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Electrochemical Selective Leaching and Deposition of Ag, Au and Pt from electronic waste

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In this work, selective electrochemical leaching of compact anodes, made from electronic waste (ewaste) powder containing metals such as silver (Ag), gold (Au) and platinum (Pt), was studied in presence of copper (Cu), nickel (Ni), Tin (Sn) and zinc (Zn), as well as metal selective deposition from solutions generated during electrochemical leaching. Thermodynamic analysis, potentiodynamic polarization and potentiostatic techniques were used to establish the conditions that promote selective leaching and deposit of Ag, Au and Pt in 10% HNO₃. X-ray diffraction (XRD), scanning electron microscopy (SEM) and inductively coupled plasma (ICP) spectroscopy were used to validate the results. Findings showed that selective electrochemical leaching for precious metals (Ag, Au and Pt) was possible at potential ranges between 1.1 to 1.17 V vs. SCE. Leaching was favored by the formation of metallic oxides (i.e., NiO₂, Cu₂O and SnO), which limits the leaching of interfering elements that are present in high concentrations in the e-waste, such as Cu. It is also indicated that four regions of deposit was found in region I (from -0.2V to -0.21V vs. SCE) and region II (at -0.25V vs. SCE). While region III and IV (above -0.3V), copper is the predominant species that produces more uniform and shining deposits.

Keywords: Electrochemical leaching, selective deposit, e-waste, Pt, Au, Ag and Cu.

1. INTRODUCTION

Technological progress in continuous development of new generation devices has promoted the indiscriminate replacement of electronic equipment in its middle useful life [1]. Garbage dumps are

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saturated with e-waste by the lack of awareness, from consumers, of the responsibility to recycle their electronic equipment and the negative effects of not doing so [2]. The lack of sustainable technologies for e-waste recycling has led to illegal, toxic and insecure extraction of the metal fraction they contain. Some rudimentary methods of illegal extraction of valuable metals such as incineration or acid extraction (with sulphuric acid, thiosulphates, cyanides or aqua regia) are used without any regulation [3, 4]. In many countries, most of the efforts are directed towards the recycling of different plastic and glass parts, delegating to other countries the selective recovery of mayor economic interest metals [5]. For this reason, it is necessary to optimize the recovery processes of metals from e-waste and the reduction of contaminant residues.

Several studies on the recovery of metals from e-waste involve a large amount of solvents that generate high levels of toxicity and limited percentage of recovery [6-10]. Some techniques are capable to recover high concentrations of the metals but not to permissible levels or including more processes, increasing this way the costs of the metal recovery. Electrochemical techniques are a great alternative for the metals recovery due to their low cost of operation and the possibility to be able to handle low concentration electrolytic media, which allows decreasing of their environmental impact. However, while current studies have considered the deposits of some of metals present, these have not included an in-depth study of the possible influence of the rest of the metals in e-waste multi-elemental system [11-15].

Xiu and Zhang [16] studied Cu deposit from printed circuit boards (PCB's) leached solutions using supercritical water as the oxidizing agent. In the electrochemical part (deposition), they achieved a Cu deposit recovery of 84.2% with current density of 20mA/cm², during 11 h of treatment in 1M HCl, which was used as the electrolytic medium. During the electrolysis process, it was observed that deposits of Cu were partially oxidized to Cu₂O, which represented an interfacial limitation in the oxidation or deposit processes. Meanwhile, the literature contains only a few studies related to the recovery of precious metals from e-waste. Fogarasi [17] studied the Cu deposit from a solution obtained from the chemical (acid) leaching of PCB's. They proposed a chemical and electrochemical reactor using HCl and FeCl₃ as electrolytes, with the purpose of dissolving the PCB plastic parts. A deposit of Cu with purity of 99.95%, with a flow velocity of 400 mL/min and a cathodic potential of -0.135V vs. Ag/AgCl/KCl_{SAT} was achieved. A solid residue was obtained in the sludge containing important metals such as Ag, Au, Sn, Pb, Zn, Fe and Ni, which will require more stages conducted for their recovery. Fogarasi also pointed out that there are still several problems to solve in terms of metal recovery from e-waste, such as improving selectivity and reducing reagent consumption.

