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INNOVATIONS IN WEEE RECYCLING

Screening of Non-cyanide Leaching Reagents for Gold Recovery from Waste Electric and Electronic Equipment

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Abstract

The importance of gold recycling from waste electronic and electrical equipment (WEEE) is continuously increasing due to raising gold demand and the need for new recycling methods for this complex waste. In state-of-the art processes gold is recovered in the copper route. In necessary pre-treatment steps, a significant loss of gold occurs. Furthermore, in this process the gold is bound for a longer time period in a copper phase and is separated in a mixture with other noble metals, which needs further treatment. A direct gold extraction from WEEE by selective leaching and precipitation would have many advantages. Due to raising social awareness of the ecological impacts of cyanidic gold extraction and environmental specifications, cyanide cannot be used as gold extractant in modern processes. Therefore, over the course of this study, two experimental sets have been conducted on each of six non-cyanide leaching reagents to test their feasibility and compare them against each other. Aqua regia and iodine/iodide leaching systems were the most successful reagents, yielding 100% of gold while showing very fast leaching rates. A comparison between the two successful reagents was carried out, with the results favoring iodine leaching due to its high selectivity for precious metals and reduced environmental impact.

Keywords Gold · Leaching · Cyanide alternative reagents · WEEE recycling · Electronic scrap · Cyanide-free · Iodine · Thiourea · Thiosulfate · MSA · LSSS

Background

Potential for PMs Recycling from WEEE

Nowadays, the world is witnessing the greatest technological leap in history of humanity, with high-tech electrical and electronic equipment becoming almost essential in everybody's life. Producing equipment ranging from refrigerators and air conditioning systems to mobile phones and computers, the industry of electrical and electronic equipment (EEE) is of the utmost importance to today's modern world. As a consequence thereof, the amount of e-waste generated globally is increasing annually, as the global e-waste monitor of the United Nations University shows (Fig. 1). Not only this, the e-waste generated per capita is also increasing despite the increasing number of Earth's inhabitants. In 2014, already around 42 Mt of e-waste was generated, with an expected upward trend in the following years [1].

Gold has excellent chemical resistance and electrical conductivity. These featured properties of gold make it a useful material for the electronic industry, where it is used as coating for electrical contacts. Gold also has high importance as save funds, due to its high price which results from its rareness and chemical resistance. Besides that, it is used in jewelry, coinage, ornaments, gilding, etc.

Recovery of metals from electronic waste can be achieved by various methods such as pyro-, hydro-, electro-, and biometallurgical techniques. Although pyrometallurgical recycling of WEEE is an established process throughout the world, the focus of researchers has shifted to hydrometallurgical methods in the past two decades [2, 3]. With relatively low investment costs and reduced environmental

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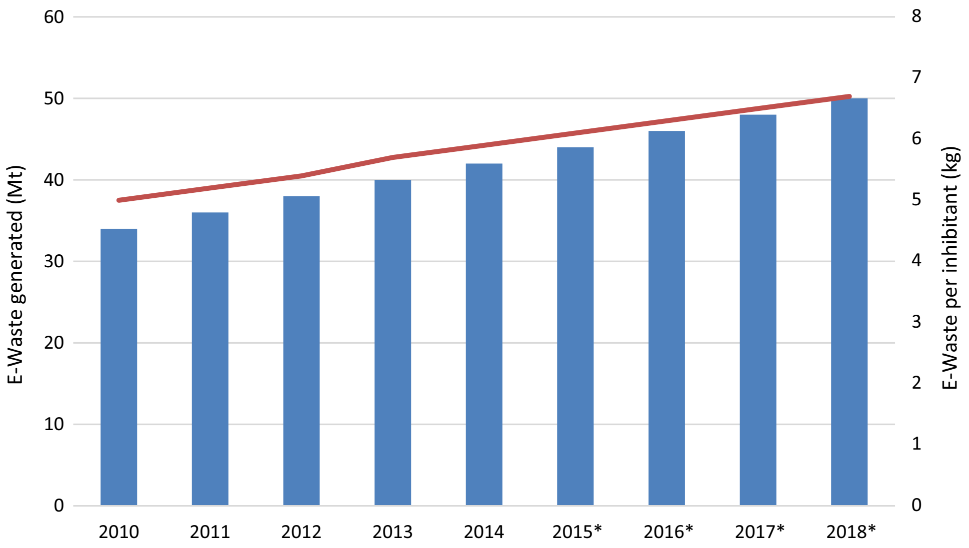

Fig. 1 E-waste generated globally per year (bars) and E-waste generated per inhabitant (line). Data from 2015 are forecast [1] (color figure online)

impacts, hydrometallurgical processes can serve as a viable substitute for pyrometallurgical techniques. The focus of researches over the past years has been on the recovery of precious metals (PM), due to their significantly higher value share in WEEE, compared to base metals [3, 4].

Of course, the mere presence of these valuable materials is not sufficient to attract metallurgical companies to explore the recycling option along with the primary routes. But the interesting fact is that the concentration of precious metals in WEEE is much higher than in ores [5], as clear from Fig. 2. Besides this economic advantage, the secondary production of precious metals has a much lower negative impact on the environment than the extraction of these metals from their ores, where thousands tons of ore are moved and leached with cyanide [6].

Challenges of Hydrometallurgical PM Recovery

The outstanding chemical resistance of gold becomes a disadvantage in hydrometallurgical processes. Capable leaching reagents like cyanide, chloride, or sulfur complexes are mostly aggressive and very toxic [9, 10]. Therefore, we face environmental problems during chemical processing of gold. Cyanide leaching is the dominating technique to recover gold from primary resources for longer than 100 years, due to its low cost, low reagent consumption, and alkalinity. The dominance of this reagent results from a cost-efficient and technical effective process with high yield and adequate dissolution rates.

