CHEMICAL ENGINEERING TRANSACTIONS

VOL. 88, 2021

A publication of AIDIC
The Italian Association
of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Petar S. Varbanov, Yee Van Fan, Jiří J. Klemeš

ISBN 978-88-95608-86-0; **ISSN** 2283-9216

DOI: 10.3303/CET2188023

Hydrometallurgical Methods for Extracting Non-ferrous Metals from Electronic Gadgets

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This article explores an environmentally friendly method of complex processing of printed circuit boards of cell phones in order to extract gold and other valuable components without cyanides. Thiourea was used as reagents for leaching gold and silver. A nitric acid-based solder solvent was used to separate the electronic components and gold plating from the printed circuit boards. To eliminate the harmful effect of copper on thiourea, the printed circuit boards were not crushed at the gold recovery stage. As a result, Ag 51 % and Au 89 % were extracted at t = 60 °C and a thiourea concentration of 12 g/L. The presented method is environmentally friendly in comparison with cyanide methods of gold recovery and effective in terms of the amount of gold recovery.

1. Introduction

The demand for precious metals gold, silver, platinum, palladium remains traditionally stable today. In April 2021, the price for 1 ounce of gold was US$ 1,761.68; silver US$ 25.614 (LBMA, 2021). In 2019, the world production of gold was 3,300 t/y, silver 26,000 t/y. In 2020, gold production was 3,200 t/y, silver 25,000 t/y. The main producers of these metals are China, Australia, Russia, the United States, Canada, Peru, Ghana, Indonesia, South Africa. Kazakhstan produced 100 t/y of gold in 2020 (USGS, 2020), and 1,315.7 t/y of silver (Ep, 2020). Precious metals are used in the production of juvenile products, medical equipment, ingots, coins, electronic household products and equipment (USGC, 2021). In 2019, the structure of gold consumption is as follows: ~34.06 % in investment, ~57.9 % in jewelry, in technology: electronics ~7.14 %, other industry ~1.5 %, dentistry ~0.4 %. And gold is mainly used as a wire for assembling semiconductors and for coating contacts (WGC, 2020). In 2019, the use of silver was: electrical and electronics 30 %; jewelry and silverware 26 %; coins and medals 12 %; photography 3 %; and other 29 % (USGS, 2020). In the world, revenue from e-waste processing in 2019 amounted to 8.721×10^9 $. For the period 2020-2027, 4.7 % revenue growth is expected from e-waste recycling (Research Dive, 2021). According to the US Geological Survey, the world's known reserves of precious metals at the end of 2020 were: gold 53 kt, silver 500 kt, reserves of MPG (platinum group metals) can be approximately 100 kt (USGC, 2021). Mineral reserves of gold and other precious metals at the current level of consumption will only last for 17-18 y. Therefore, the expansion of the material and raw material base of sources of precious metals is of great importance. Such sources can be man-made waste, which is formed during the production of, for example, copper.

Technogenic sources of gold can also serve as tailings of gold-extracting factories. Secondary waste, which includes electronic waste, can also serve as a material base for the production of these metals. With the development of the electronic industry, the demand for electronic equipment is growing more and more and the amount of electronic waste such as computers, gadgets, smartphones is increasing (Baldé et al., 2020).If e-waste is not recycled, the precious metals used for the production of electronics (Sethurajan et al., 2019) will be excluded from economic circulation, ending up in landfills. And elements such as lead, cadmium, mercury, nickel and antimony entering the soil together with electronic waste will pollute the environment (Sahan et al., 2019).

Paper Received: 4 May 2021; Revised: 24 August 2021; Accepted: 2 October 2021
Please cite this article as: Shoshay Z., Sapinov R.V., Sadenova M.A., Varbanov P.S., 2021, Hydrometallurgical Methods for Extracting Non-ferrous Metals from Electronic Gadgets, Chemical Engineering Transactions, 88, 139-144 DOI:10.3303/CET2188023

This article will discuss the methods of complex processing of electronic waste in order to extract precious metals and other valuable components.