Recent studies conducted by Lekka [18] reported the feasibility of recovering Au through deposits from a solution obtained with PCB's leaching in aqua regia. They also used synthetic solutions, intentionally adding specific concentrations of different metals in order to observe the influence of Cu on the behavior of the system. It was found that Cu caused a shift of the Au reduction potential to more negative potentials, as well as resulted in a significant increase in current due to the high concentration of Cu. This last, coupled with the low concentration of Au present in the solution, caused a situation where the gold reduction peak could not be distinguished in voltammograms. For this reason, the solution was enriched with Au. Using this approach, a reduction potential for this metal was found at 0.55V vs Ag/AgCl/KCl_{3M}. In this way, it was stablished that metals concentration in the

system will cause significant changes in the reduction potential of precious metals, making difficult to recover them selectively.

Although the literature contains a large amount of data about recovery of metals from e-waste [6-15], these do not consider factors such as the sample source, interference of different metals present in the e-waste multi-elemental system and the possible interference produced by oxides formation for the selective electrochemical leaching and selective deposition of metals from e-waste. Hence, the focus of this work was to study the selective electrochemical leaching of compact anodes made from e-waste powder containing metals such as Ag, Au and Pt in presence of copper Cu, Ni, Sn and Zn. Moreover, selective deposition of these metals from leaching solution obtained was also studied.

2. EXPERIMENTAL

2.1 Sample characterization

The sample was provided by the company "Corporación de Valores Reciclados S.A. de C.V" and was obtained from a process of several separation stages and a general milling of electronic waste. This resulted in a multi-element metal powder that can be marketed as a compacted metal.

An exhaustive characterization was performed to define the content of the metals present in the sample, specifically Ag, Au, Pt, Cu, Ni, Zn, Sn by scanning electron spectroscopy (SEM), x-ray diffraction (XRD) and inductively coupled plasma spectroscopy (ICP).

For SEM analysis, scanning over the e-waste powder surface was done in two sample regions (A and B) with a scanning electron microscope JEOL JSM-6300 at high vacuum, equipped with a detector of dispersive energies (EDS), an acceleration voltage of 20kV and a detector distance of 16mm. As far as the XRD analysis is concerned, a Siemens D5000 x-ray diffractometer with Co-k α 1 radiation source was used, the X-ray beam influenced the sample during 10min at 20kV, whereby a diffractogram was obtained with the predominant phases in the sample.

For ICP analysis, 1g of sample was leached by heating with HNO₃ and HCl in a 2:1 ratio for 15 minutes. A Perkin Elmer Inductively Coupled Plasma spectrometer was used, with radial and axial detector positions.

2.2. Thermodynamic study

Pourbaix diagrams of Ag, Au and Pt species were made using the HSC Chemistry $5.1^{\text{(B)}}$ chemical reaction and equilibrium software. The simulation was performed considering 2.4M HNO₃ at 25 °C and Ag, Au and Pt concentrations obtained by ICP. Thermochemical data base used contains values for 17000 chemical compounds, referenced properly into the software.

2.3 Electrochemical study

2.3.1 Leaching stage

Electrochemical study for Au and Pt plates was conducted in a three electrode cell connected to a Princeton Applied Research® potentiostat/galvanostat equipment version 263A, controlled by PowerSuite® software. A saturated calomel electrode (SCE, E = 0.242 V vs. a standard hydrogen electrode) was used as reference electrode and a counter electrode of titanium (Ti) in all the experiments. Briquettes (1.2x0.5x3cm) were produced by compacting 10g of e-waste metal powder to 25 tons in a hydraulic press and they were employed as working electrodes. Potential sweeps were carried out in anodic direction at 25mVs⁻¹.

