

EFFECT OF H₂O₂ AND MnO₂ AS OXIDATORS OF GOLD AND COPPER LEACH PROCESSES FROM PRINTED CIRCUIT BOARDS

Yudha Pratesa, Aji Wibisono, Wahyuaji Narottama Putra,

Yunita Sadeli, A. Zakiyuddin and Sri Harjanto

Department of Metallurgical and Materials Engineering, Universitas Indonesia

Kampus Baru UI, Depok, 16424

E-mail: sri.harjanto@ui.ac.id

Received: 7 January 2019

Revised: 12 March 2019

Accepted: 26 March 2019

ABSTRACT

EFFECT OF H₂O₂ AND MnO₂ AS OXIDATORS OF GOLD AND COPPER LEACH PROCESS-ES FROM PRINTED CIRCUIT BOARDS. In general, electronic waste management in the form of printed circuit boards (printed circuit boards / PCBs) is carried out by the process of removing components and taking precious metals that are easily recycled. However, in Indonesia, the recycling process for extracting precious metals has not been much processed, even though they contain precious metals such as copper and gold. This research was conducted to find a more economical and environmentally friendly treatment process by using an oxidizer of Hydrogen Peroxide (H₂O₂) and Manganese Oxide (MnO₂) and reducing the level of HCl used. Observation of metal leaching results using Atomic Adsorption Spectroscopy (AAS) showed the value of recovery (recovery) of gold and copper reached 59.1% and 59.8% for 0.5M HCl + 2.5% H₂O₂. However, the recovery value of copper has reached its optimum point at the addition of 1.5% H₂O₂. The use of 3% & 5% MnO₂ results in recovery values of 12% and 24% for gold and copper. Observation of the cross section shows the dissolution of the copper metal from the PCB and accompanied by a change in the color of the solution from clear to green, the more concentrated the more the amount of dissolved copper metal shows the characteristic of CuCl solution. The results of the comparison of the two types of oxidizers show that H₂O₂ is better than MnO₂ in producing higher Cu and Au metals more than 3 times.

Keywords: Oxidizing, Leaching, HCl, Printed Circuit Board

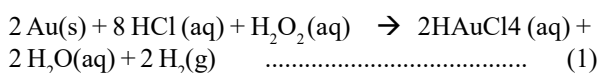
ABSTRAK

PENGARUH H₂O₂ DAN MnO₂ SEBAGAI OKSIDATOR EMAS DAN TEMBAGA HASIL PROSES PELINDIAN DARI PAPAN SIRKUIT TERCETAK. Pada umumnya pengolahan limbah elektronik berupa papan sirkuit tercetak (*printed circuit board/PCB*) dilakukan dengan proses pelepasan komponen dan pengambilan logam berharga yang mudah didaur ulang. Namun demikian di Indonesia, proses daur ulang untuk mengekstraksi logam berharga belum banyak diolah, meskipun terkandung logam berharga seperti tembaga dan emas. Penelitian ini dilakukan untuk mencari proses pengolahan yang lebih ekonomis dan ramah lingkungan dengan menggunakan oksidator Hidrogen Peroksida (H₂O₂) dan Mangan Oksida (MnO₂) dan menurunkan kadar HCl yang digunakan. Hasil pengamatan logam hasil pelindian menggunakan Atomic Adsorption Spectroscopy (AAS) menunjukkan nilai perolehan kembali (*recovery*) emas dan tembaga mencapai 59.1% dan 59.8% untuk 0.5M HCl + 2.5% H₂O₂. Namun, nilai *recovery* tembaga telah mencapai titik optimum pada penambahan 1.5 % H₂O₂. Penggunaan 3 % & 5 % MnO₂ menghasilkan nilai *recovery* sebesar 12% dan 24% untuk emas dan tembaga. Pengamatan penampang melintang menunjukkan terjadi pelarutan logam tembaga dari PCB dan disertai perubahan warna larutan dari bening menjadi kehijauan yang semakin pekat semakin banyaknya jumlah logam tembaga terlarut menunjukkan ciri larutan CuCl. Hasil perbandingan dari kedua jenis oksidator menunjukkan bahwa H₂O₂ lebih baik dari MnO₂ dalam menghasilkan perolehan logam Cu dan Au yang lebih tinggi lebih dari 3 kalinya.

Kata kunci: Oksidator, Pelindian, HCl, Papan Sirkuit Cetak

INTRODUCTION

Urban mining is mining using community waste as raw materials. Electronic waste has the potential to become as good as natural ore. At the present time, various methods are being developed to recycle electronic waste such as pyrometallurgical, hydrometallurgical (leaching) and electrometallurgical processes. The impact of the pyrometallurgy process from this process is the emission of CO_2 gas and hazardous vapors from printed circuit boards (PCB). An alternative way to this process is by using leaching methods. The key is the selection of leachate in order to reduce waste processing and be more economical. Harjanto et al., 2006 found that a mixture of HCl and H_2O_2 succeeded in leaching stainless metals such as platinum and palladium from residual automotive catalyst waste [1]. The addition of H_2O_2 as an oxidizer in HCl can help manufacture free chloride in solution which will make the reaction of dissolving valuable metals such as gold. Chemical reactions that occur in this leaching are [2]



Small chlorine ions are expected to be easier to penetrate through the protective layer of the PCB. While the reason of using Manganese Oxide as an alternative oxidative in this study because manganese oxide is a by-product waste from steel processing and is a strong oxidizing agent. Research by Behnamfard 2013, states that using sulfuric acid and H_2O_2 and getting recovery of gold and copper which is quite high but after going through several stages of the process, it is considered less economical. [3-5]. The highest gold acquisition process is the use of king water (a mixture of HNO_3 and HCl are concentrated in a ratio of 1: 3), but this leachate is very corrosive so it is very difficult to handle in its application. Another leachate that is commonly used to leach gold is cyanide acid, [6,7] but the use of cyanide acid is very limited because of the potential to cause deadly poisons.

