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Improving Hydrometallurgical Methods for Processing Tin-containing Electronic Waste

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This article provides an overview of methods for processing electronic waste (mobile phones, smartphones, printed circuit boards). The possibility of extracting tin from the waste of printed circuit boards of mobile phones using hydrochloric acid is shown. Established that the deposition of tin from the productive solution occurs due to cementation - an electrochemical displacement reaction between a cementing metal (aluminum) and a cemented ion (tin). The possibility of intensification of the process using a vibrating installation is evaluated. An environmentally friendly and efficient method for processing tin-containing electronic waste is proposed.

1. Introduction

According to preliminary data from the analytical company Gartner, the release of smartphones in 2019 amounted to $1.5·10^9$ units (Gartner, 2019). At the same time, according to forecasts by the International Data Corporation (IDC), the market for high-tech devices in the field of information technology (IT) will lose $ $30·10^9$ over the next 5 y due to a decrease in sales of personal computers (PCs) and will decrease by a third within 10 y. However, smartphone sales will not suffer and will only increase (IDC, 2018).
It is also important to say that the situation with COVID - 19 has shown the important role of smartphones in modern society. So in Kazakhstan, in connection with the introduction of quarantine, training in schools, colleges, and institutes was carried out remotely. At the same time, training was carried out both with the help of personal computers and with the help of smartphones. This shows that smartphones from a simple multimedia and communication tool have become an integral part of the distance learning system.
The production of smartphones consumes a large number of metals, non-metallic materials, and energy for their production. A modern smartphone consists of many electronic and other components. The main elements of a smartphone are the case, the printed circuit board, the battery, and the display (Gu et al., 2019). Using a solder consisting of tin and other elements, electronic components are mounted on a printed circuit board. Tin is also present as compounds with indium in the liquid crystal screen (LCD) of the telephone.
However, components of smartphones also include elements such as lead and zinc, which, if released into the environment, form toxic compounds (Singh et al., 2019), and environmental pollution leads to the death of up to 3 million people per year (Morganti and Stoller, 2017). Or these metals whose content in mineral reserves is critical and their recycling is necessary to replenish limited reserves. For example, tin, which the US Department of the Interior included in the list of 35 important minerals in 2018 (U.S. Geological Survey, 2019). It is also necessary to take into account that the content of tin and other elements in the waste of printed circuit boards of mobile phones is much higher than in mineral ore (Wansi et al., 2017), and the secondary processing of these metals saves a large amount of energy and reduces the emission of CO_2 into the atmosphere.
Along with tin, noble metals, such as Au, Ag, and Pd, which are used to make contacts and electronic elements of a smartphone are of particular interest. All these elements, consisting of metal and non-metallic parts, are closely integrated, which, coupled with the small size of the gadget elements and the design not intended for

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disassembly, makes it extremely difficult to process them. The priority in the processing of smartphones belongs to noble metals and copper, due to their high content (Xiu et al., 2015). All these facts indicate the importance of organizing the comprehensive recycling of smartphones using new technologies. These methods should ensure environmental and economical safety and can be commercially attractive.

Based on a review of current trends, it was found that the recycling of mobile devices is an acute issue in all countries. So, in China, the leader in the sale of smartphones, over the past 5 y, phone sales amounted to 400-500·10^6 units/y, and their recycling amounted to only 1-2 % annually (Ecns.cn, 2017). Figure 1 presents information on the number of smartphone sales (iPhone, LG, OPPO, Samsung, Xiaomi, and others) by region of the world in 2019, and the recycling of smartphones in some countries of the world. In countries such as the United States, the European Union, and Japan, sales amounted to about 150, 190, and 31·10^6 smartphones/y. A report from the World Economic Forum “A New Circular Vision for Electronics” showed that smartphone recycling in these countries was no more than 20 % (WEF, 2019). In Kazakhstan, over the same period, the number of smartphones sold was approximately 1.6·10^6 units, and the total number was more than 25·10^6 units. Recycling of obsolete, malfunctioning, and waste gadgets in Kazakhstan is practically absent. Reliable official information on the recycling of smartphones in most countries is difficult to provide for various reasons, but it is known that even in developed countries, recycling does not exceed 20 %. Given all of the above, the study of the amount of valuable components contained in electronic scrap, and the possibilities of their extraction and reuse remains an urgent task.

