic phases were obtained and they are shown in Table 2. The weight percentage concentrations of Ag, Au and Pt are 11.1%, 6.6% and 6.8%, respectively. Besides, concentrations of Cu, Ni, Zn and Sn with 18%, 19%, 19.7% and 18.8% respectively, were found.

Table 2 Metal e-waste estimated concentrations by DRX

Pattern	Phase	Weight Percentage %
96-901-3053	Ag	11.1
96-210-4030	Pt	6.8
96-901-3036	Au	6.6
96-900-8571	Sn	18.8
96-901-3016	Cu	18
96-901-1600	Zn	19.7
96-901-8571	Ni	19

The differences between SEM and DRX in the mass percentage of Cu, can be attributed, the technique nature. SEM is a semicuantitative analysis, just a scanning of the sample. While DRX, takes a view of the phases angles contained in the sample. So that it is necessary, to use a more precise technique like ICP, that reveals, all phases content.

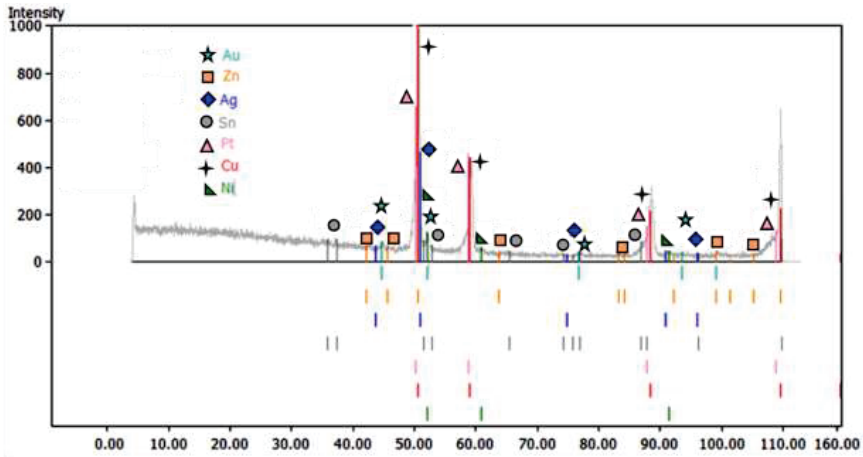


Figure 2 E-waste sample diffract pattern obtained by DRX.

Table 3 shows concentrations obtained by the ICP technique, where the weight percentage content of Ag is 0.05%, Au is 0.04 % and Pt is 0.0043%. It is important to mention, that most metals contained in e-waste, are present as solders or recovered metal parts. Differences between these results and those presented in Table 1 and 2, can be attributed; to the sample pretreatment. While ICP can reveal all metals, because the acid digestion, X-Ray diffraction and SEM-EDS don´t. These results (table 3) demonstrate that the e-waste are a potential source of precious metals, because of the amount in the sample in comparison to the mining usual concentration, which usually have a smaller percentage of Au, Ag and Pt of 0.000567, 0.01 and 0.0004% respectively.

Table 3 E-waste sample concentrations obtained by ICP.

Element	ppm	Weight percentage %
Cu	18324.00	97.64
Ni	168.82	0.90
Zn	155.52	0.83
Ag	9.82	0.05
Au	8.40	0.04
Sn	99.66	0.53
Pt	0.80	0.0043
Total		100

The results of XRD and ICP verify the presence of significant amounts of Ag, Au, Pt, Cu, Ni, Zn and Sn metals.

To carry out the selective electrochemical leaching of a multielemental metallic sample it is necessary to know the potential ranges in which metals are leached. It is therefore compulsory to carry out a thermodynamic study by constructing Pourbaix diagrams that provide information on

the potential of the oxidation processes of each metal. However, it is essential to consider this study as an approximation to the real system, because it does not take into account the nature of electrodes and interactions between all metallic elements present.

Thermodynamic study

Figure 4 (a, b, c, d, e, f, g) shows the Pourbaix diagrams obtained for Ag, Au, Pt, Cu, Ni, Zn and Sn with $9.1x10^{-5}$M, $4.2x10^{-5}$M, $4.1x10^{-6}$M, $2.88x10^{-1}$M, $2.86x10^{-3}$M, $2.4x10^{-4}$M, and $8.39x10^{-3}$M concentrations respectively, whereas a concentration of 10% HNO_3 and pH 1.03 electrolyte is used.

