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Dedicated to prof. dr. I. C. Popescu
on the occasion of his 70^{th} anniversary

DISSOLUTION OF BASE METALS FROM WPCBs USING $Na_2S_2O_8$ SOLUTION

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ABSTRACT. The present work aimed to evaluate the performances of Cu, Zn and Ni dissolution from Waste printed circuit boards (WPCBs) obtained from mobile phones (MP) using different solid:liquid ratios (SLR) and oxidant concentration (C_{ox}). It was found that the increase of C_{ox} at constant SLR increases more the performances of Zn and Ni dissolution than it does for Cu. In contrast, the increase of SLR from 1:5 to 1:15 at constant C_{ox} diminished the dissolution efficiency of Ni by 79 %, of Zn with 55 % and in the case Cu by 22 %. The experimental results revealed that the most favorable conditions for the dissolution of Zn, Ni and Cu are provided at the SLR of 1:5 and 0.42 M $Na_2S_2O_8$.

Keywords: *base metals, persulfate, WPCBs, leaching, solid:liquid ratio*

INTRODUCTION

The current industrialization processes and continuous technological innovations led to accelerated and frequent replacement of electric and electronic equipments (EEE), especially computers and MP, leading to more rapid accumulation of waste electrical and electronic equipments (WEEE). Worldwide annual amount of WEEE is about 20-30 million tons and it is estimated that between 2010 and 2020 it will grow of 2 to 4 times. The EU produces around 8 million tons of WEEE every year, with an annual growth of 3-5 % [1]. Given that today MPs have become the most ubiquitous electronic

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product, they contribute significantly to the increased quantities of WEEE. In 2013, the number of MP subscriptions was approximately equal with the world population [2]. It is estimated that 100 million MP and 17 million computers are discarded annually considering that the lifespan of MP is 1-2 years and of computer 2-5 years [3, 4]. Since MP and computers include in their structure printed circuit boards the annual accumulation of WPCB reaches 1.5-2 million tons, which represents 3 % of the total WEEE [5, 6]. Most studies show that WPCBs include several major categories of materials: ferrous, non-ferrous metals, ceramics and plastics [7, 8]. Among them, in terms of quantity, with highest percentage is Cu, 17-40 %, and by value Au and Ag. Therefore, the recovery of metals from WPCBs found in MP is an ongoing concern as it contributes to the reduction of the negative impact on the environment and to the conservation of the natural metal resources [9, 10]. In the recent decades several research studies have been conducted for the development of processes able to recovery metals from MPs WPCB [5]. Thus, it have been used various procedures as: mechanical [11-13]; pyrometallurgical [14-16]; bio-leaching [17-19]; by using supercritical fluids [20, 21] and hydrometallurgical ones [1, 5, 22, 23]. Compared with the pyrometallurgical processes, the hydrometallurgical processes make possible the use of renewable leaching medium that can be reused in the process thereby reducing the amount of solution used and consequently the production costs [3].

On this basis, the current study focused on the dissolution of base metals from WPCBs removed from MP by using $Na_2S_2O_8$ which is an efficient and selective leaching agent. In this way, it was achieved the separation of base metals which are concentrated in the leaching solution from the precious metals (Au, Ag) that remain in the residue. For this purpose, the influence of C_{ox} and of the SLR on the performance of the leaching process of base metals from MPs' WPCBs was studied.