All potential values were reported respect to SCE. Polarization potentiodynamic and potentiostatic responses for the e-waste sample with electrochemical leaching, were evaluated. Surface of already processed briquette was characterized by XRD. All the solutions generated in the electrochemical study were characterized by ICP.

2.3.2 Deposit stage

A 500 ml volume of solution derived from the electrochemical leaching during 600s of the ewaste briquette was prepared. The produced solution was characterized by ICP.

In the study of Ag, Au and Pt electrochemical deposition, a Ti working electrode, a counter electrode of Ti-RuO₂ and a SCE as reference electrode, were used. The solution of the cell was the leached of the e-waste briquettes. The potentiodynamic sweep initiated in cathodic direction with a scanning speed of 25mVs^{-1} , in a potential window that was progressively increased from -0.2V to - 0.95V. The potentiostatic transients were obtained by imposing potentials of -0.2V to -1.0V during 150s using the leached solution. The produced deposits were characterized by SEM.

3. RESULTS AND DISCUSSION

3.1 Characterization of the sample

An exhaustive analysis was performed with SEM/EDS, XRD and ICP techniques in order to identify the elements present in the sample and their content; including precious metals (Au, Ag and Pt) present in the e-waste samples. Although, SEM-EDS and XRD techniques are semi-quantitative, they provide a first indication of the presence of the metals in e-waste powder; with the ICP technique, it was determined the concentration contained of the metals of interest.

3.1.1 SEM/EDS Characterization

Figure 1 shows a micrograph of the e-waste powder provided by the company "Corporación de Valores Reciclados S.A. de C.V", with a 20X magnification. It can be seen that the metallic particles

have an irregular morphology due to the grinding from which they come. White areas in the image correspond to plastic remnants coming from the original e-waste structure. Table 1 (first column) shows the weight percentages of metals contained in the sample, obtained by SEM/EDS semiquantitative analysis.



Figure 1. SEM image obtained on e-waste powder at 20X.

Table	1. Met	al percentages	contained in	e-waste	powder	sample,	obtained	by	SEM-EDS,	DRX	and
	ICP te	chniques.									

	SEM-EDS	DRX	ICP
Cu	56.9	18	97.64
Ni	23	19	0.90
Zn	0	19.7	0.83
Ag	0.08	11.1	0.05
Au	10.02	6.6	0.04
Sn	10	18.8	0.53
Pt	0	6.8	0.0043

Table 1 shows the metals of interest, Au and Ag, obtained by SEM-EDS with content percentages of $10.02\%_{w/w}$ and $0.08\%_{w/w}$, respectively. The metals with the highest concentration were Cu and Ni, with 56.9% w/w for Cu, 10% w/w for Sn and 23% w/w for Ni, while Pt was not observed.

3.1.2 XRD Characterization

Figure 2 shows a diffractogram of the e-waste powder obtained by XRD. The highest intensity peaks correspond to the interest phases of Pt, Ag and Au in addition Cu, Zn, Ni and Sn. Table 1 also shows the concentrations of all metal species, obtained by indexing diffractogram. In the second column the concentration of precious metals in the sample are quite different from that obtained by SEM-EDS, showing a distribution more uniform with XRD and the presence of platinum, which was not observed in SEM-EDS analysis. It is important to emphasize that SEM-EDS observations are

semiquantitative and depend on the area used to the study, same case with XRD; however, with ICP there is no place to doubts about content of the metallic elements.



Figure 2. Diffractogram obtained by XRD on e-waste powder sample.

3.1.3 Chemical characterization by ICP

Table 1 (third column) shows the metals concentration present in the e-waste powder, obtained by ICP with one gram of sample. Here, it is important to remark the presence of Pt in a concentration that could be valuable. These results confirm that precious metals are present (Au, Ag and Pt) in the e-waste sample, assuring that e-waste is a potential source of these metals due to the amount found, in comparison with quantities obtained by mining extraction that are relatively smaller (i. e. Au 0.000567%, Ag 0.01% and Pt 0.0004%, in one gram of sample). In addition, considering factors such as extraction time, cost and environmental impact, the deposits can be obtained in an easier way.

