



Article

The Effect of the Redox Potential of Aqua Regia and Temperature on the Au, Cu, and Fe Dissolution from WPCBs [†]

Heini Elomaa , Sipi Seisko, Tero Junnila, Tuomas Sirviö, Benjamin P. Wilson, Jari Aromaa  and Mari Lundström *

Laboratory of Hydrometallurgy and Corrosion, Department of Chemical and Metallurgical Engineering, School of Chemical Engineering, Aalto University, P.O. Box 16200, FI-00076 Espoo, Finland; heini.elomaa@aalto.fi (H.E.); sipi.seisko@aalto.fi (S.S.); tero.junnila@aalto.fi (T.J.); tuomas.sirvio@aalto.fi (T.S.); ben.wilson@aalto.fi (B.P.W.); jari.aromaa@aalto.fi (J.A.)

* Correspondence: mari.lundstrom@aalto.fi

[†] This paper is an extended version of our paper published in 6th International Conference Quo Vadis Recycling, High Tatras, Slovak Republic, 6–9 June 2017.

Received: 22 August 2017; Accepted: 31 August 2017; Published: 1 September 2017

Abstract: Constant growth in waste electrical and electronic equipment (WEEE) levels necessitates the development of new, commercially viable recycling processes. Waste printed circuit boards (WPCBs) are a sub-group of WEEE that are of increasing interest due to their relatively high level of valuable metal content including Au, Ag, and platinum group metals (PGMs). Currently, precious metals like gold are mainly recycled from WEEE streams through copper smelting/refining; however, the possibility to peel gold from WPCBs prior to smelting, could offer advantages for recycling. In this study, the suitability of aqua regia for selective or partially selective gold leaching from un-crushed WPCBs was investigated. The redox potential of aqua regia solutions and the dissolution efficiencies of Au, Cu, and Fe from WPCBs were investigated at different temperatures (40–80 °C) and concentrations (2–32%) in batch leaching tests. The redox potential of aqua regia solution was found to depend on concentration and temperature. It is suggested that Au dissolution in aqua regia requires dissolved Cu²⁺ ions originating from the WPCB material to work. Au extraction (>50%) was shown to require a redox potential >700 mV with [Cu²⁺] > 2500 ppm, as a potential >850 mV alone was insufficient without cupric ions. Significant amounts of Au and Cu could be dissolved with only minor Fe dissolution at ≥8% aqua regia at 80 °C. Results suggest that leaching of uncrushed WPCBs in 8% aqua regia (T = 80 °C) can provide the opportunity for partial Au recovery prior to further processing.

Keywords: waste printed circuit boards; gold leaching; copper leaching

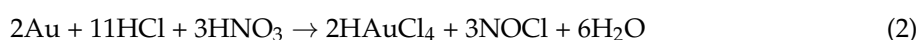
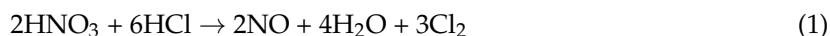
1. Introduction

In the past decades, the amount of waste electric and electronic equipment (WEEE) has been constantly growing, which influences the development of recycling processes. WEEE can be divided in many categories, which are defined in the EU/2012/19 [1] directive. The most valuable sub-group within WEEE are waste printed circuit boards (WPCBs) that contain significant amounts of valuable metals such as Au, Ag, and PGMs, increasing the interest towards the recycling of WPCBs and the recovery of valuable metals.

The difficulty of recycling WEEE lies in the heterogeneity of the materials. Aqua regia is the traditional medium for dissolving gold and platinum group metals in acid digestion, which is a common method of analyzing valuable metals [2]. In acid digestion, precious metals, such as gold,

are first leached in boiling aqua regia and after filtration analyzed by atomic absorption spectroscopy (AAS) or inductively coupled plasma mass spectroscopy (ICP). The drawback of pure aqua regia, however, is the aggressive and corrosive nature of the concentrated lixiviant. Veit et al. [3] concluded that aqua regia is usually used on the laboratory scale, but not industrially widely applied as hydrometallurgical process media. Additionally, Yannopoulos [4] stated that the dissolution of gold in aqua regia is used in analytical chemistry for either volumetric or gravimetric determinations of the soluble gold.