RESULTS AND DISCUSSION

The influence of SLR and $Na_2S_2O_8$ concentration on the dissolution degree of Cu, Zn and Ni

Preliminary tests showed that $Na_2S_2O_8$ is a strong oxidizing agent capable to selectively dissolve only Cu, Zn and Ni from WPBCs involving the following main chemical reactions:

$$Cu + Na_2S_2O_8 \rightarrow CuSO_4 + Na_2SO_4 \quad (1)$$

$$Zn + Na_2S_2O_8 \rightarrow ZnSO_4 + Na_2SO_4 \quad (2)$$

$$Ni + Na_2S_2O_8 \rightarrow NiSO_4 + Na_2SO_4 \quad (3)$$

In order to determine the optimal conditions required to achieve advanced metal solubilization the dissolution degree of Cu, Zn and Ni was evaluated at various C_{ox} and SLR. Fig. 1 presents the results obtained for the dissolution of Cu at the SLR of 1:5, which reveals that the dissolution degree of Cu increases at constant value of SLR with the increase of C_{ox}. However, it seems like the dissolution rate reaches a maximum at 0.84 M $Na_2S_2O_8$ considering that is no significant differences between the performances obtained at 0.84 M and 1.26 M $Na_2S_2O_8$. This can be explained considering the fact that the dissolution process is controlled by diffusion. Thus, the accumulation of the reaction products will lead to the decrease of their diffusion from the reaction surface to the solution volume, significantly reducing the global rate of the process.

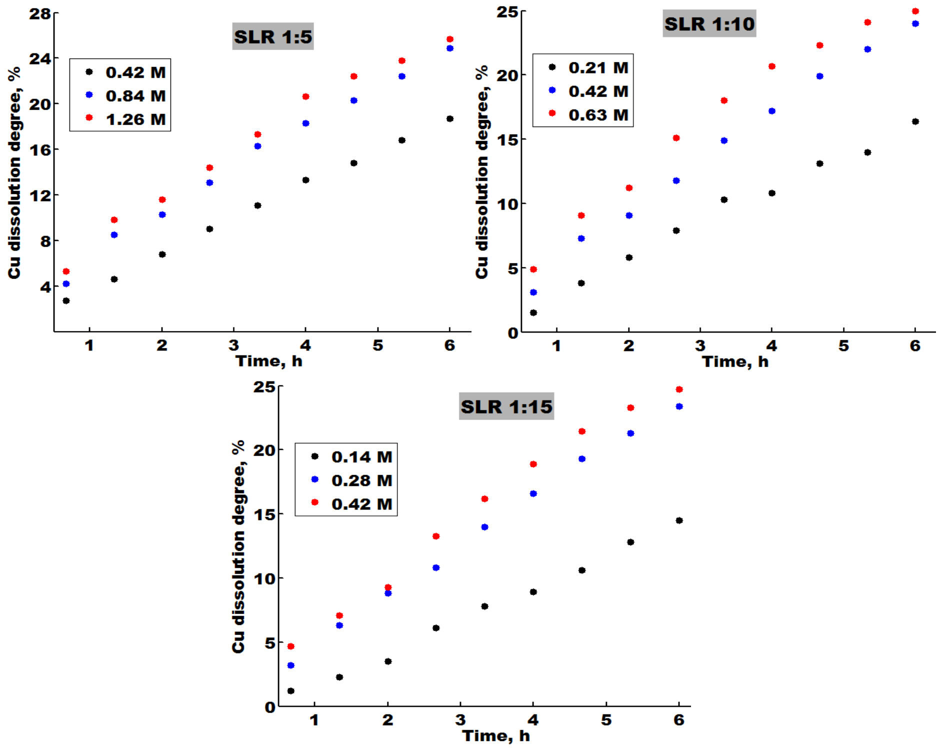

Figure 1. Cu dissolution degree vs. time at different $Na_2S_2O_8$ concentrations and SLR

Similar tendency can be observed from the results obtained for Cu at the SLR of 1:10. According to the data shown in Fig.1, the Cu dissolution degree values increased by 53 % between 0.63 M and 0.21 M $Na_2S_2O_8$, while between 0.63 M and 0.42 M $Na_2S_2O_8$ it was modified only with 4 %. In contrast, at the SLR of 1:5 the Cu dissolution degree values differed only by 36 % between the highest and lowest C_{ox}, which can be accounted to the lower volume of the leaching solution at SLR 1:5 than at SLR 1:10. As a result, the accumulation of reaction products in the solution reduced the reaction rate more at SLR 1:5 than at SLR 1:10 even if the C_{ox} were higher at SLR 1:5.

