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HYDROMETALLURGICAL RECOVERY OF TIN AND LEAD FROM WASTE PRINTED CIRCUIT BOARDS (WPCBs): LIMITATIONS AND OPPORTUNITIES

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In this paper, possibility for selective Pb and Sn recovery, using three different solutions of NaOH, HCl and HNO_3, from WPCBs containing low concentrations of Pb and Sn is presented. According to obtained results, over 98 % of Pb can be leached using 2 M HNO_3 solution at 80 °C and over 90 % of Sn using 2 M HCl solution at 80 °C, independently. However, more comprehensive analysis of obtained results indicated adverse interactions between said leaching agents, creating doubts if such leaching and recovery step could be incorporated in an integral hydrometallurgical route for selective base and precious metals recovery from WPCBs.

Key words: hydrometallurgy, WPCBs, recycling, tin, lead

INTRODUCTION

WPCBs, as a key value component of electronic waste contain approximately 30 % of metals, 40 % of plastic and 30 % of glass fiber materials [1]. This materials and components variety makes recycling of WPCBs very complex and demanding process. Pyrometalurgical processing as a traditional method for electronic waste recycling allows only partial separation of metals, why further hydrometallurgical and electrochemical processing is required [2]. In recent years, development of hydrometallurgical routes for WPCBs recycling as more exact, more predictable and easily controlled is emphasized [3]. Numerous studies using various leaching agents are reported, commonly focused on copper [4,5] and precious metals [6] recovery. Yet, tin and lead presence in form of solder alloy significantly complicates their leaching properties. Studies using bioleaching [7], alkaline [8], nitric [9], hydrochloric [9,10] or fluoroboric acid [11] as a leaching agent are reported. Among these processes, usage of fluoroboric acid, with addition of specific oxidizing agent, ensures high efficient Pb and Sn recovery. However, high operating costs restrict application of this process option to WPCBs enriched in Pb and Sn content. Main goal of this study was investigation of selective Pb and Sn recovery, using common and cost effective leaching agents, NaOH, HCl and HNO_3, from WPCBs containing Pb and Sn below 5 %. Results obtained after extensive optimization of various process parameters reviled that over 98 % of Pb can be leached using 2 M HNO_3 solution at 80 °C and over 90 % of Sn using 2 M HCl solution at 80 °C independently. However, more comprehensive analysis of obtained results indicated adverse interactions between said leaching agents, creating doubts if such leaching and recovery step could be incorporated in integral hydrometallurgical route for selective base and precious metals recovery from WPCBs.

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EXPERIMENTAL WORK

Materials. In presented research, mechanically treated WPCBs, obtained from WEEE recycler were used. Results of full material characterization are reported in previous study of authors [4]. Chemical composition of sample was determined by a combination of X-ray fluorescence spectrometry (XRF) and atomic absorption spectrometry (AAS) using Thermo Scientific Niton Analyzer XL3t and Perkin Elmer 4000 spectrometer respectively. Determined composition was as follows: 27,1 % Cu; 2,5 % Pb; 3,3 % Sn; 1,2 % Fe; 2,1 % Zn; 0,2 % Ni.

Methods. Tests were performed using three different solutions: NaOH, HNO_3 and HCl. Leaching tests were performed using three neck glass leaching reactor equipped with cooler with condenser, stirrer, pH and temperature control and chemicals addition system. Phase separation was performed using vacuum filtration unit. In each leaching test, mass of 100,0 grams of WPCBs was leached with corresponding leaching solution. Optimization of process parameters was performed trough investigation of time, temperature, acid/alkali concentration and oxidizing agent influence on overall process efficiency, while solid:liquid ratio and stirring rate were set constant to 200 g/dm^3 and 300 rpm, respectively. Leaching efficiency was determined by analyzing concentration of metals in solution and in residual solid after leaching, using AAS.

RESULTS

Alkaline leaching of tin and lead. In order to investigate leaching efficiency of Pb and Sn using NaOH solution, series of tests with variable parameters were performed. In these tests variable parameters were NaOH concentration, oxidizing agent, leaching time and temperature. Prior to process optimization, influence of oxidizer addition on leaching efficiency was investigated using O_2, H_2O_2 and Meta nitro benzoic acid (MNB). Due to fact that increased time, temperature and alkali concentration may cause precipitation of metal hydroxides, NaOH concentration, time and temperature were set to 1 M, 3 h and 70 °C respectively.