Hydrochloric acid in the presence of oxidants such as nitric acid, oxygen, cupric or ferric ions and manganese dioxide can dissolve gold [4]. Aqua regia is the combination of three parts concentrated hydrochloric to one part concentrated nitric acid and is well known to vigorously attack gold. The reactions for gold leaching in aqua regia can be described as in Equations (1)–(3) [4,5]:



Concentrated aqua regia has been proven to be efficient lixiviate for the simultaneous leaching of gold, silver, and palladium [6]. However, research by Zhang and Xu [7] suggested that aqua regia leaching of WEEE is not selective and can aggressively digest both base and precious metals concurrently. According to Lekka et al. [8], aqua regia was found to be an efficient leaching solution for metals from PCB powders. In addition, Sheng and Etsell [9] investigated the leaching of gold from computer circuit boards using aqua regia after pre-leaching the base metals by nitric acid. Furthermore, Park et al. investigated the dissolution of gold, silver, and palladium from PCBs, and they suggested a method for recovering precious metals by aqua regia leaching. For gold, a liquid–liquid extraction with toluene and recovery as nanoparticles using dodecanethiol and sodium borohydrate was suggested. Park et al. stated that aqua regia is efficient leachant for PCBs as gold, silver, and palladium can be separated at the same time [6]. This study aims at investigating diluted aqua regia as a potential media for selective or partially selective leaching of visible gold from PCBs. Simultaneously the dissolution of copper and iron is investigated.

2. Experimental

2.1. Material

In this study, the dissolution of gold available for leaching on WPCBs was investigated in aqua regia solutions batch leaching tests. Additionally, the redox potential of aqua regia solutions was studied to ascertain any correlation between the potential and gold leaching phenomenon.

The challenge in non-crushed WPCB leaching is the non-homogeneous nature of the raw material. In this study, WPCBs originating from industrial telecommunication center PCBs were used. This type of raw material provides relatively homogeneous nature as one side of the WPCBs is entirely gold coated, (Figure 1a). Larger electronic components such as capacitors and transistors were removed from the surface of the WPCB, thus standardizing the raw material. For the batch leaching tests, the raw materials was not crushed, but cut to ca. 5 cm × 5 cm squares. This in order investigate whether gold can be dissolved selectively or semi-selectively from the WPCBs, simultaneously minimizing base metal dissolution from the WPCB structure. Total gold and silver content in the raw material was analyzed using a Pb-fire assay (Labtium, Outokumpu, Finland), whereas other metal contents were determined by the total digestion. The chemical analysis of the gold in raw material (Parallel Samples 1 and 2) is presented in Table 1. Two samples were analyzed by the fire-assay method, and the results showed remarkable variation in precious metals, even with two parallel GFAAS analysis, due to challenges in the analysis of this kind of secondary raw material. In addition, the crushing conducted prior to

analysis is suggested to decrease the sample precious metal content, as the precious metals are known to enrich into dust fraction, remaining partially in the crusher [10].

Table 1. Parallel chemical analysis of waste printed circuit board (WPCB) raw material (Samples 1 and 2) used in leaching experiments, element amount presented as mg/kg of WPCB. For Sample 2, only Au and Ag were analyzed (n.a. = not analyzed).

	Au	Ag	Cu	Fe	Sn	Al	Ni	Pb	Zn
Sample 1	372	570	250,000	37,300	11,670	49,800	8830	30,000	14,600
Sample 2	421	245	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

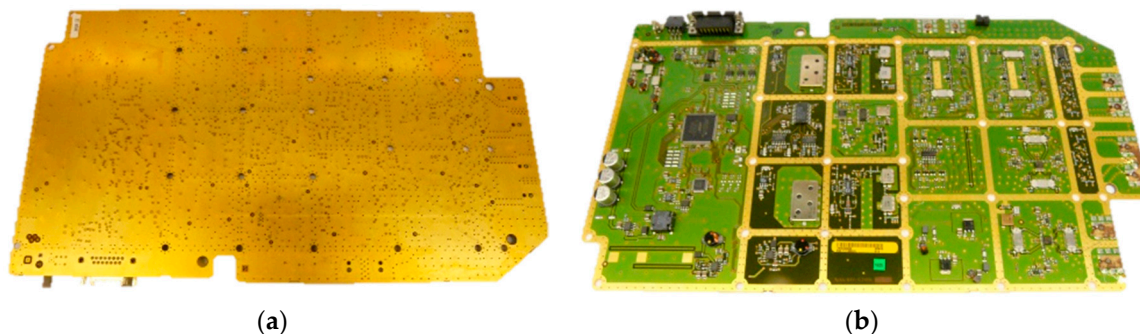


Figure 1. The WPCB raw material investigated: (a) the gold-coated side; (b) the side where larger electronic components have been removed.