A big disadvantage of cyanide is its high toxicity. The leaching process generates high amounts of contaminated waste water that can cause severe damage to the operators and environment. Besides this, the leaching rate of cyanide is significantly slower compared to other reagents like halides, which is also considered a big disadvantage [11].

A series of environmental accidents around the world raised concerns about this reagent in society. In areas near gold leaching industry, cyanide can pass soil and even contaminate the underground water. The cyanide concentration in these areas is too high for micro-organism

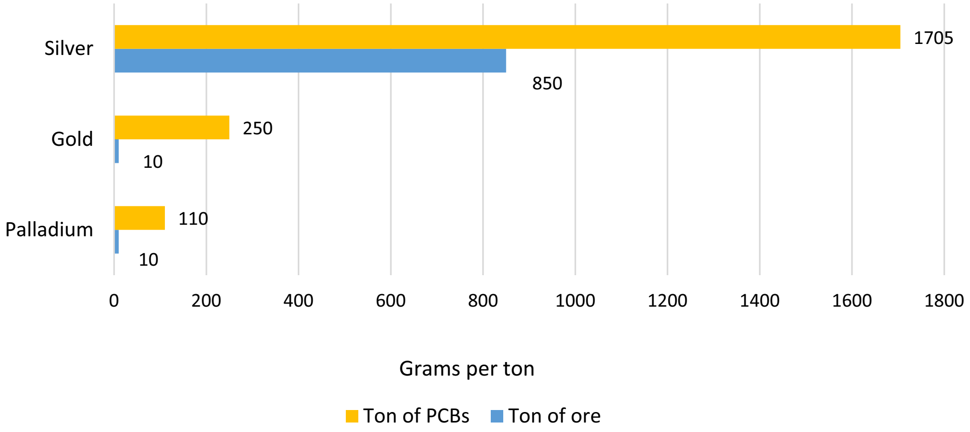

Fig. 2 Precious metals content in PCBs versus primary ores [5, 7, 8] (color figure online)

transformation to less harmful complexes whereby long-term environmental problems arise [11]. Another big disadvantage of cyanide is the low leaching efficiency of refractory sulfide minerals or gold resources that contain copper or carbonaceous preg-robbing materials. Additionally, these resources afford a higher demand of cyanide and decrease the dissolution yield. Generally, an average gold extraction yield of 50–80% can be obtained by heap or 99% by conventional leaching [11, 12].

For these reasons, researchers have diverted their attention to non-cyanide leaching processes, with some of these processes making remarkable progress which may lead them to be eligible substitutes for cyanide in the future [2, 13]. In the following subsections, the most common non-cyanide reagents like aqua regia, iodine, thiosulfate, and thiourea will be discussed. Moreover, an introduction to less common reagents like lime sulfur synthetic solution and methanesulfonic acid will also be included.

Non-cyanide Leaching Reagents

This publication offers a thorough literature review not only on the most common non-cyanide leaching reagents for gold (thiosulfate, thiourea, halogenides), but also on novelty reagents such as methanesulfonic acid (MSA) and lime sulfur synthetic solution (LSSS). Moreover, the experimental trials conducted during this study does not focus on only one leaching reagent, but on six different leaching reagents with the aim of comparing their feasibility as gold leaching reagents. Uniform and controlled process parameters were considered to produce comparable results.

Aqua Regia

Aqua regia is a mixture of concentrated nitric and hydrochloric acid, known as royal water because of its ability to dissolve gold. Neither of the two acids alone are able to dissolve gold, but a mixture of 3:1 molar ratio of them is used for this task. The powerful oxidizing nitric acid dissolves an infinitesimal amount of gold, forming trivalent gold ions. The dissolved gold ions react with chloride ions provided by hydrochloric acid to form tetrachloroaurate anions [11, 14]. The dissolving reaction is shown in the following equation:

$$\mathrm{Au} + \mathrm{HNO_3} + 4\mathrm{HCl} = \mathrm{AuCl_4^-} + \mathrm{H^+} + \mathrm{NO} + 2\mathrm{H_2O}. \quad (1)$$

The effectiveness of aqua regia as a leaching reagent was studied by several researchers. For example, Sheng and Estell [15] used aqua regia for precious metal leaching from computer chips due to its ease, flexibility, low cost, and very fast leaching rates. They investigated the effects of parameters like temperature, *S*/*L* ratio, and retention time on the process. They concluded that higher temperatures result in faster leaching rates. They also found that the optimum S/L ratio needed to fully dissolve the computer chips was 1:2 ml/g, which is considered a great advantage due to the small amount of reagent needed. Moreover, they concluded that mechanical agitation was not necessary for the process, due to the self-agitation of the system resulting from the release of nitrous oxide and chlorine vapors that cause bubbling and frothing of the solution [15]. Unfortunately, aqua regia leaching process does come with a couple of major disadvantages which make it more difficult to apply than cyanide. Highly poisonous chlorine gas is emitted during the process, therefore strict safety measures must be applied in order to avoid any damages. The other disadvantage is the highly corrosive and oxidizing conditions needed for the process, hence requiring special stainless-steel rubber-lined equipment to withstand these conditions [3]. Moreover, it was observed by Park and Fray [14] that silver and palladium precipitate at the bottom of the system and do not dissolve in aqua regia like gold does. Silver reacts with chlorine forming precipitated silver chloride and reacts with palladium to give a red palladium precipitate ($\mathrm{Pd(NH_4)_2Cl_6}$) [14].