The increase of the SLR to 1:15 increased even more the difference between the performances obtained at the lowest and highest C_{ox}. Fig. 1 shows that the Cu dissolution degree at 0.42 M $Na_2S_2O_8$ is almost twice compared to the one obtained at 0.14 M $Na_2S_2O_8$. It is important to note that the Cu dissolution degree dropped only with 4 % for the highest $Na_2S_2O_8$ concentrations with the increase of the SLR from 1:5 to 1:15 while for the lowest C_{ox} it changed with 29 %. Considering that the concentrations are decreasing with the increase of the SLR, it is evident that the diffusion rate of the oxidant from the bulk of the solution to the reaction surface will decrease as well. Moreover, since the duration of the experiments was the same, the increase of the SLR (volume) reduced significantly the amount of oxidant which could reach the reaction surface in time. This is the reason why significant difference were accoutered only at the lowest C_{ox} regardless the SLR.

In comparison to Cu, the dissolution of Zn is more strongly affected by SLR and C_{ox} variations considering the significant difference between the reactivity of the two metals. The dissolution of Zn (Table 1) occurs the most rapidly at the lowest SLR (1:5) reaching the highest dissolution degree of 94 % at 1.26 M $Na_2S_2O_8$. It is also obvious that regardless the SLR the dissolution degree of Zn differs more between the lowest and middle C_{ox} than between the middle and the highest C_{ox}. For instance, the dissolution degree of Zn increased with 106 % between 0.42 and 0.84 M $Na_2S_2O_8$ while between 0.84 and 1.26 M $Na_2S_2O_8$ with only 20 %. As a result, the dissolution degree of 38 % obtained in 6 h at 0.42 M $Na_2S_2O_8$ can be achieved in 100 min at 0.84 M $Na_2S_2O_8$ and in less than 1 h at 1.26 M $Na_2S_2O_8$. It can be noticed that (Table 1) the performances of the dissolution process of Zn were reduced significantly by the increase of SLR. Nevertheless, similarly to the dissolution of Cu, the dissolution degree values of Zn were diminished more at the lowest C_{ox} than at the highest. Therefore, the increase of the SLR from 1:5 to 1:15 lowered dissolution degree with 55 % for the lowest C_{ox} and with 26 % for the highest.

Table 1. Zn dissolution degree (%) vs. C_{ox} and SLR

SLR	Conc.	Time, min								
g:mL	M	40	80	120	160	200	240	280	320	360
1:5	**0.42**	4.2	8.3	14	20	24	28	31	33	38
	0.84	9.6	27.5	46	54	63	68	71	74	79
	1.26	14.1	45.6	67	79	84	88	91	93	94
1:10	**0.21**	3.5	6.4	9	12	15	19	22	26	30
	0.42	9.0	19.0	31	37	45	50	58	64	66
	0.63	8.2	19.3	33	48	63	71	78	81	84
1:15	**0.14**	1.6	4.6	6	8	10	11	14	15	17
	0.28	8.9	14.0	18	21	26	30	35	40	47
	0.42	9.0	16.8	27	33	45	54	59	65	69

The influence of SLR and $Na_2S_2O_8$ concentration on the dissolution process of Ni was also evaluated. It was found that Ni has higher dissolution rate at the SLR of 1:5 and 1.26 M $Na_2S_2O_8$ than Cu, achieving a dissolution degree of 44 % (Fig. 2). The results also revealed that the influence of the studied experimental conditions on the performances of Ni dissolution were more similar in their tendency with the ones obtained for Zn than the ones for Cu. However, at the SLR of 1:5 and 1:10 (Fig. 2) the dissolution degrees of Ni for the middle concentrations were closer to the ones obtained at the lowest concentrations. This means that Ni dissolution is more strongly affected by C_{ox} increase at the above mentioned SLRs than in the case of Zn, especially after 120 min of processing.