2.2. Methods

The gold leaching experiments were carried out in aqua regia solutions with varying concentrations, the molar ratio of the nitric to hydrochloric acid kept constantly at 1:3 with dilution to distilled water. Table 2 outlines the concentration of the aqua regia solutions investigated. Additionally, the amounts of free chlorides in solution—calculated based on the hydrochloric acid molarity—is also shown.

Table 2. Aqua regia concentrations and corresponding chloride concentration in the redox test series (R1–R1) and in the batch leaching test series used in WPCB leaching (L1–L5). In addition, the temperature range investigated in the test series R1–R10 and L1–L5 is presented.

Aqua Regia Concentration	Redox Test Series	Batch Leaching of WPCB, Test Series	Chloride [Cl [−]], M
0.01%	R1 (25–80 °C)		0.003
0.1%	R2 (25–80 °C)		0.026
0.5%	R3 (25–80 °C)		0.129
1%	R4 (25–80 °C)		0.257
2%	R5 (25–80 °C)	L1 (40–80 °C)	0.515
4%	R6 (25–80 °C)	L2 (40–80 °C)	1.030
5%	R7 (25–80 °C)		1.286
8%	R8 (25–80 °C)	L3 (40–80 °C)	2.058
16%	R9 (25–80 °C)	L4 (40–80 °C)	4.116
32%	R10 (25–80 °C)	L5 (40–80 °C)	8.233

The redox potential of aqua regia solutions (R1–R10) was studied at eight different temperatures: 25, 30, 35, 40, 50, 60, 70, and 80 °C. The solution redox potential was measured by immersing a reference electrode (vs. Ag/AgCl, Red Rod ref 201) in solution with a platinum wire. A Lauda Immersion Thermostat A100 provided temperature control. For the batch leaching experiments (L1–L5), WPCBs were cut into ca. 5 × 5 cm pieces, and the experiments were conducted at 40 °C and 80 °C in a 1 dm³ glass reactor, heated by Aqualine AL 25 water bath with thermostatic control. The rate of oxygen sparging (1 NL/min) and rotational speed (100 rpm) were kept constant in every experiment. Leaching time was 2 h. Solution sampling was conducted with a glass pipette at time intervals of 1, 3, 5, 10, 20, 30, 60, and 120 min for subsequent analysis by atomic absorption

spectroscopy (AAS, Thermo Scientific iCE 3000 Series, Waltham, MA, USA). Solutions samples were filtered, and 2 drops of 50% nitric acid were added to the samples in order to prevent sedimentation.

Solution additions were performed in order to maintain the liquid/solid ratio and mitigate the effects of evaporation. The evaporation was determined during a 2 h leaching test in all studied temperatures, and the evaporating volume of liquid added at 10 min intervals. All redox potentials were measured using Ag/AgCl in saturated KCl as reference electrode (Red Rod ref 201) and platinum as the counter electrode.

3. Results and Discussion

3.1. Redox Potential

Figure 2 shows the measured redox potentials in investigated solutions (R1–R10) at temperatures between 25 and 80 °C. The results show that the redox potential increases both with the increase in aqua regia concentration and with increases in temperature. The redox potential was shown to range from 540 to 900 mV vs. Ag/AgCl and obeyed the Nernst equation—i.e., the well-known relationship between reduction potential, temperature, and concentration (activity) of the electroactive species—except at the most dilute point, 0.01% aqua regia, as demonstrated by the data presented in Figure 2.