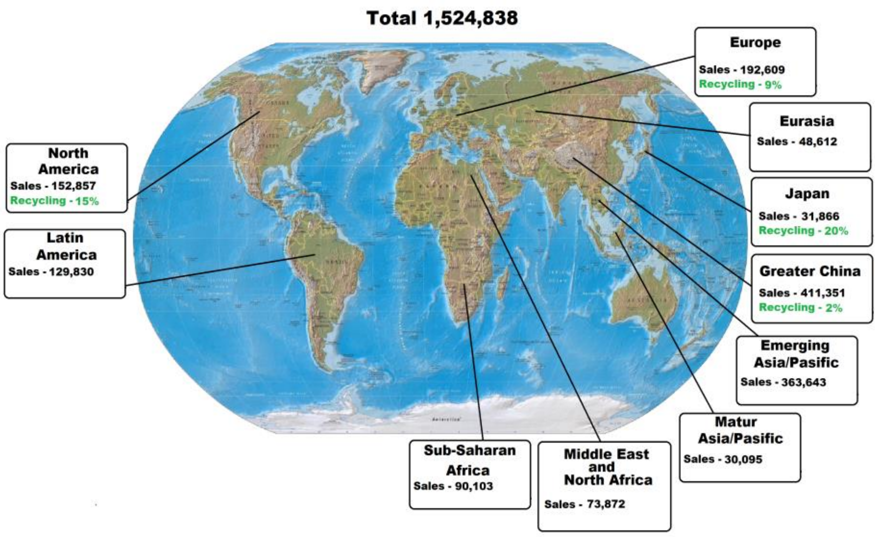

Figure 1: Global smartphone sales and telephone waste recycling in some countries in 2019 (10^3 units)

Currently, there are various approaches to the processing of all the main parts of smartphones - batteries, LCDs and printed circuit boards with electronic components. For the processing of printed circuit boards, which contain the largest number of valuable metals, pyrometallurgical, hydrometallurgical and combined methods can be used. With pyrometallurgical methods, telephone wastes are processed at high temperatures. With hydrometallurgical methods, telephone waste is recycled using various acids and alkalis. To extract all the valuable components from the printed circuit boards to the fullest extent possible, at the initial stage of processing it is necessary to separate its constituent parts from the telephone body and then the electronic components from the printed circuit board. It should be noted that the dismantling of smartphones, as a rule, is carried out manually. A common method of separating components from the printed circuit board is to heat the printed circuit board to the melting point of the solder and to mechanically or otherwise affect it. There are also methods for processing printed circuit boards without preliminary separation of components when the selective extraction of metals is carried out by crushing the printed circuit boards in an assembly in several stages (Jeon et al., 2019). There are other more complex methods for separating electronic components. After the elements are separated, they are sorted, which is essentially a preliminary enrichment operation, and subjected to appropriate processing. A number of authors suggest technologies in which it is proposed to extract only noble metals from the entire mass of electronic scrap (Kasper and Veit, 2018), in other methods only copper is extracted (Wang et al., 2018).

Despite the many existing methods for extracting tin from printed circuit boards of computers, it revealed that the topic of extraction of tin from printed circuit boards of telephones was poorly covered.

This makes the study of the comprehensive extraction of all valuable metals (including tin) from spent cell phones quite necessary. Probably, the same processing methods can be applied to the printed circuit boards of telephones as to computer circuit boards. The most promising for printed circuit boards are hydrometallurgical processing methods (Wang et al., 2018). They are selected also for processing method telephone printed circuit boards. Yang et al. (2017) indicate positive results when using leaching as a reagent for processing printed circuit boards of HCl, H_2SO_4, HNO_3, and other acids. The main parts of a modern mobile device are shown in Figure 2. The illustration shows the whole variety of valuable components that need to be recycled.