3.2 Thermodynamic study of Ag, Au and Pt in nitric acid system

Figure 3 (a, b and c) shows the Pourbaix diagrams obtained for Ag, Au and Pt. For its construction, the concentrations obtained by ICP $(9.1 \times 10^{-5} \text{M}, 4.2 \times 10^{-5} \text{M} \text{ and } 4.1 \times 10^{-6} \text{M}, \text{ respectively})$ and a 10 % _{v/v} HNO₃ concentration (pH 1.03), were considered.

Figure 3(a) shows the Ag^+ and AgO_2 species predominance range in potential and pH. The ionic species of Ag^+ appears in a potential range between 0.55V to 1.5V at the pH of 1.03 and it has coupled the oxygen evolution reaction since 1.2V. In Figure 3(b) it is shown that Au only has complexes in Au⁺³ species. This species appears in a potential range between 1.45V to 2.0V at the working pH and haves coupled the oxygen evolution reaction in all pH range.



Figure 3. Pourbaix diagrams for the systems: a) $[Ag] = 9.1 \text{ E}^{-2} \text{ mM}$, b) $[Au] = 4.2 \text{ E}^{-2} \text{ mM}$ and c) $[Pt] = 4.1\text{E}^{-3} \text{ mM}$, in 10% HNO₃ medium.

Figure 3(c) shows that Pt complexes in species $PtO-PtO_2$, indicating that, under working conditions, Pt ionic species is not available.

The results indicate that it is possible to obtain ionic species of Au $^{(+3)}$ and Ag $^{(+)}$ but not of Pt, at the working conditions (pH and potential). Then, it would be expected that the electrochemical leaching of Pt cannot occur at all the potential range (Figure 3c). However, it is important to consider that although Pourbaix diagrams are a starting point at the beginning of an electrochemical study; these do not take into account other factors such as electrodes nature, possible interference caused by other metals presence at the interface (i. e., galvanic interactions) or the whole kinetics. In this way experimental results may differ from thermodynamic ones. Thus, it was essential to assess the potentiodynamic response of a Pt electrode with a solution of 10% HNO₃ and to corroborate the absence of Pt species after dissolution of the working electrode. In the case of Ag and Au, they were not evaluated because these metals have a good affinity with electrolytic medium producing ionic species and it has been demonstrated by several authors in literature [4].

3.1.3 Electrochemical leaching study

Figure 4 shows the voltammetric response of Pt working electrode when the potential sweep starts in the anodic direction, in a solution of $10\%_{v/v}$ HNO₃. The sweeping was carried out in a potential window from 1.5V to -0.5V and with a scan rate of $25mVs^{-1}$.



Figure 4. Cyclic voltammetry *initiated in anodic direction* obtained with a Pt electrode in $10\%_{v/v}$ HNO₃ at 25mVs⁻¹, pH 1.03.

It can be observed from the diagram that the oxidation process of Pt was carried out at a potential range of 0.8V to 1.2V, with a maximum oxidation current of 0.085 mA; while its corresponding reduction process was carried out at potential range between 0.6V and 0.2V. This

corroborates that the electrochemical leaching of Pt was possible under the working conditions. In order to identify the potential ranges where selective leaching of Pt, Au and Ag are carried out from briquettes of e-waste, anodic voltammetric response was evaluated at the potential range from 0.2V to 1.3V (Figure 5).



Figure 5. Voltammetric responses obtained on e-waste briquette in $10\%_{v/v}$ HNO₃ at pH 1.03, with potential inversion from 0.2V to 1.3V vs SCE and a scan rate of $25mVs^{-1}$.