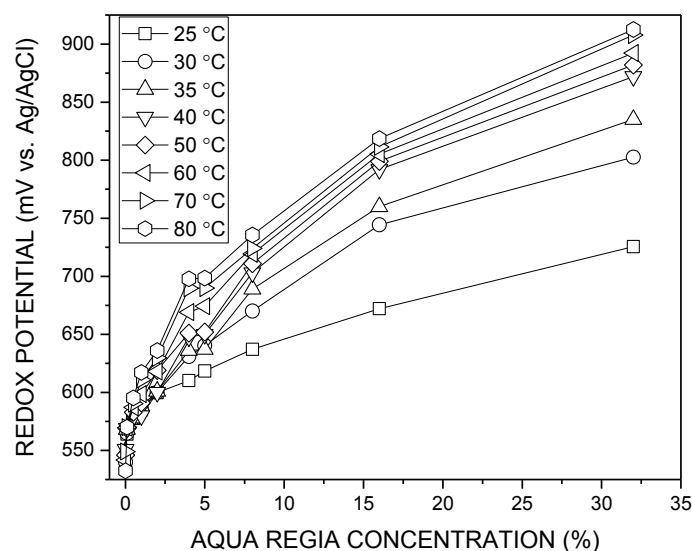


Figure 2. The redox potential of aqua regia solutions at temperatures of 25, 30, 35, 40, 50, 60, 70, and 80 °C as a function of aqua regia concentration.

3.2. Batch Leaching

During the batch leaching tests, the redox potential was measured at each solution sampling time to observe the oxidative power of the solution as a function of WPCB leaching time (Figure 3). The redox potential of the aqua regia leaching solution varied in the range 300–900 mV vs. Ag/AgCl after the raw material exposure. It can be seen that the redox potential of the leaching solution generally declined quickly after the samples were immersed into the leaching solution (aqua regia \leq 16% at $T = 40$ °C and aqua regia \leq 4% at $T = 80$ °C). This indicates that the initial leaching reactions consumed the oxidative species present in the solution. As the dissolution progressed the metal concentration in the solution increased. The applied air purging oxidized the dissolved metallic species in the solution resulting in redox potential increase with time. The opposite phenomenon, redox potential remaining in the same level or slightly increasing from the initial aqua regia potential was typical at higher concentrations and temperatures (aqua regia 32% at $T = 40$ °C and aqua regia \geq 8% at $T = 80$ °C).

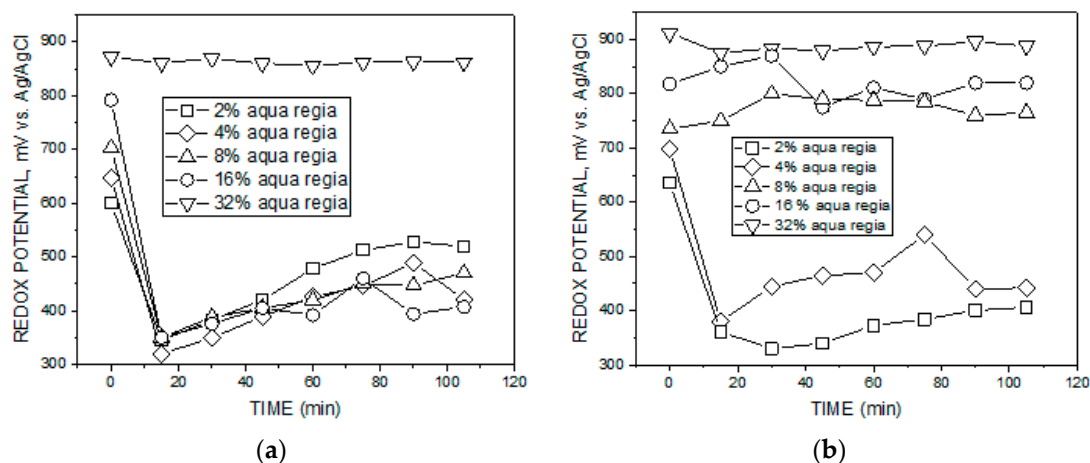


Figure 3. Aqua regia redox potential prior to raw material exposure ($t = 0$) and during the WPCB batch leaching tests (L1–L5) at temperatures (a) 40 °C and (b) 80 °C.

Figure 4 presents the PCB pieces after leaching experiments in 8% aqua regia solution at temperatures of 40 °C (a) and 80 °C (b), respectively. As can be observed, after leaching at 40 °C (Figure 4a) gold is still visible on the PCB surface. After leaching in 8% aqua regia solution at 80 °C (Figure 4b), leaching of visible Au from the WPCB material was evident and no similar shiny gold could be seen.