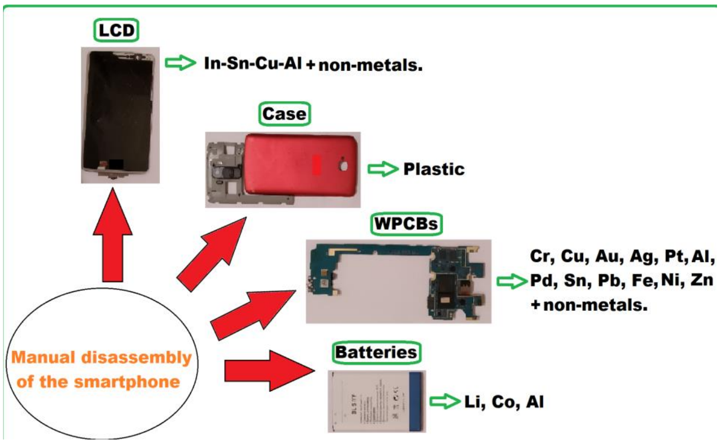

Figure 2: The main parts of a cell phone

Fragments of smartphones and other gadgets are quite large and as a result, work with them, as a rule, begins with analysis into smaller parts and grinding. Depending on the hydrometallurgical processing method used, crushing and/or grinding is preliminarily performed to appropriate particle sizes for each procedure (Yang et al., 2017). In this case, part of the metal may be lost due to the close connection of the metal and nonmetallic parts of the printed circuit board. Another factor to pay attention to is the formation of sediment from the crushed material, making it difficult to extract valuable components.

Precipitation from the productive solution is carried out in various ways. Given the value of the electrochemical potential of tin, it can be assumed that one of the effective methods for the deposition of tin from a solution can be its electrochemical contact displacement using aluminum from aqueous solutions of hydrochloric acid. This process in specialized literature is often called the term cementation. The cementation process is based on the displacement of metals with less negative potentials, metals with more electronegative potentials from the productive solution.Cementation can take place on solid surfaces of the cementing metal and using the cementing metal in the form of a powder. Cementation processes can have different kinetics. Various methods are used to intensify cementation processes, including cementation in non-stationary force fields. Non-stationary fields are those fields whose intensity is a function of time such fields can be ultrasonic, fields of electromagnetic waves, etc. Low-frequency mechanical waves (vibration) is also one of the types of such fields. The used range of vibration frequencies is in the range from 1 to $1.0 \cdot 10^5$ Hz. Most often, for the implementation of mass transfer processes, a rather narrow frequency range is used that is easily provided with conventional electromechanical and electromagnetic vibrators.

Assessment of the current state of pyro - and hydrometallurgical methods for processing electronic scrap is in favor of the second method. In this paper, the main attention is paid to the search for new technological methods or their combinations to improve the existing options for recycling tin-containing electronic waste.

2. Materials and methods

For the study, samples of printed circuit boards were selected from worn-out smartphones of various brands and types of release 2012-2014 (LG - H630D, LG - D686, Samsung SM - J100H / DS) and release 2010-2011 (Blackberry smartphone, Nokia C5). Part of the material was crushed to study the chemical composition and mixed since it will be difficult to sort them by grades and types during processing on an industrial scale.The content of valuable material components was determined using an inductively coupled plasma mass spectrometer ICP-MS 7500 cx from Agilenttechnologies (USA). Printed circuit boards were divided into large pieces of size, about 5 x 5 cm or more. Starting materials - printed circuit boards were placed in a heat-resistant laboratory glass vessel for leaching without mechanical grinding. A photograph of a portion of the starting material (LG - H630D) is shown in Figure 3. The chemical coating was not removed from the surface. An aqueous solution of hydrochloric acid - HCl with a concentration of 2 mol/L, a solution temperature of t = 75 °C, L / S = 10, and a stirring speed of 300 rpm for 6 h was used for the leaching process.

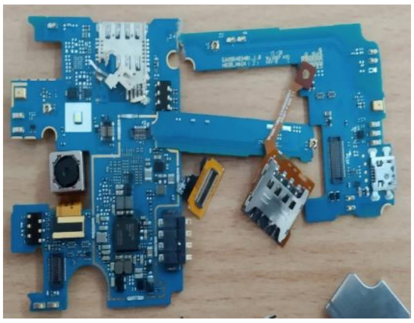

Figure 3: Smartphone circuit board (LG - H630D)

3. Results and discussion

The average values of the content of valuable components in the waste of printed circuit boards of mobile phones and smartphones are presented in Table 1.