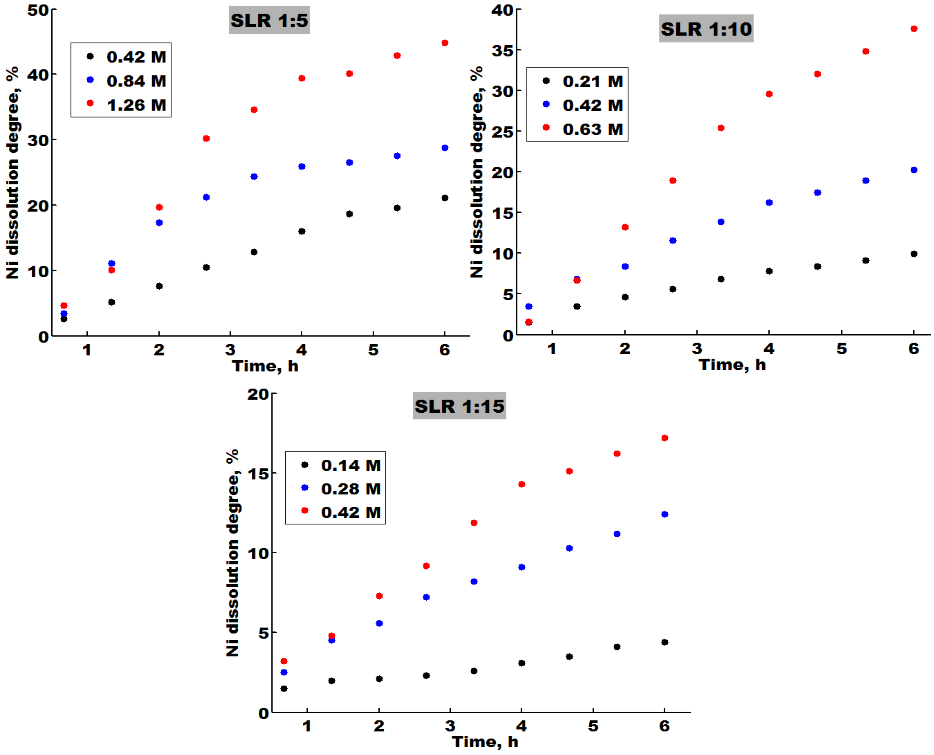

Figure 2. Ni dissolution degree vs. time at different $Na_2S_2O_8$ concentrations and SLR

On the other hand, at the SLR of 1:15 the dissolution degrees of Ni (Fig. 2) and Zn (Table 1) have similar tendency with the increase of C_{ox}. Still, it is remarkable that the dissolution rate of Ni drops more at the lowest concentration with the increase of SLR than for the other two metals. Hence, the increase of the SLR from 1:5 to 1:15 reduced the dissolution degree with more than 80 % for the lowest C_{ox} and with 56 % for the highest one. It is also worth noting that among the metals, Ni has the lowest dissolution degrees at 0.14 M and 0.21 M $Na_2S_2O_8$ concentrations. For example at 0.14 M $Na_2S_2O_8$ the dissolution degrees of Cu and Zn are comparable while for Ni are 4 times smaller than for the other two metals, which means that it could be separated from Cu and Zn by selective leaching.

The influence of SLR and $Na_2S_2O_8$ concentration on the dissolution efficiency of Cu, Zn and Ni

The impact of secondary reactions Eq. (4) on the leaching of metals can be quantified by the dissolution efficiency (%/g) defined as the ratio between the dissolution degree of the metal (%) and the amount of $Na_2S_2O_8$ (g) used in the experiment.

$$2H_2O + 2Na_2S_2O_8 \rightarrow 2H_2SO_4 + 2Na_2SO_4 + O_2 \qquad (4)$$

Fig. 3 shows that for constant SLR the dissolution efficiency of Cu decreases with the increase of C_{ox} which means that the increase of the amount of oxidant in the same volume of leaching solution favors more the secondary reactions than the dissolution of Cu. In contrast, the increase of SLR at constant amount of $Na_2S_2O_8$ affects the same way the primary and secondary reactions since it gives the same performances for the middle and highest concentrations. Only at the lowest oxidant concentrations has the increase of SLR different impact on the dissolution of Cu and oxidant degradation.