Halogenides

Iodine/iodide leaching is one of the most promising non-cyanide leaching processes. It has been researched extensively in the past few years, in an attempt to improve gold recovery from the pregnant solution and decrease the costs related to the reagent by trying to reuse it. As a part of the halides leaching techniques, iodine solutions have fast leaching rates similar to that of the chlorine solutions (aqua regia) [16]. It is also worth noting that among halogens, the gold–iodine complexes are the most stable in aqueous solutions [12].

Regarding the chemistry of the solution, it is understood that the slightly water-soluble iodine reacts with the present iodide ion (that may come from dissolved potassium iodide) to form a soluble tri-iodide ion that serves as an oxidant for the elemental gold during the process [16] with reactions shown below [17]:

$$\mathrm{I_{2\,(aq.)}} + \mathrm{I^-} \leftrightarrow \mathrm{I_3^-} \quad (2)$$

$$2\mathrm{Au} + \mathrm{I_3^-} + \mathrm{I^-} \leftrightarrow 2\mathrm{AuI_2^-}. \quad (3)$$

The studies conducted in iodine solutions are mainly performed in the presence of hydrogen peroxide. Through experimental trials, the great importance of adding hydrogen peroxide to the system was shown, with one study [16] reporting a very low percentage of gold dissolution (35%) when no hydrogen peroxide was added. According to Chen et al. [18], almost all present gold (97.5%) in the used PCBs was dissolved, being leached under their concluded optimum conditions.

Iodine/iodide leaching has several advantages that make it a very attractive route for precious metals recovery. First of all, this process has fast leaching rates with very good selectivity for precious metals. Iodine solutions are neutral or weakly alkaline so there is no corrosion whatsoever. Moreover, iodine solutions are considered non-toxic compared to other available methods. Unfortunately, this method has not been applied on an industrial scale yet despite of its advantages large due to the relatively high prices of iodine. In order to overcome this problem, efforts are being made to decrease these costs by trying to reuse the leaching solution multiple times [13].

Two other important halide leaching reagents with a similar dissolution reaction to iodine are bromine and chlorine. These reagents are strongly oxidizing and show much higher dissolution rates than cyanide leaching. The dissolution reaction can be summarized in the following equations [12, 19, 20]:

$$\mathrm{Au} + 2\mathrm{Br}^- + 2\mathrm{Br} = \mathrm{AuBr}_4^- + \mathrm{e}^- \tag{4}$$

$$\mathrm{Au} + \mathrm{Cl}^- = \mathrm{AuCl} + \mathrm{e}^- \tag{5}$$

$$\mathrm{AuCl}_2^- + 2\mathrm{Cl}^- = \mathrm{AuCl}_4^- + 3\mathrm{e}^-. \tag{6}$$

The chloride and bromide complexes are less stable than gold iodide, wherefore gold can be more easily reduced to be separated in metallic form. These reagents were already tested to recover gold from sulfide ores in lab scale and showed a good performance concerning extraction rate and yield. Besides the advantages, chlorine and bromine leaching were not implemented into industrial application due to their highly corrosive properties, high reagent costs, and volatility [12, 20].

Thiosulfate

For leaching precious metals, there are two common types of thiosulfates used ammonium thiosulfate and sodium thiosulfate. Thiosulfate reacts with metallic gold to form aurothiosulfate complex ($\mathrm{Au(S_2O_3)_2^{3-}}$). In this process, there are two important additives needed for feasible leaching: ammonia and copper sulfate.

Copper sulfate works as a catalyst and an oxidizing agent, forming a stable cupric tetra amine complex when it reacts with ammonia which acts as a stabilizer for the aurothiosulfate complex formed [21]. Moreover, ammonia is important for hindering gold passivation [22]. The reaction is described by the following equations [3]:

$$\mathrm{Au} + 5\mathrm{S_2O_3^{2-}} + \mathrm{Cu(NH_3)_4^{2+}} \leftrightarrow \mathrm{Au(S_2O_3)_2^{3-}} + 4\mathrm{NH_3} + \mathrm{Cu(S_2O_3)_3^{5-}} \tag{7}$$

$$2\mathrm{Cu(S_2O_3)_3^{5-}} + 8\mathrm{NH_3} + \frac{1}{2}\mathrm{O_2} + \mathrm{H_2O} \leftrightarrow 2\mathrm{Cu(NH_3)_4^{2+}} + 2\mathrm{OH^-} + 6\mathrm{S_2O_3^-}. \tag{8}$$

Tripathi et al. [21] have studied the effects of parameters like ammonium thiosulfate concentration, copper sulfate concentration, and pH value along with the effect of the sample geometry. They found out that using their concluded optimum conditions on different types of sample geometries resulted in different gold yields where only 56.7% of gold was recovered from the shredded sample, while leaching a complete PCB garnered a 78.8% recovery. They attributed this difference to the higher dissolution of copper in the case of shredded samples (due to larger surface area) which results in higher losses of thiosulfate ions by its conversion to tetrathionate.

Thiosulfate leaching process has high selectivity for precious metals and its non-toxicity. It also offers an alkaline medium for leaching, hence it is a non-corrosive process. Despite its potential environmental benefits, its relatively slow leaching rates along with its high reagent consumption makes it a less attractive route in comparison to other available methods [3].

Thiourea

Thiourea (also known as sulfurized urea) was synthesized for the first time in 1868 [13] and for the past few years, using it as a gold extraction reagent has been researched showing considerably promising results. Thiourea is an organic compound that has the ability to react with gold to form a cationic complex soluble in an acidic medium [12]. The leaching rate during this process is highly dependable on the thiourea and oxidant concentrations, along with the pH value.