Figure 4a, shows that the formation of Ag^{+} ionic species and AgO_2 oxides is favored in the conditions tested. The Ag^{+} ion species is favored in a range of electrochemical potential imposed between 0.55V to 1.5V vs SCE at pH 1.03. Moreover, it is observed that the leaching of the ionic species of Ag^{+} can be affected by the oxygen evolution reaction from the electrochemical potential of 1.17V.

Figure 4b shows that Gold produces only one ionic specie, Au^{+3}, which predominates in a range of electrochemical potential imposed between 1.45V and 2.0V vs SCE at pH 1.03. Furthermore, it is noted that production of Au^{+3} is always coupled with oxygen evolution; because it is presented to less anodic potentials (1.17V) respect to the working pH.

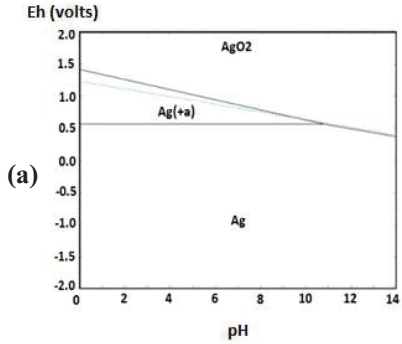
Figure 4c shows that the production of oxidized Pt species is favored; PtO, PtO_2, throughout the pH range, without the production of platinum ionic species.

In Figure 4d the presence of ionic species, Cu^{+2} and oxidized copper, Cu_2O and CuO, are observed. The production of the ionic species Cu^{+2} is favored in the range of electrochemical imposed potential between 0.4V and 2.0V vs SCE at pH 1.03 and whose production is carried out, coupled to the oxygen evolution reaction from 1.17 V vs SCE.

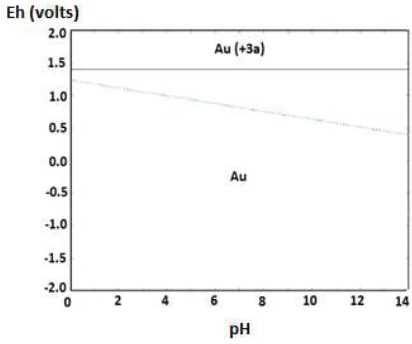
In Figure 4e, the ionic species of Nickel, Ni^{+2}, oxidized, NiO, and hydroxylated, $Ni(OH)_3$, are observed. The production of the ionic species, Ni^{+2}, is favored in the range of electrochemical potential from -0.3V to 2.0V vs SCE. In addition there is the coupled reaction of oxygen evolution from 1.17V during leaching of nickel.

In Figure 4f, the ionic species of Zinc, Zn^{+2}, and oxidized ZnO, are observed. Production of the ionic species Zn^{+2} is carried out at electrochemical potentials between -0.7V to 2.0V vs SCE. In addition, the oxygen evolution reaction, observed from 1.17V, affects leaching process of zinc Zn^{+2} species.

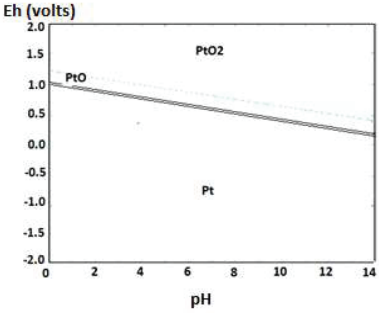
Figure 4g shows that the production of ionic species Sn^{+2} and oxide SnO_2 is possible; however, the ionic species Sn^{+2} are favored in a small range of electrochemical potential of -0.1V to -0.25V vs SCE.