As presented on Figure 1, usage of both, H_2O_2 and MNB, showed significant improvement of process kinetic. However, presence of H_2O_2 in leaching solution may cause partial transformation of Sn to metastannic acid, according to reaction:

$$Sn + 2H_2O_2 \rightarrow SnO_2 \times H_2O(s) + H_2O \qquad (1)$$

Therefore in further tests, organic oxidizer, MNB was used.

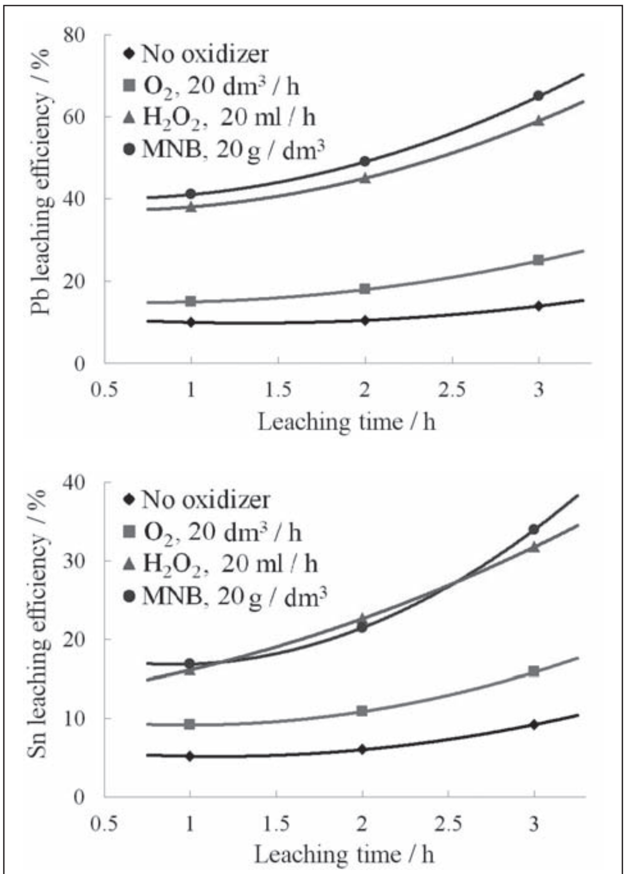

Figure 1 Influence of oxidizing agents on Pb and Sn leaching efficiency

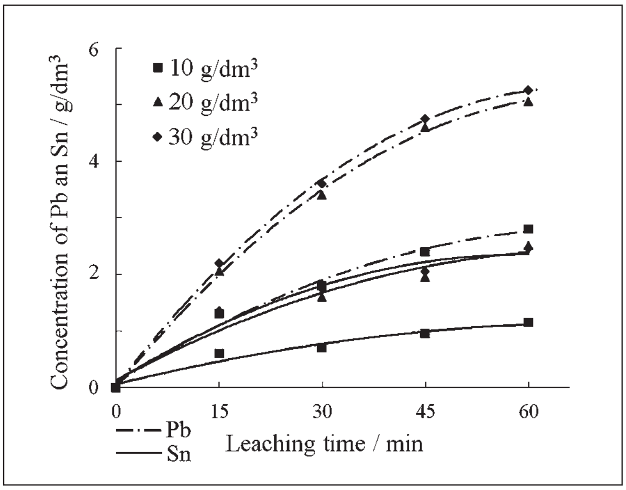

Figure 2 Influence of MNB concentration on Pb and Sn leaching efficiency

Furthermore, as presented on Figure 2, increase of MNB concentration insignificantly affects leaching efficiency, why in further tests MNB concentration was set to 20 g/dm³.

Influence of temperature (60; 70; 80 and 90 °C), NaOH concentration (0,5; 1; 2 and 3 M) and leaching time (1; 2; 4 and 6 h) were investigated and summary of all process parameters variations and obtained efficiencies are presented in Table 1.