It is widely regarded that the system of ferric ions with sulfuric acid is the most effective system, garnering the best results with thiourea. It has been discovered that the presence of an oxidant like $\mathrm{Fe^{3+}}$ in the system facilitates the oxidation of precious metals, hence catalyzing the whole process making it almost 4 times faster than without the presence of an oxidant [11, 23, 24]. The reaction of gold with thiourea in both cases can be described by the following equations[25]:

$$\mathrm{Au} + 2\mathrm{SC(NH_2)_2} + \frac{1}{4}\mathrm{O_2} + \mathrm{H^+} \leftrightarrow \mathrm{Au[SC(NH_2)_2]_2} + \frac{1}{2}\mathrm{H_2O} \tag{9}$$

$$Au + 2SC(NH_2)_2 + Fe^{3+} \leftrightarrow Au[SC(NH_2)_2]_2^+ + Fe^{2+}. \quad (10)$$

Thiourea leaching has been investigated by various researchers. Wu et al. [26] conducted experimental trials to find the optimum parameters for this process, reporting that metal yields for gold and silver were 91.4 and 80.2%, respectively. Another study by Zhong et al. [27] showed that for the same retention time (1 h) the optimum parameters were different from the previously mentioned study, signifying that more research is needed in this field in order to reach closer values for the optimum parameters of the process.

Thiourea leaching has several advantages like fast leaching rates and high efficiency [13]. It is also regarded as a low-toxicity environmentally friendly process, but this perception is starting to change as some reports claim that thiourea is a suspected carcinogen, with some concerns also emerging about its environmental impact [12]. The main reason hindering thiourea leaching from being industrially applied until now is its poor stability compared to other reagents. During the process, the thiourea is oxidized into disulfide formamidine which initially helps in increasing the leaching rate. After a while when its concentration increases, it is prone to decompose generating elemental sulfur which forms a passive layer on the gold particle, thus hindering its dissolution. Moreover, a great amount of reagent is consumed during this process [28].

MSA

Methanesulfonic acid (MSA) is a non-oxidizing acid with the chemical formula of (CH_3SO_2OH) that belongs to the class of organosulfur compounds. MSA is mainly known in the metallurgical field as the standard electrolyte for preparing lead and tin electroplating baths. Various studies have been conducted to test the feasibility of leaching base metals with MSA, but this is not the case for precious metals leaching which is still an under-researched topic.

In 1995, Gernon [29] filed for a European patent regarding precious metals leaching using MSA, taking silver as a representative for precious metals. He figured that injecting air or even oxygen was not sufficient to leach precious metals, so he used the stronger hydrogen peroxide as an oxidizing agent. Using various physical forms of pure silver as the raw material, Gernon studied the influence of the materials' geometry on the feasibility of the process, while discovering the optimum conditions for this method that is best described by the following equation [29]:

$$2Ag + 2CH_3SO_2OH + H_2O_2 \leftrightarrow 2AgO_3SCH_3 + 2H_2O. \quad (11)$$

From his experimental trials, Gernon concluded that the physical form of the silver used was one of the most important factors affecting the feasibility of the process, with this fact being demonstrated by the following table (Table 1).

MSA offers various functional and environmental advantages that make it an attractive leaching route. MSA has high metal salt solubility, high conductivity which make it a good electrolyte, high stability, along with low toxicity and biodegradability [30]. The main challenge against using this method to leach precious metals from electronic scrap is its high leaching selectivity favoring less noble metals over precious metals, which led Gernon [29] to preferably use high purity silver in his experimental trials.

LSSS

Lime sulfur synthetic solution (LSSS) is a potential leaching reagent for precious metals introduced by Zhang [31]. LSSS is synthesized by mixing elemental sulfur, lime (quick or slaked), and water at elevated temperatures and mechanical stirring [32]. The main components of this synthesized solution are CaS_x and CaS_2O_3, with polysulfide and thiosulfate responsible for the leaching function. The reaction of the solution with gold is represented below [33]:

$$2Au + 2S^{2-} + H_2O + 1/2O_2 \leftrightarrow 2AuS^- + 2OH^- \quad (12)$$

$$2Au + 4S_2O_3^{2-} + H_2O + 1/2O_2 \leftrightarrow 2Au(S_2O_3)_2^{3-} + 2OH^-. \quad (13)$$

The LSSS needs some additives like sodium sulfite, copper sulfate, and aqueous ammonia to enhance its leaching capabilities. Ying and Lu [33] have investigated this method, reporting that the main parameters affecting the feasibility of the process were the concentrations of these additives along with the retention time and temperature. According to this study, the process yielded about 92% of gold and 90% of silver under optimum working conditions. They reported an optimum S/L ratio of 1:3, which is considered to be one of the greatest advantages of this method (because it decreases the reagent cost) along with its fast leaching rates and non-toxicity [33].

Table 1 The effect of silver form on the retention time [29]

Geometry	Amount of Ag used (g)	Time for dissolution (h)
Flakes	5.6	0.5
Coins	0.1	10
Needles	5.5	24

Experimental

The experimental trials conducted during this study intended to show the major differences between the leaching reagents and compare their feasibility regarding precious metals leaching from electronic scrap. For each reagent, there were six trials divided into two sets of experiments with each of them composed of three trials.