In Figure 5, an increase in the oxidation current can be observed with the imposition of anodic potentials. This increase was attributed to the leaching of the metals present in the briquette as Ag, Au, Pt, Cu, Ni, Zn and Sn. However, it should be noted that from 0.7V the increase of current was slightly higher. This behavior is due to the superficial modifications on the briquette, attributable to an increase in the surface area due to the detachment of metallic particles from the briquettes, which releases new active spaces; as well as, to oxygen evolution reaction achieved at that potential. In addition, a higher increase of current was observed above 1.2V, likely by a transpassivation phenomenon, due to dissolution of a passive film present on the briquette surface. In order to obtain more precise data on the surface changes in the briquette and behavior of the metals leaching, a potentiostatic transients analysis was also carried out in a potential range between 0.2V and 1.2V in a solution with $10\%_{v/v}$ HNO₃ (Figure 6).



Figure 6. Potentiostatic transients obtained from e-waste briquette in $10\%_{v/v}$ HNO₃ at pH 1.03, imposing potentials from: (a) 0.2V to 1.2V vs SCE and (b) 1.0V to 1.19V vs SCE, during 600s.

In Figure 6a, it can be observed that by increasing gradually the anodic potential oxidation current increases too, but above 0.8V the changes in current are irregular. In addition, a greater increase of the current occurs between 1.1V and 1.2V. This fact was attributable to three important contributions in e-waste multi-elemental system. These were a) material detachment, because metal powder is compacted without any support, and while it is leaching it tends to detach from the briquette; b) the oxygen evolution reaction that can be observed macroscopically above 0.8V and c) a passive layer formation occurs, similar to what Deyab and Keera [19] observed. In this way, a detailed study was conducted on e-waste briquette at potential range from 1.0V to 1.2V, under the same work

conditions (Figure 6b). An irregular behavior in the potentiostatic transients response was observed, with current increase and decrease, attributed to the formation of a passive layer or galvanic interactions of metals on the briquette surface.

Xiu and Zhang [16] established that Cu is partially oxidized, probably due to its interaction with the medium. Deyab and Keera [19] found the formation of a passive layer on a carbon steel electrode with hydrochlorhidric acid. In this system, they found that after a potential area identified by an oxidation peak where the ferrous ion dissolution is carried out, it produces a solid oxide at the surface, which causes the anodic current to decrease, indicating passive zones generation (partial passivity) at working electrode surface. Considering the high concentration in which the Cu is present in the system, its high affinity with the electrolytic medium and the energy supplied, it is very likely that the formation of a partial passive layer occurs over briquettes surface. In order to corroborate this hypothesis, it was needed to characterize the generated solutions to identify the metals that are being leached in each imposed potential; besides characterizing the briquette surface by XRD to verify metallic oxides formation.

Figure 7 shows the concentrations obtained by ICP of the solutions generated in the previous potentiostatic transients study. These concentrations indicate that leached metals increase in the solution as anodic potential increases. The Cu presents a very active behavior leaching to from 0.2V and increase in large quantities between 0.8V to 1.0V, where it reaches its maximum value. However, at 1.1V, their leaching decreases drastically and it is precisely at this potential where Au begins to be leached. Furthermore, it was observed that Ag and Pt begin to leach from 0.2V, but above 1.1V and close to 1.2V was where highest amount are achieved, likely due to less interference of Cu by a passive layer generation.



Figure 7. Metal concentrations obtained by ICP from leached solutions produced at the potentiostatic transients evaluations.

Figure 8 shows the diffractogram obtained by XRD on the electrochemical modified briquettes surface at 1.17V during 300 seconds. Presence of metal oxides was evident on the briquette surface,

where higher oxides concentration were NiO₂, Cu₂O and SnO, followed by ZnO and AgO (see Table 2). Thus, the results indicates that to achieve Ag, Au and Pt leaching, it is necessary to work at potentials above 1.1V and close to 1.2V, where passive layer formation mainly by Cu, Ni and Zn oxides occurs, which limits Cu leaching and favors interest metals leaching. It is also important to mention that the deviation in Pt leaching behavior with respect to what is observed in Pourbaix diagrams is likely due to the presence of other elements (i.e. Cu, Zn, Ni, Sn, Ag and Au), which favors its leaching. Thus, it is pertinent to attribute to the generation of a passive layer those differences produced in the anodic current during leaching and the appearance of a potentials zone where selectivity occurs, that is to say, where we have least Cu interference.