Table 1 **Process parameters / leaching efficiencies using NaOH**

Test No.	Temp. / °C	NaOH / M	Time / h	Efficiency, / %	
				Sn	Pb
1	60	1	3	31,2	58,3
2	70			33,4	64,2
3	80			38,1	63,5
4	90			54,4	61,7
5	90	0,5	3	21,3	30,1
6		1		54,4	61,7
7		2		47,7	59,3
8		3		41,4	51,7
9	90	1	1	57,0	69,2
10			2	62,4	71,6
11			4	49,4	54,5
12			6	34,7	48,1

As presented, increase of temperature increases Pb and Sn leaching efficiency, giving the best results at 90 °C. However, increase of NaOH concentration and leaching time, caused decrease of leaching efficiency which corresponds to fact that excessive presence and exposure to NaOH lead to intense precipitation of metal hydroxides, limiting leaching efficiency to around 60 % and 70 % for Sn and Pb respectively. In order to verify decrease in leaching efficiency, solid residues after Test No. 5 – 12 were washed, dried and sieved, using 100 μm mesh, separating fine powder of metal hydroxides from rest of solid residue. Obtained powders were weight and analyzed for chemical composition using XRF. According to results presented in Table 2, mass percentage of obtained powder increases with increase of NaOH concentration and time, confirming promotion of metal hydroxides precipitation.

Table 2 **Percentage and chemical composition of hydroxides / wt. %**

Test No.	wt. %	Zn	Pb	Sn
5	5,2	24,2	19,2	52,8
6	7,3	26,2	21,1	48,5
7	7,9	25,8	21,7	51,2
8	8,1	26,4	20,1	49,4
9	5,8	24,1	19,8	51,4
10	7,2	26,5	22,4	49,8
11	7,8	21,8	18,9	54,8
12	8,2	24,8	21,5	48,5

Leaching of Pb and Sn using HNO_3. In order to investigate Pb and Sn leaching efficiency using HNO_3, influence of time (1; 2 and 3 h), temperature (70; 80 and 90 °C) and acid concentration (1; 2 and 3 M) was studied. Summary of all process parameters variations and obtained process efficiencies are presented in Table 3.

Table 3 **Process parameters / leaching efficiencies using HNO_3**

Test No.	Temp. / °C	HNO_3 / M	Time / h	Efficiency / %	
				Sn	Pb
13	70	1	1	16,1	56,3
14	80			14,3	78,2
15	90			14,1	82,8
16	80	1	1	14,3	78,2
17		2		12,6	>98
18		3		10,1	>98
19	80	2	1	12,6	>98
20			2	10,4	>98
21			3	4,8	>98

As presented, Pb leaching efficiency is intensive and influenced by increase of temperature and HNO_3 concentration, giving the highest leaching degree (>98 %) already at 80 °C, 2 M and 1 h. On contrary, Sn dissolution in HNO_3, as expected, was at very low level, in all tests below 15 %, affected by transformation of Sn to highly insoluble metastannic acid ($SnO_2 \times H_2O$) in accordance with reaction:

$$Sn + 4HNO_3(a) \rightarrow SnO_2 \times H_2O(s) + 4NO_2(g) + H_2O \quad (2)$$

Further increase of HNO_3 concentration and leaching time promote said transformation, resulting in further decrease of leaching efficiency. Pb recovery from leaching solution was performed by precipitation using 4 M NaCl solution at room temperature. Obtained solid precipitate of $PbCl_2$, was filtered, washed and dried. Procedure was repeated on solutions obtained from Test No. 16 – 21. Chemical composition of obtained precipitates was determined by XRF analysis and presented in Table 4.

As presented, Ag presence was determined in each precipitate, suggesting that leaching and recovery of lead using HNO_3 is followed with partial dissolution of Ag, even at lower concentrations of HNO_3.

Table 4 **Chemical composition of obtained $PbCl_2$ precipitate / wt. %**

Test No.	Pb	Ag	Sn	Cu
16	92,5	6,7	0,04	0,01
17	91,8	7,9	0,07	0,03
18	88,9	10,9	0,05	0,02
19	91,3	8,3	0,08	0,05
20	91,2	8,5	0,09	0,01
21	85,5	14,2	0,11	0,03

Leaching of Pb and Sn using HCl. In next series of tests, Pb and Sn leaching efficiency using HCl was studied. Influence of temperature (60; 70 and 80 °C), acid concentration (2; 4 and 6 M) and time (1; 3 and 6 h) was investigated. Summary of all process parameters variations as well obtained process efficiencies are presented in Table 5.