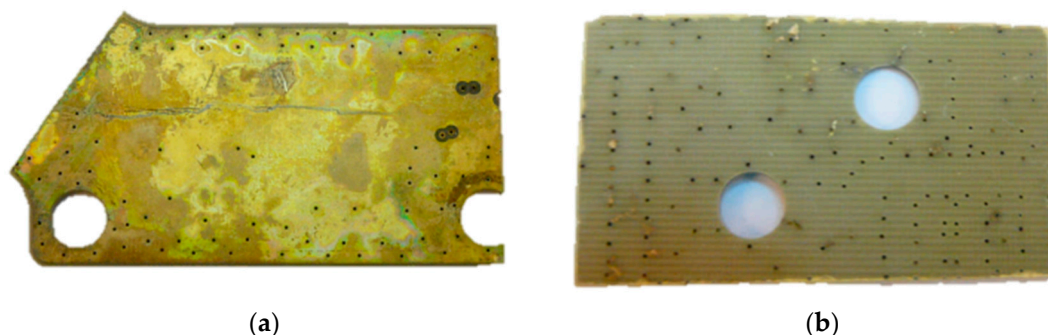


Figure 4. The WPCB pieces after leaching experiment L3 in 8% aqua regia at temperatures (a) 40 and (b) 80 °C.

Two-hour batch leaching experiments (L1–L5) were conducted with aqua regia leaching solution concentrations 2–32% for the WPCB material. The dissolution of Cu and Au is presented in Figures 5 and 6 as normalized to the dissolution of these elements in 32% aqua regia at 80 °C (L5, the most aggressive leaching media). This in order to define the metal extraction efficiency into the solutions compared to maximum extraction into the solution.

Figure 5 shows that, generally, an increase in temperature increases Cu extraction in the solution. At 32% aqua regia ($T = 80$ °C), 30 min was enough for maximum Cu dissolution (Figure 5a); however, the maximum Cu dissolution could also be also achieved at 16% ($T = 80$ °C) after 120 min of leaching (Figure 5c). The lower temperature ($T = 40$ °C) was shown to leach only minor amount of Cu with $t \leq 60$ min. When solution analysis was compared to the original Cu content in the WPCB solid raw material (Table 1), the maximum Cu recovery that could be achieved in any of the leaching experiments was 61%. The Cu recovery of 61% can be explained by the fact that only part of the copper is available for leaching in the non-crushed WPCB material, whereas a big part of Cu is in the laminated WPCB structure not exposed to the leaching solution.