Position / °2 Theta

Figure 8. Diffractogram obtained by XRD on e- waste briquette surface electrochemically modified during 300 seconds at 1.17V vs SCE.

Table 2. Metallic oxides percentages	obtained on e-waste br	riquette surface electroc	chemically modified
during 300 seconds at 1.17V v	's SCE.		

Pattern	Phase	%			
96-901-6309	NiO ₂	51.4			
96-900-5770	Cu ₂ O	26.8			
96-901-2141	SnO	17.4			
96-230-0114	ZnO	2.6			
96-231-0066	AgO	1.8			
		100			

3.3 Deposit study

Some authors [20-22] have developed an effective strategy to determine the ranges where the selective deposit of metals is carried out. This experimental strategy allows researchers, by cyclic

voltammetry measurements, to obtain a reduction potential as an anodic charge function. Slope changes are attributed to surface modifications due to deposit or co-deposit of metals.



Figure 9. Cyclic voltammograms obtained on Ti plate electrode from e-waste leached solution, with potential inversions from: (a) -0.2V to -0.25V and (b) -0.25 to -0.95 V vs SCE with scan rate of 25mV/s.

Figure 9 shows voltammograms initiated in cathodic direction at ranges of: a) -0.2V to -0.25V, b) -0.25V to -0.95V, with a sweep rate of 25mV/s. In all tests the electrodes arrangement Ti/Ti-RuO₂ and the leached solution of e-waste were used. It can be observed that in all voltammograms there is a reduction process (C1) that starts from 0V to -0.25V, attributed to metals deposit. When the sweep was reversed, one oxidation processes appears (a1) in a potential range between 0.4V to 0.2V vs SCE attributed to leaching of metals deposited during the direct sweep. It can also be observed that the oxidation peak current density (a1) increases as cathodic switch potential increases, due to an increase in species concentration deposited on the Ti electrode.

Figure 9b shows that from the switch potential of -0.3V, voltammograms presents two reduction processes (c1 and c2) in the potential range between 0V to -0.4V and of -0.4V to -0.9V, which were attributed to deposit of metals, as well as to the electrolytic medium reduction. In addition, two crosses at -0.4V and -0.3V can also be seen in the voltammetric responses, indicating Ti surface modification due to new deposits formation. Anodic current (peak a1) density increases as the cathodic switching potential increases, until -0.7V, but above this potential the current density of peak a1 decreases, due to coupling of reaction of hydrogen evolution at reduction process c2. It was also observed that a displacement of oxidation peak a1 occurred towards values that were more positive, which is characteristic of co-deposits redissolution. Thus, in order to elucidate the certain potentials where deposits and co-deposits of Ag, Au and Pt are carried out in the presence of Cu, Ni, Zn and Sn, the anodic charge was determined as a function of the cathodic switching potential.



Figure 10. Associated anodic charge (Qa) obtained on Ti plate electrode from e-waste leached solution, with the cathodic switching $E_{-\lambda}$ potential between -0.2V to -0.95V vs SCE.

Figure 10 shows the graph of anodic charges as the cathodic switching potential (E_{λ}) function, where four regions of potentials with different slopes are shown. Region I goes from -0.2V to -0.22V, region II from -0.22V to -0.3V, which can also be called transition zone, region III from -0.3V to -0.7V and finally region IV from -0.7V to -0.95V.