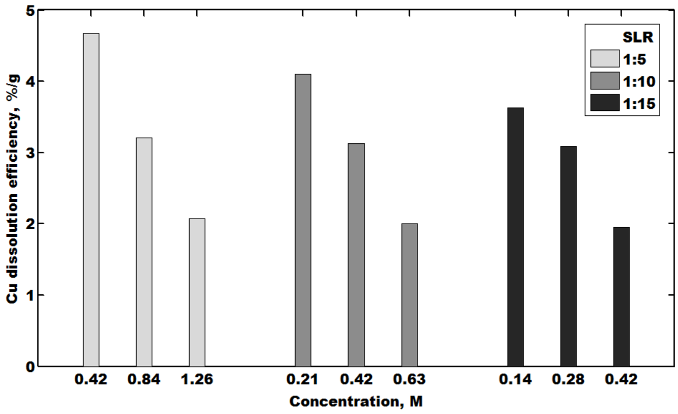

Figure 3. Cu dissolution efficiency vs. C_{ox} and SLRs after 6 h of leaching

Regardless the C_{ox}, the negative influence of SLR increase can be noticed in the case of Zn dissolution as well, (Fig. 4). It can be observed that the middle concentration gives the best performance at each SLR, reaching the highest value of 9.82 %/g at 0.42 M $Na_2S_2O_8$ and SLR 1:5. This tendency can be explained considering that Zn can be dissolved by H_2SO_4 and $Na_2S_2O_8$ as well. As a result, the increase of the amount of oxidant will increase the dissolution rate of Zn, but at the highest concentrations (12 g $Na_2S_2O_8$) it will favor more the secondary reactions.

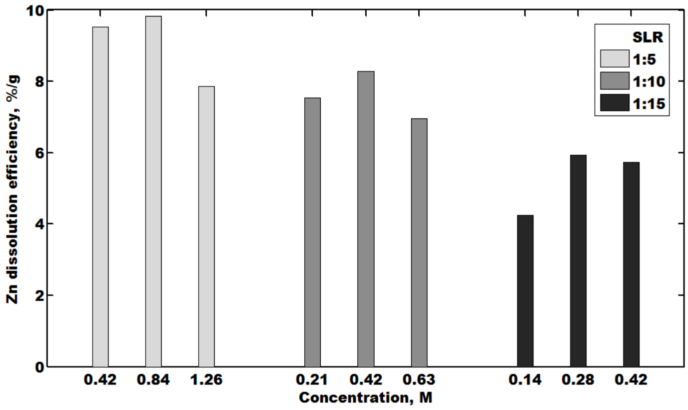

Figure 4. Zn dissolution efficiency vs. C_{ox} and SLRs after 6 h of leaching

Differently from Cu and Zn, in the case of Ni the dissolution efficiency is more strongly affected by the increase of SLR, dropping sharply between the SLRs of 1:5 and 1:15 by 4 times. Therefore, the highest value for the Ni dissolution efficiency (5.27 %/g) is obtained at the SLRs of 1:5 and 0.42 M $Na_2S_2O_8$ (Fig. 5).