Feed Materials

The first set of experiments served as a test for the gold leaching capacity of each reagent. These trials were conducted on a gold-coated copper material, which shows a similar composition to electrical contacts. By using this material, the unpredictable factor of the high heterogeneity of WEEE could be excluded. In this set, one parameter only was varied in the leaching conditions in order to test its effect on the process. To prepare the raw material used in this set, a gold-plated cooling device made of copper was mechanically cut into approximately equal rectangular specimens having a flat surface and a thickness of 1 mm, as shown in Fig. 3.

On the other hand, the second set of experiments concerning the leaching solutions were always carried out with the exact same leaching conditions, but on three different types of electronic scrap: central processing unit (CPUs), random access memory (RAMs), and pyrolyzed RAMs that have been previously prepared at IME. The CPU and RAM were selected in order to enable a qualitative optical evaluation of the leaching ability of each reagent on real and untreated materials, which show a completely different geometry and surface. The superficial gold of CPUs gold pins and RAMs “gold finger” facilitates the leaching process and helps in determining the success of the process visually as seen in Fig. 4. Additionally, the selectivity of the reagents was tested with these materials due to the presence of different metals in the pregnant leaching solution. The pyrolyzed material was milled and sieved to achieve a grain size smaller < 90 µm. It was important to include a pulverized raw material to see the leaching effect on a small particle size and a high reaction surface material.

Fig. 3 Specimens for the first experimental set (color figure online)

Leaching Tests

All leaching solutions were stirred by an agitation speed of 300 rpm, and all trials were performed at room temperature (except for first set of aqua regia leaching, when temperature was the investigated variable). It should be noted that the leaching conditions of the second set were also used for the first except the parameter under investigation.

For the first set of experiments, each gold-plated specimen was leached with a 50 ml solution, which was a sufficient amount fixed for all leaching reagents. The second set of experiments was always carried out with a 150 ml for each trial. These amounts (50 and 150 ml) were chosen to ensure an excess of leaching reagent for complete reaction and to enable the comparability of the experiments. The weight of the pyrolyzed RAMs used in all trials was always 5 g.

Regarding the retention time, it was 3 h for all trials except for thiosulfate leaching, which due to expected lower leaching rates, the samples where left for 24 h. In Table 2, an overview on the parameters used for each leaching reagent in both sets is displayed.

All trials were conducted using magnetic stirrers and glass beakers, with the whole setup being inside a fume hood at all times. For the experiments including CPUs and RAMs as raw materials, a clamping device was used to hold the CPU or RAM while immersing a part of it in the agitated solution, in order to show the difference between the leached and unleached parts of the specimen. All samples taken from the CPU and RAM trials were not chosen for analysis, since their individual composition varies from piece to piece and cannot be analyzed without destroying the sample. The leaching trials with these samples will be evaluated just visually.

For each individual trial, three samples were taken from the leaching solution at different times in order to assess the progress of the process over time. After drawing a small

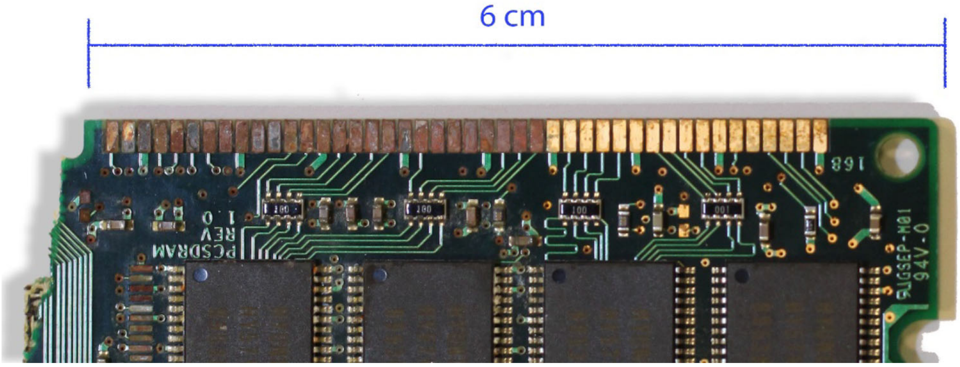

Fig. 4 Difference between leached and unleached "gold finger" (sample used for 1% iodine leaching) (color figure online)

Table 2 Summary of experimental conditions

Reagent	Parameter in 1st set	Values of specified variable parameter	Parameters of 2nd set (also valid for 1st set)
Aqua regia	Temperature	25, 50, 75 °C	3:1 ratio of $HCl:HNO_3$
Iodine	I_2 conc.	1, 3, 5% (w/v)	2% I_2 (w/v), 1.5% H_2O_2 (v/v), I_2:KI molar ratio 1:10
Thiosulfate	Cu^{2+} conc.	0.01, 0.03, 0.05 M	0.2 M $(NH_4)_2S_2O_3$, 0.3 M NH_4OH, 0.05 M Cu^{2+}
Thiourea	Thiourea conc.	10, 30, 50 g/l	40 g/l TU, 8 g/l H_2SO_4 and 0.01 M Fe^{3+}
MSA	MSA conc.	10, 40, 70%	70% (v/v) of solution made of diluted 10% MSA, 30% H_2O_2 (v/v)
LSSS	NA	NA	Solution 2:1.3:60 mass ratio for $S:Ca(OH)_2:H_2O$, 0.1 M Na_2SO_3, 0.5 M NH_4OH and 0.03 M Cu^{2+}

portion of the leaching solution from the beaker using a pipette, it was filtered using an organic filter in order to separate undissolved materials. All samples were prepared by diluting the filtered pregnant solution with distilled water to a ratio of 1:10. Moreover, 1 ml of the acidic or alkaline aqueous solution used to prepare the reagent was added to the diluted sample to stabilize the pH value in order to avoid any belated precipitation from occurring, which can compromise the integrity of the sample making it unsuitable for chemical analysis.