The metal content of printed circuit board waste (WPCBs) reaches 40 % by weight and has 60 different chemical elements, so WPCBs should be considered as a valuable secondary source of noble metals (Wang et al., 2020). One of the varieties of electronic scrap, the number of which is growing rapidly, is various electronic gadgets, such as smartphones, tablets, etc. These types of electronic waste are particularly valuable because of the high content of precious metals found on printed circuit boards in the form of sputtering and in electronic components (Wang et al., 2020). Hydrometallurgical processing methods are optimal from the point of view of ecology (Sapinov et al., 2020), with the separation of printed circuit boards and electronic components on them, without joint grinding. The separation of printed circuit boards and electronic components occurs by chemical dissolution of the solder. Thus, the electronic components that contain precious metals will be separated from the board. However, the surface of the boards also contains deposited gold. Therefore, before the subsequent processing of the printed circuit board, the gold coating must be removed from the surface of the board. After that, the electronic board is crushed, and the copper is extracted from it in various ways. The electronic parts also go through crushing, after which the material is leached. Traditionally, cyanides are used as reagents for the leaching of gold, while the recovery of gold is 88 %. Modern methods of hydrometallurgical processing are based on the use of various reagents and approaches to achieve optimal performance in terms of economic efficiency and environmental components. Thus, ammonium and sodium thiosulfate is proposed as a reagent for leaching gold. However, gold recovery in this case is 75 % and 70 % (Kasper et al., 2018). Compared to traditional leaching methods, thiourea $CS(NH_2)_2$ is less toxic, does not harm the environment, and has high gold leaching rates (Li et al., 2018). Thiourea initially dissolves Ag and Au in acidic solutions to form stable sulfate salts when iron ions Fe^{3+} are added (Gu et al., 2019).

However, the leaching of gold with thiourea has limitations when processing raw materials containing copper, since thiourea decomposes in the presence of copper (Mudila et al., 2020). A common method for disposing of e-waste is shredding it together with electronic components (Moosakazemi et al., 2020). In this case, the use of such environmentally friendly reagents as thiourea for gold leaching becomes difficult due to the decomposition of thiourea upon contact with copper. Therefore, it would be logical to find a way to recycle e-waste without such disadvantages. Therefore, a method is required with the preliminary separation of the gold plating from the printed circuit board (and the copper contained in it) before its subsequent dissolution with thiourea. Smartphone WPCBs contain large amounts of copper. Therefore, a method is needed with the preliminary separation of the gold plating from the printed board and the copper contained in it, before its subsequent dissolution with thiourea. This paper discusses the processing of cell phone WPCBs for gold recovery in aqueous thiourea solution.

2. Materials and methods

2.1 Experiment description

Figure 1 shows a diagram of the experiment. To eliminate the harmful effect of copper, at the first stage, the gold sputtering is separated with the help of a solder dissolver.