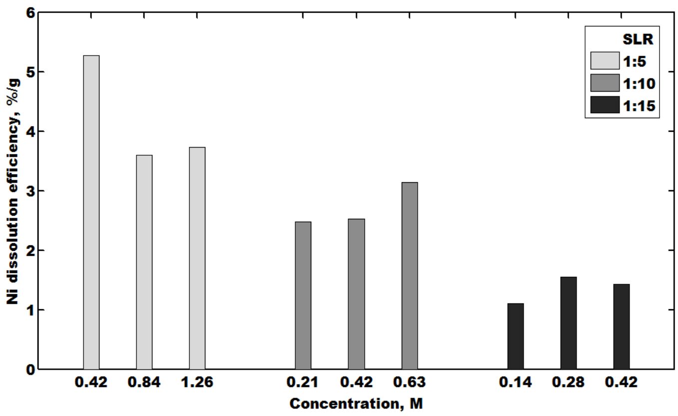

Figure 5. Ni dissolution efficiency vs. C_{ox} and SLRs after 6 h of leaching

On the other hand, the influence of C_{ox} depends on the value of the SLR probably due to the fact that Ni is more noble metal than Zn; being more hardly dissolved by H_2SO_4 resulted from the degradation of the oxidant.

CONCLUSIONS

The current paper proved that the dissolution of Cu, Zn and Ni from WPCBs obtained from MP can be performed with high efficiency and selectivity by using $Na_2S_2O_8$ solutions. The dissolution degree values obtained for various experimental conditions showed that Zn has the highest dissolution degree (max. 94.3 %) followed by Ni (max. 44.8 %) and Cu (max. 25.7 %), regardless the SLR or C_{ox}. It was also found that the dissolution rate of Zn and Ni are more strongly affected by the increase of SLR and concentration than Cu due to their higher reactivity. The results revealed that the increase of the SLR favors more the secondary reaction than the dissolution of metals. Moreover, there are significant differences between the performances obtained for Ni, Cu and Zn considering that the increase of SLR from 1:5 to 1:15 lowered the dissolution efficiency of Ni by 79 % while in the case of Zn 55 % and for Cu only 22 %. Based on the dissolution degree and dissolution efficiency values, the overall conclusion is that the most favorable conditions for the dissolution of Zn, Ni and Cu are provided at the SLR of 1:5 and 0.42 M $Na_2S_2O_8$.

EXPERIMENTAL SECTION

The leaching tests were carried out using 8 g of WPCB samples resulted from the mechanical processing of waste MP. Each WPCB was cut into about 18 pieces with an area of approx. 1 cm^2 and then mixed to obtain a relatively homogeneous material. The samples were subject to leaching tests (Table 2) with duration of 6 hours at room temperature using $Na_2S_2O_8$ solutions of different concentrations (0.14-1.26 M) and SLRs (1:5-1:15).

Table 2. Experimental conditions for the leaching tests

Mass of WPBC	Mass of $Na_2S_2O_8$	Solution volume	$Na_2S_2O_8$ conc.	S:L ratio
g		mL	M	g:mL
8	4	40	0.42	1:5
		80	0.21	1:10
		120	0.14	1:15
	8	40	0.84	1:5
		80	0.42	1:10
		120	0.28	1:15
	12	40	1.26	1:5
		80	0.63	1:10
		120	0.42	1:15

To determine the metal content a first dissolution was performed using aqua regia with duration of 24 hours. The undissolved material from the structure of WPCB was separated by filtration. The composition of the WPCB sample is shows in Table 3.

Table 3. Composition of the WPCB sample and of the metallic part

Material	Cu	Au	Ag	Zn	Ni	Pb	Sn	Fe	Non metals	Total
	wt.%									
WPCB sample	18.3	0.03	0.12	1.5	1.7	0.6	2.26	0.4	75.09	100

The solutions were sampled during the leaching test in order to determine the concentration of dissolved metals at different moments. The solid residue separated by leaching tests was further treated for 24 hours with aqua regia for complete dissolution of metals in order to determine the dissolution degree of each metal. The samples collected at different leaching stages and mineralized with aqua regia were analyzed for metal content with an atomic absorption spectrometer (AVANTA PM, GBC - Australia).

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