Figure 11. Potentiostatic transients obtained on Ti plate electrode from e-waste leached solution in 10% HNO₃ at pH 1.03, imposing potentials from: (a) -0.2V to -0.25V vs SCE and (b) -0.3 V to -0.9V vs SCE, during 150s.

It is expected that in each one of these regions of potentials, selective deposition of metals contained in e-waste leached solution occurs. In addition, positive slopes values (m1=0.013 and m2=0.08) can be observed in regions I and II, were this decreases as the potential became more negative. It is likely that here the deposits of metals present in small quantities was carried out due to lower magnitudes of charges, while negative slope values (m3= -0.0258 and m4 = -0.0001) can be observed in regions III and IV, with an anodic charge higher. However, Region III shows a significant increase in the charge when potential was more negative. This increase is attributed to the massive co-deposit of metals present in greater proportions, such as Cu, on the previously deposited metals.

Thus, the results in Region I can be attributed to the precious metals (Ag, Au and Pt) deposit. Region II can be attributed to active metals (Ni, Zn and Sn) co-deposit over the previous metals deposits made in region I. Region III is attributed to Cu massive co-deposit on the previously deposited metals; this shows a significant increase in the anodic charge, while in region IV Cu continues depositing but with hydrogen evolution reaction coupled.

Some authors that have applied this experimental strategy, but used other electrolytic systems, fewer elements and synthetic solutions, through which they determined that selective deposit potentials have shown a different behavior in their slopes values [20-22]. However, the slopes behavior indicates that Au, Ag and Pt deposit rate decreases, which can be attributed to the Ni, Sn, Zn and Cu elements influence contained in the system over noble metals co-deposition. In terms of mass transport species there is no support electrolyte, thus the process is controlled by species migration and diffusion, which causes deposit rate to decrease. Although this result indicates that it is possible to obtain selective deposit of metals from the leached solution, it is necessary to evaluate the deposits obtained in the four regions using a potentiostatic transients analysis.

Figure 11 (a) shows potentiostatic transients responses using the leached solution of e-waste when there are imposed potentials from -0.2V to -0.3V (Region I and II) during 150 seconds. While Figure 11 (b) shows potentiostatic transients responses imposing potentials from -0.3V to -0.9V (Region III and IV) during 150 seconds. The Figure (11a) shows that potentials between -0.2V to -0.25V, the cathodic current do not increase normally, which was attributed to precious metals deposits (Au, Pt, Ag) with the interference of some active metals (Zn, Ni, Sn and Cu).





Figure 12. SEM images obtained from deposits on a Ti plate electrode in regions: (a) I and II at 4500X, (b) region III at 3300X and (c) region IV at 4000X.

Deposition resulting in an energy competition due to galvanic interactions, which prevents these noble metals, continues to be deposited. However, Cu interference cannot be completely avoided, such as Reyes-Cruz [21] as observed. For potentials above -0.25V (Figure 11b) cathodic currents significant increases gradually as the imposed cathodic potentials increases. This behavior suggests a deposit of higher concentration species in the solution such as Cu. However from -0.5V to -0.9V the increase in the reduction current is very high, indicating that there is enough energy to achieve a massive Cu deposit, in addition to the hydrogen evolution reaction. Hence, it was necessary to characterize deposits obtained to define which species are deposited preferably in each region of potentials.