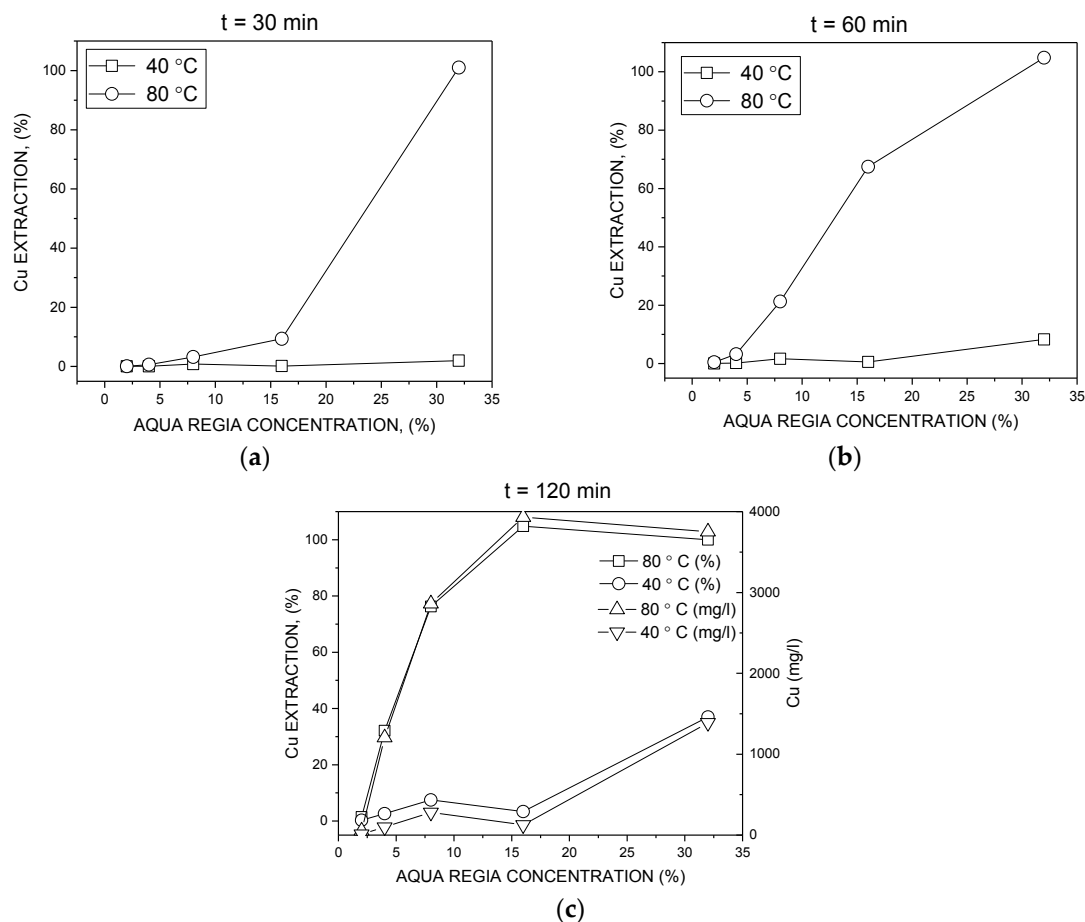


Figure 5. The extractions of copper at $t = 30$ min (a); $t = 60$ min (b); and $t = 120$ min (c). Extraction presented as % at left y-axis (a–c) and mg/L at right y-axis (c).

The determination of the Au recovery was challenging, as the recoveries calculated (solution analysis vs. initial solid analysis in Table 1) gave Au extraction values $>100\%$. This is due to the error margins related to the WPCB-type material pre-treatment, during which the sample is crushed and part of the Au can also be lost to the crusher as gold dust [10]. Additionally, the gold analysis from this type of secondary raw material is not straightforward. Table 1 shows remarkable variation, even between two identical samples. Therefore, the Au extraction was observed as the relative recovery, i.e., versus the maximum dissolved amount of gold achieved. Figure 6 shows that, generally, an increase in temperatures increases Au extraction in the solution. At 32% aqua regia ($T = 80$ °C), 30 min was sufficient for maximum Au dissolution. Equally high Au extraction could not be achieved in any of the more dilute aqua regia solutions. Additionally, leaching times ≤ 60 min (Figure 6a,b) did not provide maximum Au dissolution in any other conditions than at 32% aqua regia. The lower temperature ($T = 40$ °C) was shown not to leach Au. However, it can be seen that 8% aqua regia at $T = 80$ °C was able to dissolve over half of the maximum leachable gold at $t = 120$ min.