Eh (volts)
AgO2
Ag(+a)
Ag
pH

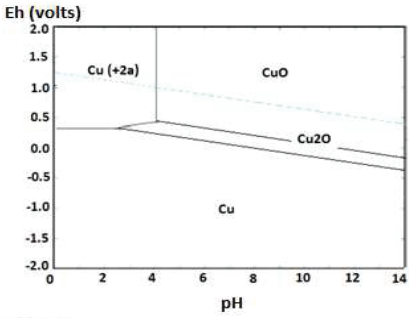
(a)


Eh (volts)
Au (+3a)
Au
pH

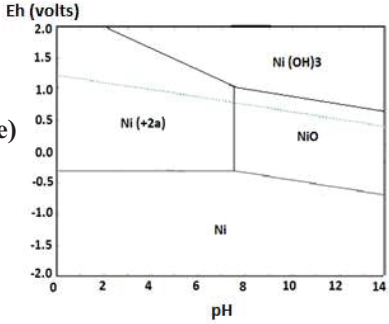
(b)


Eh (volts)
PtO2
PtO
Pt
pH

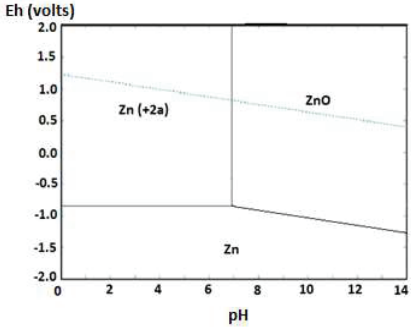
(c)


Eh (volts)
Cu (+2a)
CuO
Cu2O
Cu
pH

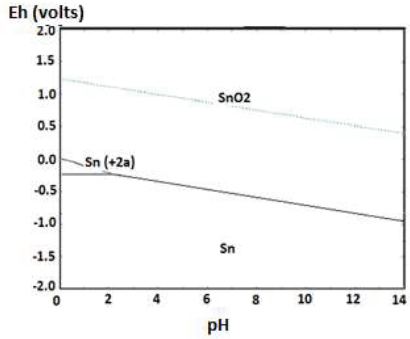
(d)


Eh (volts)
Ni (OH)3
Ni (+2a)
NiO
Ni
pH

(e)


Eh (volts)
Zn (+2a)
ZnO
Zn
pH

(f)



(g)

Figure 4 Pourbaix diagrams for a) Ag , b) Au, c) Pt, d) Cu , e) Ni, f) Zn and g) Sn considering pH 1.03 nitric acid concentration.

Taking into account the above, redox reactions under standard conditions for ionic metal species, which are expected to carry out under the conditions of this work are:

$$Cu^{2+} + 2e^- \leftrightarrow Cu^o \quad E^o = 0.34 \tag{1}$$

$$Ni^{2+} + 2e^- \leftrightarrow Ni^o \quad E^o = -0.250 \tag{2}$$

$$Zn^{2+} + 2e^- \leftrightarrow Zn^o \quad E^o = -0.73 \tag{3}$$

$$Sn^{2+} + 2e^- \leftrightarrow Sn^o \quad E^o = -0.36 \tag{4}$$

$$Au^{3+} + 3e^- \leftrightarrow Au^o \quad E^o = 1.49 \tag{5}$$

$$Ag^{+} + e^- \leftrightarrow Ag^o \quad E^o = 0.799 \tag{6}$$

$$Pt^{2+} + 2e^- \leftrightarrow Pt^o \quad E^o = 1.2 \tag{7}$$

It is worth mentioning that these equilibriums are affected by the specific conditions of the real system, and there can be deviations in the values of potential to which the leaching process is held.

Therefore, the thermodynamic results indicate that it is possible the Ag^+ and Au^{+3}ionic species existence, without platinum; under working conditions. However, these results do not take into account other important factors such as the electrodes nature or interferences in the equilibrium state due to the rest metals interactions.

Conclusions

The characteristics of the metal sample evaluated were determined by verifying the amount of each metal, showing that the e-waste are a viable source for the recovery of Ag, Au, Pt, Cu, Ni, Zn and Sn.

The thermodynamic study indicated that it is possible to obtain the ionic species of Ag, Au, Cu, Ni and Zn metal at an interval of electrochemical potentials of 1.45V to 2V at a pH of 1.03. It is also noted that the tin ion species are produced in an interval of electrochemical potential of -0.1V to -0.25V vs. SCE. Conversely, the formation of platinum ionic species in this potential range and in this medium is not favored. So also it can be concluded that the HNO_3 is a suitable medium for the leaching of most metals in e-waste.

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