	Region I				Region II			Region III							Region IV			
E(V) Element%	-0.2	-0.21	-0.22	-0.23	-0.24	-0.25	-0.3	-0.4	-0.45	-0.46	-0.47	-0.48	-0.49	-0.5	-0.6	-0.7	-0.8	6.0 -
Pt	24.3	13.7	20.3	3.7	0.5	21.0	1.0	1.3	1.2	1.0	1.3	0.8	1.4	0.6	1.2	0.6	1.3	1.3
Au	31.3	4.88	10.7	14.5	0.8	23.3	0.7	0.7	1.1	3.3	2.1	2.0	2.0	1.9	0.9	0.4	0.6	1.3
Ag	13.7	32.2	16.8	19.2	1.8	19.7	1.2	2.2	0.5	1.9	0.5	1.8	1.7	1.3	0.5	1.0	0.4	0.9
Cu	0.0	12.9	16.4	49.2	94.6	0.4	95.3	93.6	96.4	91.1	93.2	92.5	92.8	94.2	96.1	95.8	96.4	95.9
Zn	2.9	4.30	2.4	0.6	0.3	14.7	0.1	0.4	0.0	0.0	1.2	0.5	0.0	0.2	0.0	0.0	0.0	0.0
Ni	9.2	18.2	10.8	9.6	0.7	7.0	0.5	1.2	0.2	0.6	1.5	2.6	1.2	0.7	0.6	1.4	0.4	0.3
Sn	18.5	13.8	23.4	3.2	1.4	13.9	1.1	0.5	0.6	1.0	0.1	0.6	0.9	1.1	0.7	0.8	0.3	0.3

Table 3. Metal average percentages contained on deposits obtained from each region of potentials, by SEM-EDS.

Figure 12 shows deposits micrographs obtained from region (a) I and II with a 4500X magnification, (b) region III with a 3300X magnification and (c) region IV with a 4000X magnification. It can be seen that in regions I and II, deposits grow as a regular shape round

morphology. In region III this morphology prevails, but continues growing, while in IV region deposits grow amorphous and disordered, which is due to a great deposit rate achieved by the system.

Table 3 shows metals concentrations deposited at the four potential regions. These readings were obtained by using the SEM-EDS technique, sweeping 9 areas of Ti surface electrode and obtaining this way a concentration average in each imposed potential region.

It was possible to observe that at -0.2V, a higher concentration of precious metals deposited (Au, Pt and Ag) was obtained, with lower Cu. From -0.21V to -0.22V a small amount of Cu starts to deposit. This confirms that in region I there is a potentials zone where interest metals selective deposits can occur, with the least Cu interference. At potentials between -0.23V to -0.3V vs SCE, corresponding to region II, it can be observed that there is no trend in the amount of metals deposited due to the galvanic interactions generated between them. However, at -0.25V, a higher concentration of precious metals is deposited (Au, Pt and Ag) with Cu being the least observed. Above -0.3V, Cu is the predominant species and it produces more uniform and bright deposits as the imposed potential increases.

These results indicate that it is possible to determine potentials zone where it is possible to carry out the leaching of briquettes made from e-waste. It is also possible to find a potential zone where deposits of interest metals, i.e., precious metals, such as Au, Pt and Ag occur without too much interference of the Cu or other elements present.

4. CONCLUSIONS

Precious metals, such as Au, Ag and Pt, are more feasible to leach in potential ranges between 1.1V and 1.17V vs. SCE. This is due to that its leaching is limited by the superficial modifications of compacted briquette and metallic oxides formed (i.e., NiO₂, Cu₂O and SnO) on the interface, which allows having a potentials zone where selective leaching is achieved with the least interference of Cu.

The electrochemical results showed Pt leaching which is present in e-waste is possible at potentials from 0.2V to 1.2V vs. SCE, in spite of thermodynamic study that shown not there are Pt ionic species produced.

The anodic charge as a function of cathodic potential imposed shown four regions of deposit at potentials between -0.2 V to -0.9V vs. SCE, while a potentiostatic transients analysis and characterization studies by SEM-EDS confirmed this. Selectivity zone of precious metals deposit was found in region I (from -0.2V to -0.21V vs. SCE) and region II (at -0.25V vs. SCE), which presented positive slopes values with the less Cu interference in the e-waste multi-element system. To more cathodic potentials (above -0.3V, region III and IV), copper is the predominant species and it produces more uniform and bright deposits as the imposed potential increases.

The results obtained in this work and the significant amounts of Ag, Au and Pt present in ewaste, open the possibility of making these residues a suitable recovery source in 10% HNO₃ medium, when compared to the estimated amounts in mining production.

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