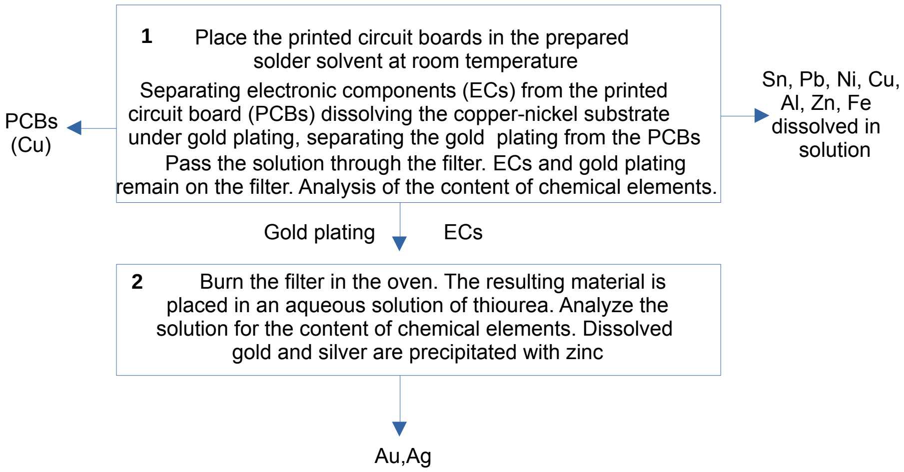

Figure 1: The scheme of the experiment

At the same time, it is assumed that the electronic components are separated for their separate processing. The experiment will study the effect on the gold leaching process of various factors - temperature and duration of the process.In the first step, the printed circuit boards are placed in a solder solvent. As a result, the solder dissolves and goes into a productive solution. This separates the electronic components from the printed circuit board. In addition to the solder, the copper-nickel base also dissolves under gold plating on the surface of the printed circuit board. Then the electronic components and gold plating are separated from the solution using a filter. In the second step, the filter is burned in an oven along with gold plating and electronic components. From the resulting material, gold and silver are leached using an aqueous solution of thiourea. Then, gold and silver are precipitated from the productive solution by electrochemical deposition, the introduction of zinc. All experiments were conducted on the premises of D. Serikbayev East Kazakhstan Technical University. Thermodynamic calculations were performed using the HSC 9 program. Profiles of the distribution of elements in the selected area were made using a scanning microscope JSM-6390LV manufactured by JEOLLtd. (Japan). The elemental composition of the materials was determined using an inductively coupled plasma mass spectrometer ICP-MS 7500 cx from Agilent Technologies (USA). The phase composition was determined using an X-ray diffractometer X'pertpro manufactured by PANalitical (the Netherlands). All reagents were of analytical purity. Chemical heat-resistant cookware was used for leaching. For processing, printed circuit boards were taken from used cell phones (Figure 2) of the brands Samsung, NokiaLumia and LG. After manual disassembly, the printed circuit boards were separated from the housings (Figure 2a). Then, the printed circuit boards were placed without grinding into a heat-resistant laboratory glass vessel to remove the solder into the productive solution and remove the gold plating without dissolution (Figure 2b). The chemical coating was not previously removed from the board surface.

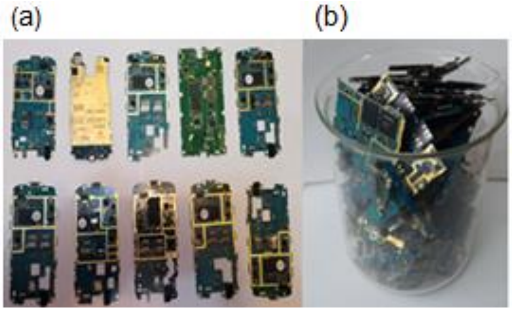

Figure 2: Boards; (a) after disassembly, (b) in a vessel

2.2 Removal of solder and copper-nickel substrate by leaching for the purpose of dismantling electronic components and removal of gold plating

To remove the gold coating applied to the surface of the printed circuit board (Figure 3), it is necessary to dissolve the solder and the copper-nickel substrate without dissolving the gold. For this purpose, an aqueous solution of nitric acid is used. In order for the reagent to selectively extract the solder and the copper-nickel substrate, it is necessary to dissolve 0.5 g of urea in distilled water (10 mL) to obtain a urea solution. Then, 5 mL of nitric acid is poured into the same solution. Urea nitrate precipitates. Add the rest of the distilled water (90 mL) and add citric acid (6 g) and mix until it dissolves.