Table 1: Average concentration of metals in samples of a mixture of printed circuit boards (wt.%)

Cu	Fe	Al	Sn	Ni	Zn	Pb	Ag	Au
28.6	3.56	1.4	2.13	1.92	0.73	0.68	0.15	0.16

During the leaching, the color of the solution changed, which from a transparent one became cloudy (Figure 4).

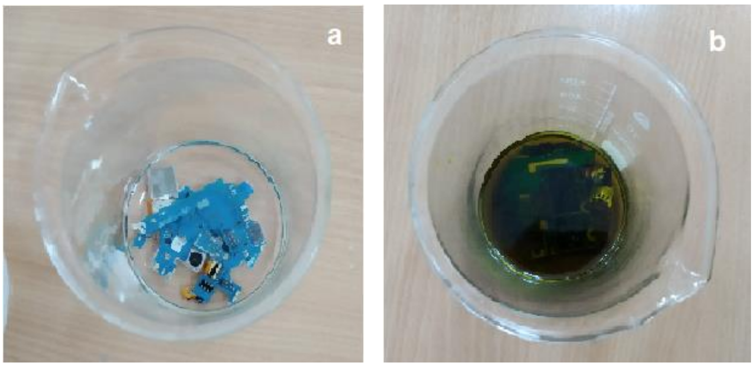

Figure 4: Smartphone printed circuit board before (a) and after leaching (b)

Elements, Al, Sn, and Pb, were extracted into a productive solution. Their extraction amounted to 86.2 %, 85.4 %, and 96 % of the average concentration of metals in the material. Copper, silver, and gold were not found in a productive solution. The degrees of extraction of various metals obtained from the printed circuit boards in the productive solution obtained from the experiment are shown in Table 2.

Table 2: Recovery of metals by leaching (%)

	Cu	Fe	Al	Sn	Ni	Zn	Pb	Ag	Au
(%)	0	41,3	1.4	85.4	3.2	0.73	96	0	0

The experiment showed that one of the difficult stages in the processing of printed circuit boards is the dismantling of electronic parts. After the leaching procedure, almost all electronic components were removed from the printed circuit boards, because the solder providing the mechanical connection to the circuit board was removed into the solution. Figure 5 (LG - H630D) shows the image of the board before (Figure 5a) and after leaching (Figure 5b). On visual inspection, no traces of solder were found on the surface of the boards. Probably, the tin during the leaching was almost completely transferred from the solder on the surface of the boards into the solution. It is assumed that in the next main stage it is necessary to ensure the extraction of the remaining noble metals. To extract tin from the solution, a cementation procedure was carried out in the presence of aluminum as a cement metal. To intensify the process of tin cementation, it is proposed to additionally apply the vibrational mixing of the medium.

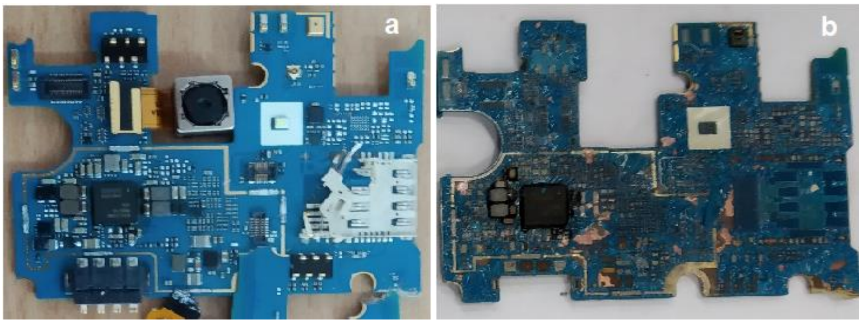

Figure 5: LG - H630D Smartphone printed circuit boards before (a) and after leaching (b)

For this purpose, a laboratory model of a vibration unit was developed and manufactured. The installation diagram is shown in Figure 6. The installation has a perforated disk with 22 cylindrical holes with a diameter of 6 mm, which performs reciprocating movements with a frequency of 25 Hz. The ratio of the diameter of the disk to the diameter of the vessel is 0.4. The power of the installation is 0.18 kW. The mortar vessel has a rubber cover to prevent the splashing of the product solution with holes for the connecting rods of the drive mechanism of the perforated disk.