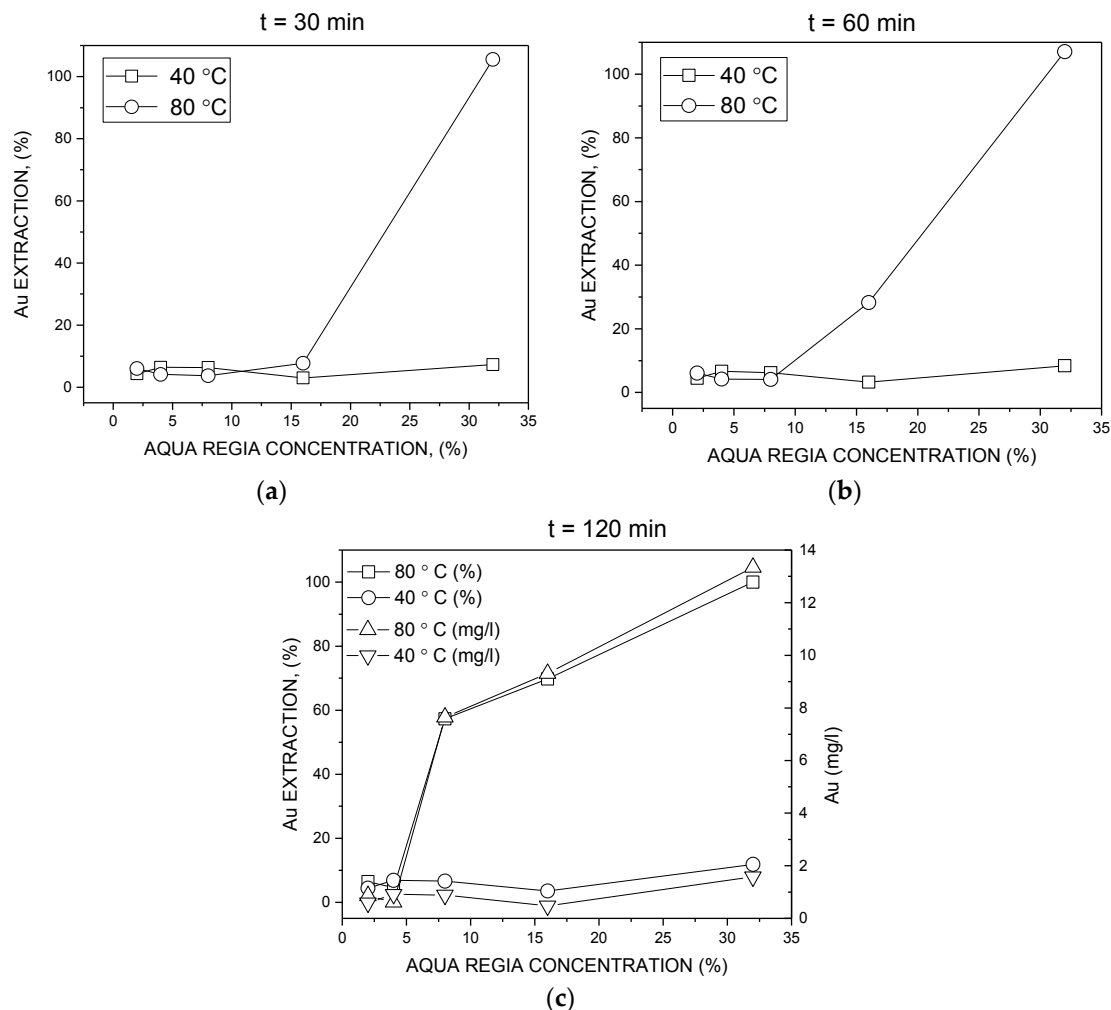


Figure 6. The extractions of gold at (a) $t = 30$ min; (b) $t = 60$ min; and (c) $t = 120$ min.

When Fe solution analysis was compared to the original Fe content in the WPCB solid raw material (Table 1), it was observed that only minor Fe dissolved. The maximum Fe extraction in any of the experiments (L1–L5) was low, ~3% (max 30.1 mg/L in solution in 16% aqua regia at 80 °C). This suggests that leaching of Cu and Au from non-crushed WPCBs is selective to Fe and that Fe present in the WPCB is mostly in the laminated structure, not available for leaching.

When Figure 3 is compared to Figures 5 and 6, it can be suggested that a high Au extraction (>50% of maximum extraction) required a redox potential >700 mV vs. Ag/AgCl (L3–L5, $T = 80$ °C) and that the maximum Au extraction was achieved at a redox potential >850 mV vs. Ag/AgCl (L5, $T = 80$ °C). However, a high redox potential (>850 mV vs. Ag/AgCl) alone was not enough to dissolve gold (L5, $T = 40$ °C). It seems that Au dissolution was heavily supported by dissolved Cu^{2+} ions, acting as gold oxidant [11], high Au extractions (>50%) being achieved in solutions with $[\text{Cu}^{2+}] > 2500$ ppm. The results indicate that 8% aqua regia ($T = 80$ °C, $t = 120$ min) can provide a process window, where 57% of the visible gold can be dissolved. Simultaneously, 44% of the Cu is dissolved. The dissolution from non-crushed WPCBs is selective towards iron. These process conditions provide the recycling operator a possibility of partially dissolving Au and Cu prior to further processing via, e.g., a primary copper refinery route [12].

4. Conclusions

The redox potential characteristics of aqua regia solutions were determined in this study and were found to increase as a function of both increased concentration and temperature. Results showed that redox potential ranged from 540 to 900 mV vs. Ag/AgCl in the studied range (aqua regia concentration = 0.01 to 32% and temperature = 40–80 °C. In addition, the redox potential measured in a pure aqua regia solution obeyed the Nernst equation with the exception of the lowest aqua regia concentration of 0.01%. The redox potentials varied between 300 and 900 mV vs. Ag/AgCl after the WPCB exposure into the aqua regia solution.