Results and Interpretation

Reference System: Aqua Regia

As expected, aqua regia leaching demonstrated very fast leaching rates, dissolving all visible gold content on the surface of the raw materials of the second set. For the first set of trials, it was concluded that the leaching rate was directly proportional to the temperature, with complete dissolution of the whole specimen (except for the epoxy resin) in < 1 h when the temperature was 75 °C. The two other specimens were also completely dissolved after 1.5 and 3 h for the 50 and 25 °C trials, respectively. Nonetheless, it was observed that at 75 °C the solution was evaporating, drastically decreasing the *S*/*L* ratio of the trial leaving the system almost dry (impractical situation) which was not the case in the trial conducted at 50 °C where almost no evaporation occurred. Due to the occurrence of full dissolution of the specimens (i.e., 100% yield for Cu and Au present in the gold-plated copper samples), it was decided that these results (10 g/l copper and 18.6 mg/l gold) will serve as a reference value for the metal yield calculations in order to compare the results of other leaching reagents against it, as the initial composition of the samples was unknown. Regarding the metal yield calculations for the pyrolyzed RAM trials, the results of the aqua regia shown in Table 3 were also taken as a reference (i.e., the shown values represent 100% yield of each of the metallic elements). Moreover, the initial chemical composition of the pyrolyzed RAMs is displayed in Table 4.

Iodine

Regarding the first set of experiments, the selected parameter under investigation was the iodine concentration. The chemical analysis conducted on the gathered

Table 3 Selected metals leached from pyrolyzed RAMs (in mg/l) by aqua regia

Cu	Fe	Ni	Sn	Au
297.0	93.8	81.4	43.4	3.1

Table 4 Initial chemical composition of pyrolyzed RAM sample showing selected elements (in wt%)

Cu	Fe	Ni	Sn	Au (ppm)
8.9	2.8	2.4	1.3	973.0

Table 5 Yield percentages of selected elements from iodine's pyrolyzed RAMs trial

Cu (%)	Fe (%)	Ni (%)	Sn (%)	Au (%)
0.0	0.0	6.5	0.0	80.0

A yield of 0.0% means that the amount of the element was so small to be detected by the analysis equipment

samples came with very promising results, with the achieved gold yields for different iodine concentrations shown in Fig. 5. Since no other elements could be measured in the pregnant leaching solution, the table just shows the gold extraction.

Moreover, it was observed that the leaching efficiency seems to slightly decrease by increasing iodine concentration in the solution, hence concluding that 1% iodine is the best concentration among the ones tested. Microscopic observations of the three samples showed, that there was no gold coating on their surface. The discrepancy in gold yield may be caused by an unsteady thickness of the gold coating or a divergence in size of the investigated specimens. In literature there is no adequate explanation for a decreasing leaching yield with higher iodine concentrations and neither a similar observation.

For the second set with iodine, the process was successful in leaching the gold on the surfaces of the RAM and the CPU. Regarding the pyrolyzed RAMs trial, the gold yield was 80% (see Table 5). Further trials should be conducted on the pyrolyzed material in order to discover weather this decrease in the yield happened because iodine solutions are less effective with this kind of material or there was simply less gold in the 5 g sample used for iodine leaching compared to the one of aqua regia (material is highly heterogeneous, so even if the weight is similar, composition might differ).

During the first experimental set, samples after 1, 2, and 3 h were drawn from the system and analyzed in order to determine the effect of the retention time on the process. The results depicted in Fig. 6 show that almost all gold was leached during the first hour of the trial (a fact clearly demonstrated by the almost horizontal lines), thus proving the very fast leaching rates of iodine-based solutions.

Thiosulfate, Thiourea

For thiosulfate and thiourea disappointing results were achieved. In case of thiosulfate, a strong passivation reaction occurred that formed an inert coating over the surface of the raw materials hindering any leaching activity. Most probably the passivated layer consists of gold or copper sulfides. A further problem for bad gold leaching with thiosulfate could be the formation of tenorites and tetrathionates, which hinder the further extraction [34]. Figure 7 shows a microscopy record of the leached surface at ×500 magnification. Of course, this coating could not be observed for the pyrolyzed RAM trial, where a significant amount of copper was leached, but there was no significant gold yield. It is assumed that due to the higher concentration of the less noble element copper, gold leaching did not occur even after 24 h. Table 6 shows the obtained results from the pyrolyzed RAMs trials of both leaching

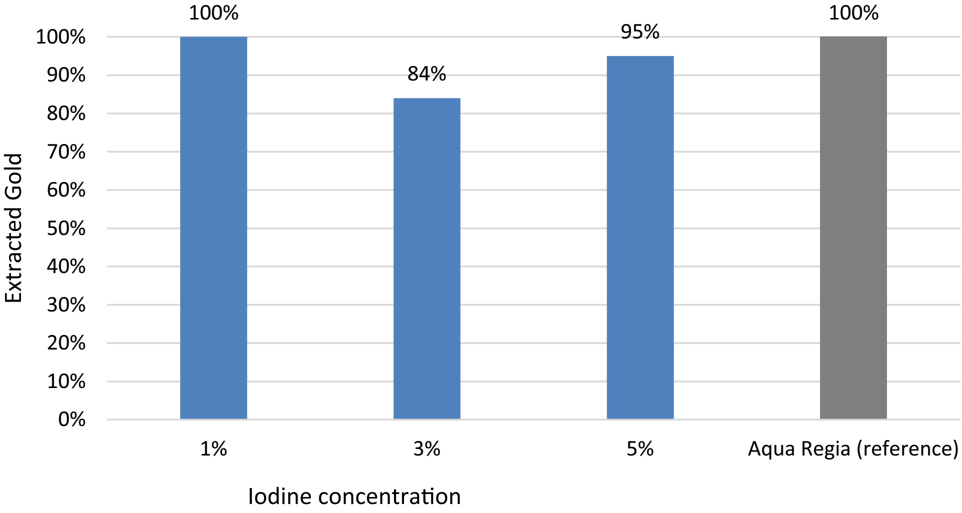

Fig. 5 Gold yield after 3 h for different iodine concentrations (color figure online)