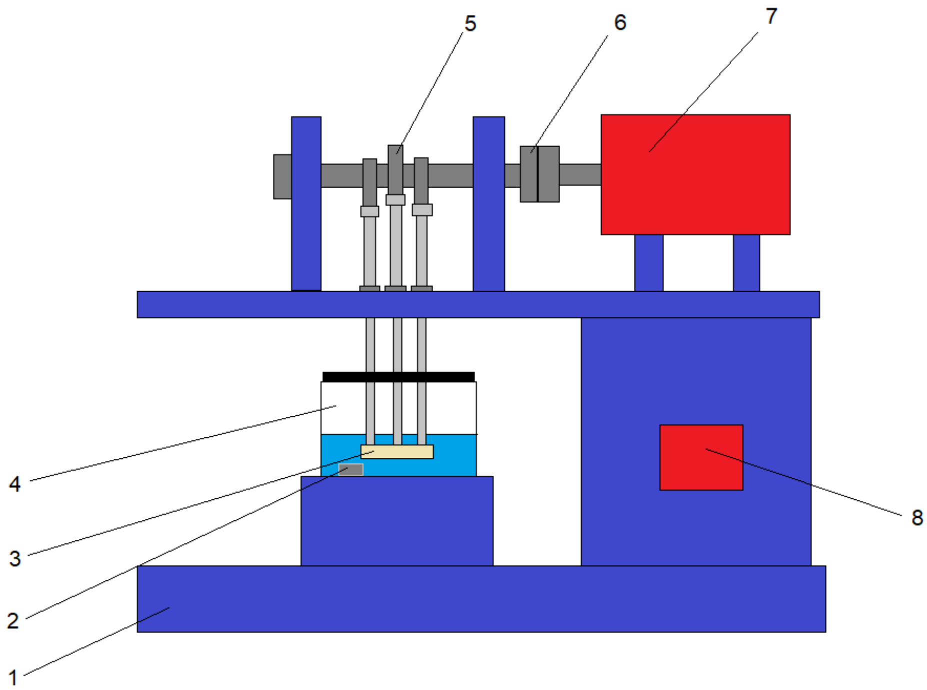

Figure 6: Vibration unit: 1 - bed, 2 - Al, 3 - perforated disk, 4 - vessel, 5 - cam mechanism, 6 - coupling, 7 - electric motor, 8 - control panel

Preliminary tests of the vibration unit have shown the effectiveness of this approach. During the cementation, a more intense course of the process was visually observed. These assumptions will be verified in more detail in the course of further research in this direction. Vibro-mixing is successfully used to intensify various heterogeneous chemical processes. As vibratory bodies, you can use perforated discs, the vibration of which will create a jet of liquid. The shape of the disc openings can also affect the intensity of the impact. If the holes have a tapering profile, then due to the narrowing, the speed of the jet will increase, and the intensity of the impact on the solution as well.

4. Conclusion

In this paper, we propose a method for pre-processing smartphones without grinding to remove the solder and simultaneously dismantle electronic components. This will allow the extraction of tin in a productive solution before the main processing in order to extract precious metals. The cementation process at the stage of deposition of tin from the productive solution, it is proposed to intensify using a vibration field. The experiment showed leaching efficiency to remove solder by exposure to HCl solution from unmilled printed circuit boards of smartphones and mobile devices of various brands and types. During leaching, the separation of electronic parts from the printed circuit boards was observed, which makes the process even more effective, since the need for a separate operation for removing the electronic parts from the printed circuit board is eliminated. Further research in the direction of the deposition of tin from the productive solution by cementation in a vibration field is also promising. The proposed technology is resource- and energy-saving and allows the effective extraction of tin from the electronic waste. The authors plan to continue research in this direction for the subsequent improvement of the extraction of precious metals from printed circuit boards of smartphones and other telephone sets.

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