The batch leaching tests for WPCB raw material suggested that high redox (>850 mV vs. Ag/AgCl) potential alone did not allow Au dissolution, but Au dissolution was heavily supported by aqua regia concentration and dissolved Cu^{2+} ions, acting as gold oxidant [11]. High Au extractions (>50%) were achieved in solutions with $[\text{Cu}^{2+}] > 2500$ ppm at redox potentials >700 mV vs. Ag/AgCl. The results indicate that 8% aqua regia ($T = 80$ °C, $t = 120$ min) can provide a process window, where most (57%) of the visible gold can be dissolved with simultaneous Cu dissolution (44%). In the investigated leaching environment, the dissolution of Au and Cu is selective towards iron.

It can be concluded that the results provide systematic data about the use of aqua regia for Au, Cu, and Fe leaching from the WPCB material. Aqua regia can be seen as a potential hydrometallurgical pre-treatment step to separate partially gold and copper from non-crushed WPCB with only minimal iron dissolution.

Acknowledgments: The authors would like to thank the Emil Aaltonen Foundation (Ympäristöystävällistä kultaa—project funding), the CMEco project (7405/31/2016), and the ARVI project funded by Finnish innovation agency TEKES for financial support. “RawMatTERS Finland Infrastructure” (RAMI) and NoWASTE-project (297962) supported by the Academy of Finland and are greatly acknowledged.

Author Contributions: Heini Elomaa and Sipi Seisko conceived and designed the experiments. Tero Junnila and Tuomas Sirviö performed the experiments. Heini Elomaa analyzed the data. Jari Aromaa and Sipi Seisko contributed to the design of experiments and analysis of the data. Heini Elomaa wrote the paper and significant contribution to writing was made by Benjamin P. Wilson and Mari Lundström. Mari Lundström is the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. European Commission. *Directive 2012/19/EU of the European Parliament and of the Council of 4 of July on Waste Electrical and Electronic Equipment*; Official Journal of the European Union: Strasbourg, France, 2012.
2. Marsden, J.; House, I. *The Chemistry of Gold Extraction*, 2nd ed.; The Society of Mining, Metallurgy and Exploration: Littleton, CO, USA, 2006; p. 650, ISBN 10-0-87335-240-8.
3. Veit, H.M.; Bernardes, A.M.; Ferreira, J.Z.; Tenório, J.A.S.; de Fraga Malfatti, C. Recovery of copper from printed circuit boards scraps by mechanical processing and electrometallurgy. *J. Hazard. Mater.* **2006**, *137*, 1704–1709. [[CrossRef](#)] [[PubMed](#)]
4. Yannopoulos, J.C. *The Extractive Metallurgy of Gold*; Van Nostrand Reinhold: New York, NY, USA, 1991; p. 281, ISBN 0-442-31797-2.
5. Cui, J.; Zhang, L. Metallurgical recovery of metals from electronic waste: A review. *J. Hazard. Mater.* **2008**, *158*, 228–256. [[CrossRef](#)] [[PubMed](#)]
6. Park, Y.J.; Fray, D.J. Recovery of high purity precious metals from printed circuit boards. *J. Hazard. Mater.* **2009**, *167*, 1152–1158. [[CrossRef](#)] [[PubMed](#)]
7. Zhang, L.; Xu, Z. A review of current progress of recycling technologies for metals from waste electrical and electronic equipment. *J. Clean. Prod.* **2016**, *127*, 19–36. [[CrossRef](#)]
8. Lekka, M.; Masavetas, I.; Benedetti, A.V.; Moutsatsou, A.; Fedrizzi, L. Gold recovery from waste electrical and electronic equipment by electrodeposition: A feasibility study. *Hydrometallurgy* **2015**, *157*, 97–106. [[CrossRef](#)]
9. Sheng, P.P.; Etsell, T.H. Recovery of gold from computer circuit board scrap using aqua regia. *Waste Manag. Res.* **2007**, *25*, 380–383. [[CrossRef](#)] [[PubMed](#)]

10. Saulny, M. The Behavior of Printed Circuit Boards in Knife Shredder and Its Effects on the Recycling Process. Master's Thesis, Aalto University, Espoo, Finland, 2015.
11. Lampinen, M.; Seisko, S.; Forsström, O.; Laari, A.; Aromaa, J.; Lundström, M.; Koiranen, T. Mechanism and kinetics of gold leaching by cupric chloride. *Hydrometallurgy* **2017**, *169*, 103–111. [[CrossRef](#)]
12. Hagelüken, C. Recycling of electronic scrap at Umicore's integrated metals smelter and refinery. *Erzmetall* **2006**, *59*, 152–161.



© 2017 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).