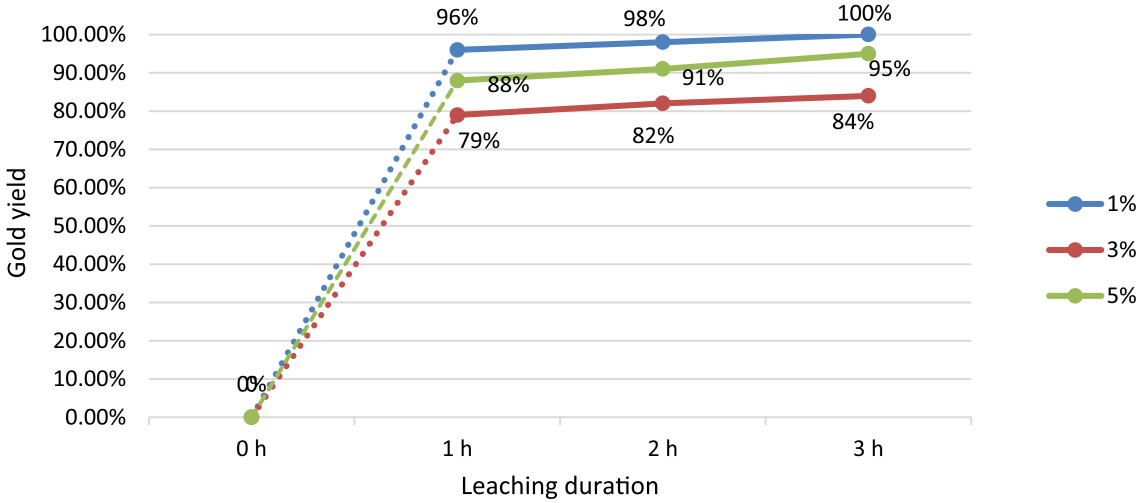

Fig. 6 Gold dissolution versus time for different iodine concentrations (dotted line is assumed) (color figure online)

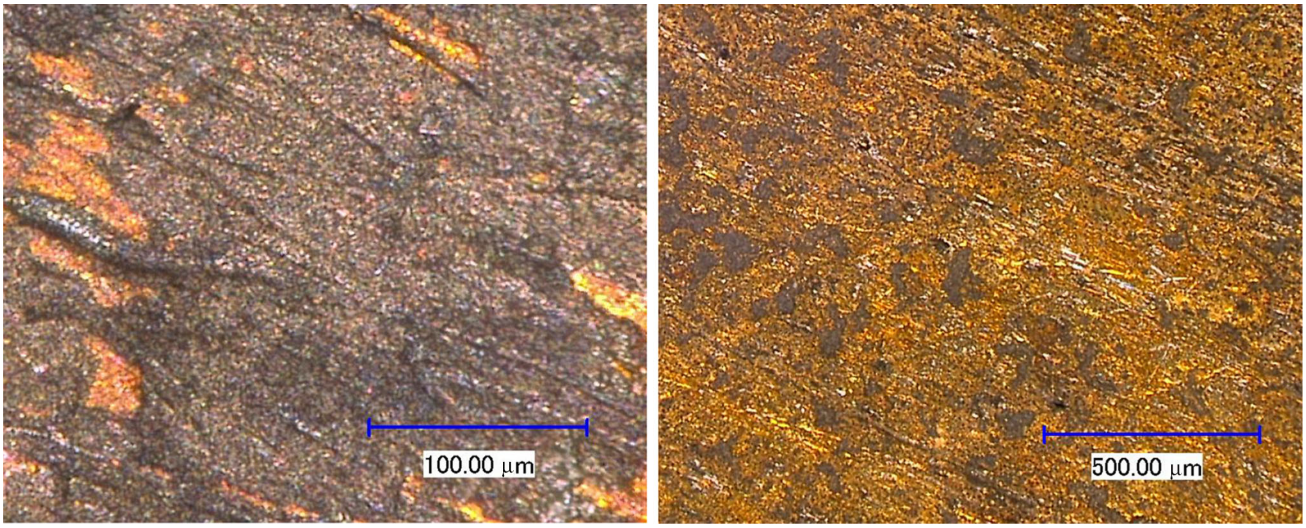

Fig. 7 Passivation of gold surface with thiosulfate (left, 0.03 M Cu^{2+} trial, magnification ×500) and thiourea (right, 30 g/l thiourea trial, magnification ×100) (color figure online)

reagents as a yield percentage (compared to Aqua regia results as a reference).

As previously discussed in "Thiourea," the reason for the disappointing results obtained from the thiourea trials can be attributed to its weak stability, where the compound formed from its oxidation decomposes overtime generating elemental sulfur that forms a passive layer over the surface of the material, thus hindering dissolution of metals. The passive layer, with similar composition to that of thiosulfate leaching (but thinner), is shown also in Fig. 7.