Table 5 **Process parameters / leaching efficiencies using HCl**

Test No.	Temp. / °C	HCl / M	Time / h	Efficiency / %	
				Sn	Pb
22	60	2	3	24,4	14,1
23	70			48,6	27,5
24	80			78,1	38,8
25	80	2	3	78,1	38,8
26		4		83,4	41,9
27		6		85,6	39,7
28	80	2	1	51,8	26,9
29			3	83,4	41,9
30			6	91,8	38,6

As presented, although increase of HCl concentration and time insignificantly increase Sn leaching efficiency, process is dominantly influenced by temperature, and increases with increase of temperature.

On the other hand, similarly as in previous tests, Pb leaching efficiency using HCl proves to be limited. This phenomenon is related to exposure of Pb and Ag to excessive amount of Cl^- ions, where on higher temperatures two step reactions between Pb and Ag with HCl occurs:

- 1st reaction: formation of $PbCl_2$ and AgCl precipitates

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s) \quad (3)$$

$$Pb^{2+}(aq) + 2Cl^-(aq) \rightarrow PbCl_2(s) \quad (4)$$

- 2nd reaction: formation of soluble Pb and Ag chloride ions

$$AgCl(s) + Cl^-(aq) \rightarrow AgCl_2^-(aq) \quad (5)$$

$$PbCl_2 + 2Cl^-(aq) \rightarrow PbCl_4^{2-}(aq) \quad (6)$$

However, upon cooling of solution and decreased solubility of formed chloride ions, reverse reactions and reformation of insoluble $PbCl_2$ and AgCl precipitate is promoted, affecting the overall selectivity of leaching process. SEM micrograph of chloride precipitate containing around 96 % of $PbCl_2$ and 4 % of AgCl, deposited on surface, is presented on Figure 3.

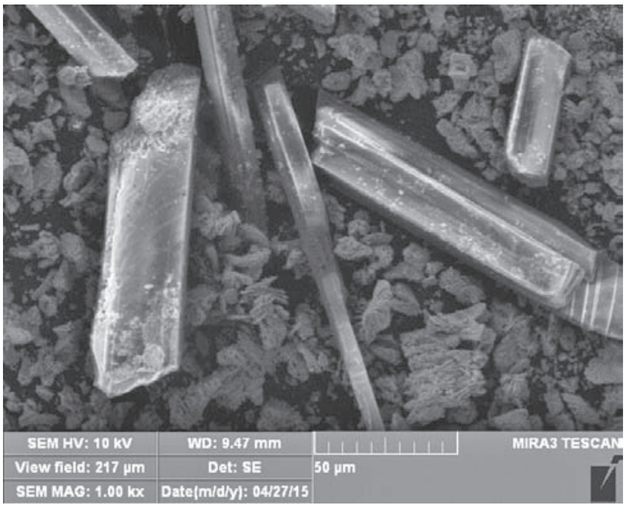

Figure 3 $PbCl_2$ and AgCl precipitate

CONCLUSION

Even though all tested methods has proven fairly efficient, either showed no satisfying selectivity, identifying this step as bottle neck of hydrometallurgical metals recovery from WPCBs. Main disadvantage of NaOH usage represents simultaneous dissolution and precipitation of metal hydroxides, imposing that use of NaOH does not represent a reliable method for Pb and Sn recovery. Usage of HNO_3 gave exceptional results for Pb leaching, above 98 %, as well possibility for simultaneous Pb and Ag leaching, upon increase of leaching time and acid concentration. However intensive oxidation of Sn to highly insoluble $SnO_2 \times H_2O$, which occurs during the leaching, leaves no possibility for simple leaching and recovery of Sn in further hydrometallurgical steps. By using HCl as leaching agent, over 90 % of Sn is leached, yet high temperature and Cl^- ions concentration causes precipitation of highly insoluble AgCl, and passivation of outer layers of Ag particles, blocking the further reaction of Ag with leaching agents. Eventually, this may led to unacceptable losses of Ag, and to disturbance of overall process economy. Therefore, it is clear that chemical composition of material represent a major decision making factor if solder leaching step should be incorporated in integral hydrometallurgical route for selective base and precious metals recovery. For materials like used in presented research, characterized with low Sn content, Sn recovery step should be avoided, due to fact that same affects overall process economy, either by applying highly expensive fluoroboric process or by usage of HCl and creation of Ag losses. Therefore, assessment should be based on techno-economic analysis in terms of process costs *vs*. revenues *vs*. losses.

Acknowledgements

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Note: The person responsible for English language is Mrs. Ranitović, Belgrade, Serbia