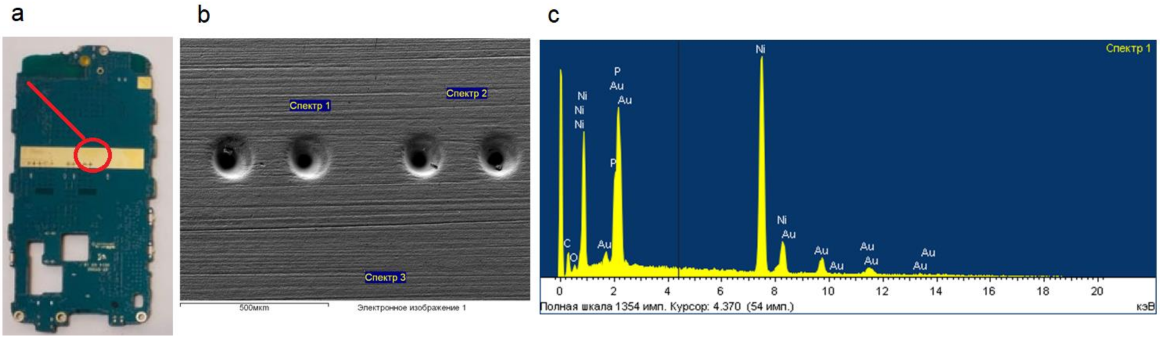

Figure 3: Distribution profiles of elements (c) over the surface of the spraying (b) applied to the surface of the printed circuit board (a)

After the citric acid has dissolved, we add the remaining nitric acid to it and the entire content of the solution is mixed again. The printed circuit boards are placed in the solution and leached for 20 min. After that, the solution is passed through the filter. On the filter, there is a gold coating separated from the boards and electronic elements that have separated from the board as a result of the dissolution of the solder. The boards free of electronic elements were washed with water and dried before crushing for further extraction of metals.

2.3 Transfer of the separated gold deposition to the productive solution

To transfer the separated gold deposition to a productive solution, the filter in the crucible is placed in the furnace. The remaining material after burning is placed in an aqueous solution of thiourea with a concentration of 12 g/L. S/L ratio = 1/10 (solid / liquid). The material is leached for 240 min at a temperature of 25 °C, 45 °C and 60 °C with stirring on a magnetic stirrer. The pH of the process was 1.5. Samples were taken every 60 min to study the kinetics of the process. To maintain the pH of the process $\mathrm{Fe}_2(SO_4)_3$ was added.

3 Results and discussion

Using the HSC9 program (Outotec Research, www.hsc-chemistry.com), pH/Eh diagrams were constructed for the Au-Ag system to predict thermodynamically stable forms of silver and gold ions at different pH values and redox potential (Figure 4). In the diagram (Figure 4a), the silver ion ($\mathrm{Ag}^{+\mathrm{a}}$) at a low potential value is reduced to the underlying form, that is, to metallic silver (Ag). The reduction of silver does not require the participation of protons, so the potential of silver does not depend on the pH value. At high potential values, silver is oxidized to the overlying AgO_2 form. Whereas for gold (Figure 4b), the overlying form is the gold ion itself $\mathrm{Au}^{+3\mathrm{a}}$and at low potential values, the gold ion is reduced to metallic gold (Au). In the diagram (Figure 4b) with gold, water reduces solid $\mathrm{AgO}_2$and $\mathrm{Au(OH)}_3$ and dissolved Au^{+3} and $\mathrm{Au}_2\mathrm{O}_3 2\mathrm{H}_2\mathrm{O}$ to metal at all pH values; therefore, gold is not oxidized by dissolved oxygen and is not affected by strong acids and alkalis. Gold is not able to form stable compounds in the presence of water. At the bottom of the diagram, metallic gold and silver are stable and do not corrode. In the right part, the metals are in solution in ionic form. In areas where metal oxides are present, a protective oxide film is formed to protect the metal surface from further corrosion.