Table 6 Yield percentages of selected elements from pyrolyzed RAMs trials of thiosulfate and thiourea

	Cu (%)	Fe (%)	Ni (%)	Sn (%)	Au (%)
Thiosulfate	125.0	0.0	11.4	0.0	0.0
Thiourea	30.6	0.0	6.5	5.0	0.0

The percentage > 100% is attributed to the cupric ions added to the thiosulfate solution

MSA and LSSS

Despite the fact that the copper-based specimens of the first set are coated with gold and no other base metals are present, the gold coatings were "peeled" of the surface of the specimens, leaving clearly visible undissolved gold flakes in the solution even after 6 h of leaching in the first set (left for 3 extra hours in the solution) of MSA trials. Nonetheless, the 10 and 40% MSA solutions displayed a

Table 7 Yield percentages of selected elements from pyrolyzed RAMs trials of MSA and LSSS

	Cu (%)	Fe (%)	Ni (%)	Sn (%)	Au (%)
MSA	120.0	na	na	na	0.0
LSSS	0.56	0.0	0.0	0.0	0.0

"na" means that these elements were not analyzed

significant ability in leaching copper, with the chemical analysis for the samples showing the dissolution of 2.76 and 0.88 g/l of copper inside the 10 and 40% MSA solutions, respectively. The analysis also showed that almost no metals were leached during the 70% MSA trial, hence proving that the relationship between leaching efficiency and MSA concentration is inversely proportional. It was concluded that MSA solutions are highly selective for base metals, therefore it is not a feasible leaching reagent for precious metals especially when the raw material is electronic scrap, where a big amount of base metals is present. Further experiments on the feasibility of MSA as a copper leaching reagent are recommended for future research. Table 7 shows the results of the pyrolyzed RAMs trials for both MSA and LSSS.

Regarding LSSS leaching, the main problem was the precipitation of large amounts of elemental sulfur that was present in the solution. The lime sulfur solution used for the trials was synthesized in the lab. The ratio of elemental sulfur to calcium hydroxide to water used to prepare the solution was 2:1.3:60, which was reported to be the best ratio for leaching gold [32]. The mixture was stirred and heated for an hour to synthesize the solution. As these parameters failed to produce a suitable leaching solution, different preparation approaches and parameters for this solution is needed to prevent this kind of precipitation that completely hindered the process.

Comparative Assessment

The main conclusion of this study is that aqua regia and iodine were the only two reagents capable of successfully dissolving gold, with almost 100% yield. The main difference between the two reagents regarding their leaching capacity was their ability to leach base metals. As mentioned before, aqua regia has demonstrated a vigorous ability in leaching not only precious metals, but base metals as well. This was not the case for iodine leaching, as the results showed that almost no base metals were leached.

Figure 8 shows the separation factor values between gold and selected base metals during iodine leaching of pyrolyzed RAMs. The separation factor was calculated to show the extent of separation between gold and base metals, according to the following formula. Moreover, the leaching of the gold-coated copper specimens did not show any copper dissolution, i.e., the gold extraction was absolutely selective.

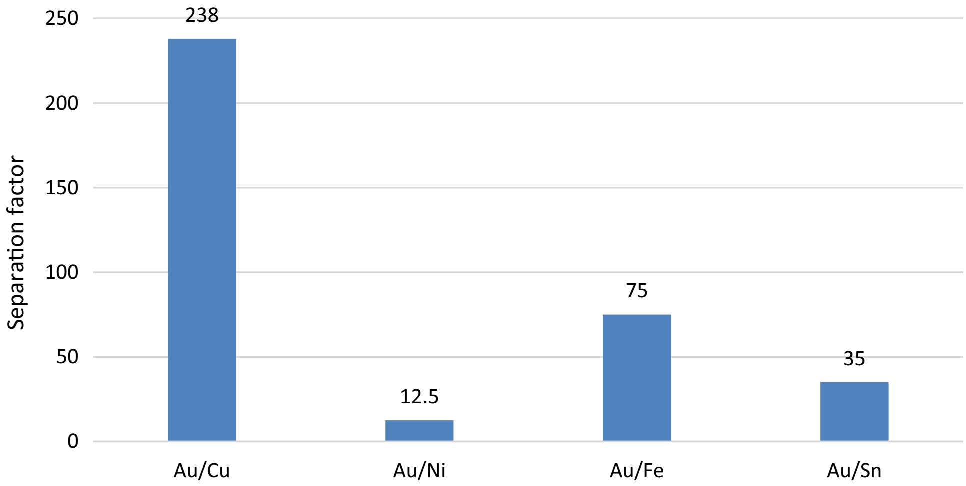

Fig. 8 Separation factors between gold and selected base metals based on the results of iodine's pyrolyzed RAMs trial (color figure online)

Table 8 Comparison between cyanide, aqua regia, and iodine as gold leaching reagents

Point of comparison	Cyanide	Aqua regia	Iodine
Dissolution rate	0.5 mg/cm^2/h [11]	> 7.5 mg/cm^2/h	> 7.5 mg/cm^2/h
Selectivity base metals/gold	High	Low	Very high
Toxicity	High	High	None

$$\mathrm{SF} = \frac{\text{Au yield}}{\text{BMs yield}} \tag{14}$$

A comparison between the two successful reagents and cyanide (shown in Table 8) was made to show their main advantages and disadvantages in order to decide which reagent is the better option and the most feasible substitute for cyanide leaching.

From the comparison, it is clear that iodine leaching has various advantages over the other two reagents. Therefore, iodine leaching will be furtherly investigated to see if it is able to produce even faster leaching rates. Winning gold from pregnant iodine solutions will also be investigated, with emphasis on the ability to reuse the leaching solution, as it is a very important aspect in the efforts of industrializing this process (due to the relatively high cost of iodine).

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