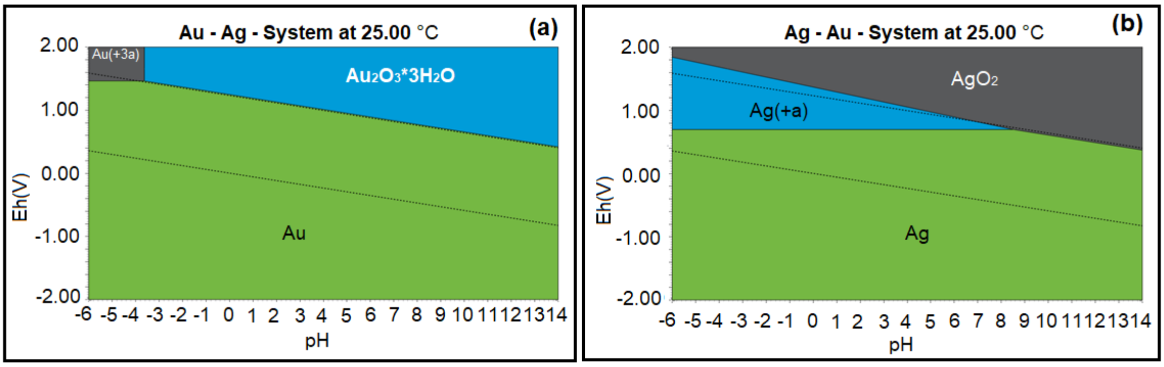

Figure 4: Diagram of pH - Eh for the Au-Ag (a) system and pH - Eh for the Ag-Au (b) system

To determine the average values of the metal content in the WPBCs of cell phones (Table 1), 8 WPBCs of phones of 2014 – 2019 brands were taken (Samsung, Nokia Lumia and LG). The WPBCs were ground to sizes less than 0.1 mm. After that, a sample was taken from this material by quartering.

Table 1: Average concentration of metals in PCB mix samples (wt. %)

Cu	Al	Sn	Ni	Zn	Pb	Fe	Ag	Au	Pd
26.4	3.9	3.2	2.3	1.2	1.7	4.2	0.2	0.35	0.1

30 min after the boards were placed in the solder removal solution, the solder was removed and the copper-nickel substrate also partially dissolved. Gilding in the form of a film (foil) began to float to the surface of the solution (Figure 5a). After the end of the reaction, the boards were removed from the solution and washed with distilled water. The productive solution with dissolved solder was filtered out. On the surface of the filter, the gilding and separated electronic elements remained (Figure 5b). Chemical analysis of the productive solution showed that the gold did not pass into the solution (Table 2). The gold-plated filter was placed in a furnace,

burned, and then dissolved in an aqueous solution of thiourea (Figure 5c). The separated chips are crushed and leached together with the separated gold plating.

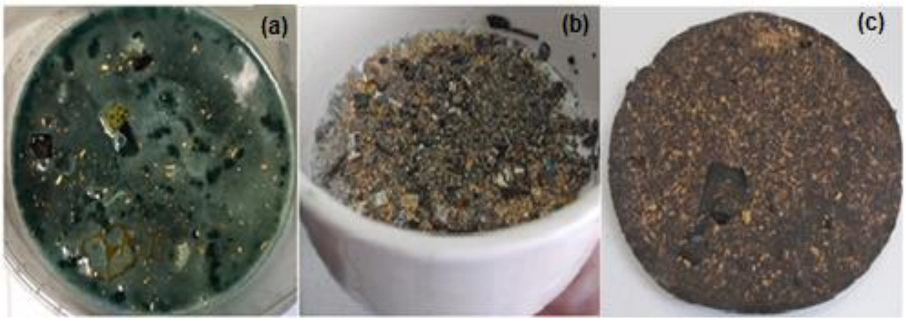

Figure 5: Solder leaching: (a) separated gold plating on the PLS surface, (b) gold plating and electronic components, (c) post-combustion material

In order to determine the degree of recovery of the solder into the productive solutionthe contents of heavy metals were determined (Table 2). It is shown that most of the solder (98 %) and some of the copper were transferred to the solution.

Table 2: Percentage of metal recovery in PLS after solder dissolution (%)

Cu	Fe	Al	Sn	Ni	Zn	Pb	Ag	Au
14	87	41,3	85,4	20	95	86	0	0

The next step was to transfer the gold deposition separated from the boards to a productive solution. To do this, the material remaining after burning the gold-coated filter was placed in a chemical dish and leached at various temperatures in an aqueous solution of thiourea. Figure 6 shows graphs of the dependence of gold extraction on the process temperature.

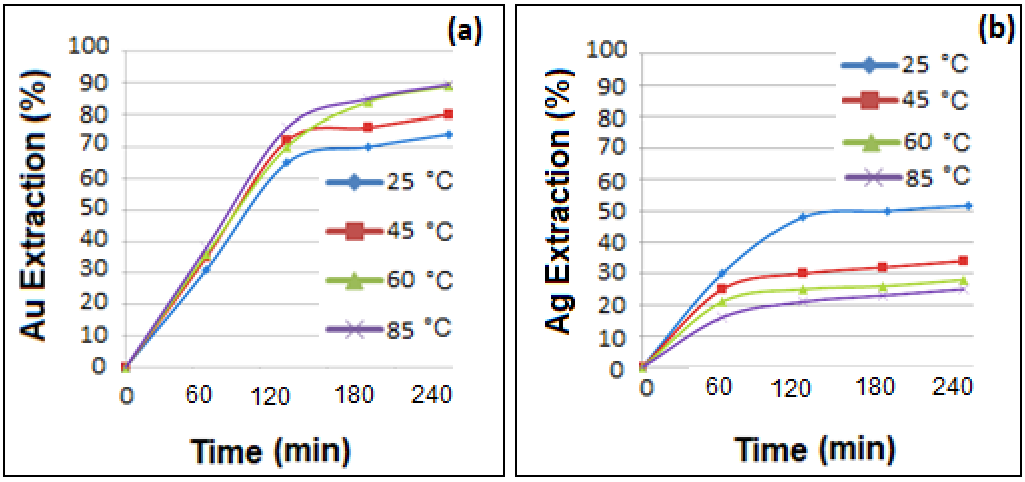

Figure 6: Recovery of (a) Au and (b) Ag at 25 °C, 45 °C, 60 °C and 85 °C

The most effective temperature for gold extraction was 60 °C (Au 89 %). The lowest extraction was at a temperature of 25 °C. An increase in temperature to 85 °C did not give a noticeable increase, (Au 89.5 %), but given that the extracted element is gold, an increase of 0.5 % can be considered effective. Table 3 shows the extracted elements at a temperature of 60 °C.

Table 3: Percentage of metal recovery in productive solution (%)

	Cu	Fe	Al	Sn	Ni	Zn	Pb	Ag	Au
(%)	0	0	0	0	0,2	0.73	0.4	51	89

The next step is the deposition of gold from the productive leaching solution. The deposition was carried out by a process of displacement by a more electronegative element. In our case, it is zinc powder. In more detail, the process of gold deposition from the productive solution will be shown in the next article of the authors.

4 Conclusions

In this paper, we studied the complex processing of printed circuit boards of cell phones in order to extract gold and other valuable components. In the first step, the solder was recovered using a nitric acid solvent. In doing so, the electronic components and gold plating on the surface were separated from the printed circuit board. Then the resulting productive solution is separated from the solid part containing gold plating and electronic components using a filter. The filter was burned in an oven and the resulting material was leached with an aqueous solution of thiourea. The gold and silver extracted into the productive solution were precipitated with zinc. 51 % of silver and 89 % of gold were thus recovered at a temperature of 60 °C. The processed printed circuit boards are further processed for grinding and copper extraction from them. This part of the experiment together with the calculation of energy costs (and carbon emissions into the atmosphere) for the extraction of all useful components, will be presented in the next work.

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