The use of Manganese oxide was inspired by the use of a galvanic corrosion process between the minerals chalcopryrite and pyrite so as to produce copper metal leaching in a solution called the galvanox process [8,9]. Nakazawa showed the formation of a copper leaching process due to the galvanic process between Manganese (IV) oxide and chalcopryrite. [9,10] Manganese oxide was chosen because of its availability in the form of iron and steel processing residues, making it quite economical to develop [11].

It is expected that from the use of these two oxidizing agents, it can reduce the concentration of strong acid HCl so that the waste from PCB processing does not damage the environment and is easy to handle. This research is carried out to look for a more economical

and environmentally friendly process using the Hydrogen Peroxide (H_2O_2) oxidizer and Manganese Oxide (MnO_2) and reduce the level of HCl used.

EXPERIMENTAL METHOD

Materials and Tools

The printed circuit board (PCB) used is from the same source, the telecommunications transmitter. The process begins with a reduction in the size of the PCB using a ProShex 3S / 6R manual cutting tool to sizes ranging from 1.0 - 2.0 cm. After that the sample is weighed with analytical scales to get the same weight for every dissolving process with a weight of 50 grams.

The process of making the solution is done by using a dilution process of 10.2 M HCl solution to 0.5 M HCl using aquades. While the H_2O_2 solution was diluted from 30% to 1.5% and 2.5%. The volume ratio of each solution in the HCl + H_2O_2 mixture is 1: 1.

A slight difference was made in the mixture of HCl + MnO_2 , namely the preparation of HCl solution with a concentration of 0.5 M of 500 ml then MnO_2 powder was added by 3% & 5% in the percentage of total weight. Type of manganese (IV) oxide analytical grade. In addition, a water solution (concentrated) was also made with concentrated concentrations of 10.2 M for HCl and 13.41 M in a ratio of 1: 3. This solution was made as an assumption that this solution could dissolve all metals in the PCB up to 100% for gold and copper.

Working Procedure

Four types of solutions were prepared as a comparison in this study. First is the king's water (aqua regia) as the control solution, which is assumed to be able to shed most of the gold inside the PCB. King water is made by mixing concentrated nitric acid (HNO_3) and concentrated hydrochloric acid (HCl) in a ratio of 1: 3. The next solution is a 0.5 M HCl solution without an oxidizer, and a 0.5 M HCl solution with an H_2O_2 oxidizer, and the final solution is 0.5 M HCl with MnO_2 .

The oxidation variation is based on the percentage of oxidizing in dissolving, that is 1.5% and 2.5%. Leaching was performed with a ratio of solid to liquid ratio of 1:50 at a temperature of 55 ° C with stirring speed using a magnetic stirrer that is 400-500 rpm for 120 minutes. After the leaching of the PCB is completed, the solution is then filtered to separate solid particles that are not dissolved. The filtering solution is then subjected to the Atomic Adsorption Spectroscopy (AAS) test.

The calculation of the recovery value of each solution is obtained by comparing the results of the AAS between the solution to be studied with King water

(aqua regia) which is used as a control solution with equation (3).

$$Recovery = \frac{Concentration (sample)}{Concentration (aqua regia)} \times 100\% \quad (2)$$

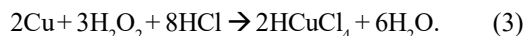
On the other hand, observations of changes in the color of the solution and physical morphology of the PCB after immersion are also carried out. Morphological observations were carried out on a cross section using an optical microscope followed by metallographic preparations using SiC sandpaper and followed by polishing using TiO₂.

RESULT AND DISCUSSION

Physical Conditions of Leached Results

Physical analysis was carried out on the results of the printed circuit board leaching process with hydrochloric acid solution, hydrochloric acid with hydrogen peroxide oxidizing agent, and aqueous (aqua regia) water solution. Color changes occur in each solution and become more concentrated with the higher levels of oxidizing given as shown in Figure 1.

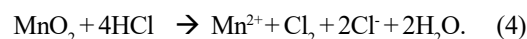
The blue color is seen due to the reaction between hydrochloric acid and copper to form the compound CuCl₂. The reaction is



This is consistent with the observations of Vogel (1990) that copper (II) salts are generally blue at low chloride ion levels and green at high chloride ion levels. [12] This is shown in the king's water yield (aqua regia) which contains high HCl concentrations showing green while 0.5 M HCl shows blue. The dark blue color shows that the amount of copper that can be dissolved by a leachate solution increases with the addition of an oxidizing agent.

While the results of leaching using blue MnO₂ formed were not as intense as the results of

leaching using H₂O₂ and found the remaining MnO₂ deposits. This shows that the low MnO₂ solubility in 0.5 M HCl solution. However. Color changes are still seen in Figure 1 and are more concentrated than without using an oxidizer. This shows that MnO₂ actually has a significant effect on leaching. The leaching mechanism by MnO₂ is initiated by the reaction



The resulting Cl₂ compound will bind Cu and Au to form AuCl₄⁻ or CuCl₂. In addition to changes in color, physical observations are carried out under cross-sectional conditions of the sample after leaching results.

Figure 2 shows the results of observations under an optical microscope showing changes in the shape of the layer is characterized by the occurrence of thinning in some parts of the copper layer on the leaching results using H₂O₂ oxidizer. However, in conditions without the addition of oxidizing agents, the leaching results are still intact. Indicates that not many layers are dissolved by the leachate solution, so the results are consistent with the color changes that occur. Much different results can be seen from leaching using aqua regia. Almost all layers have been removed after the immersion process.

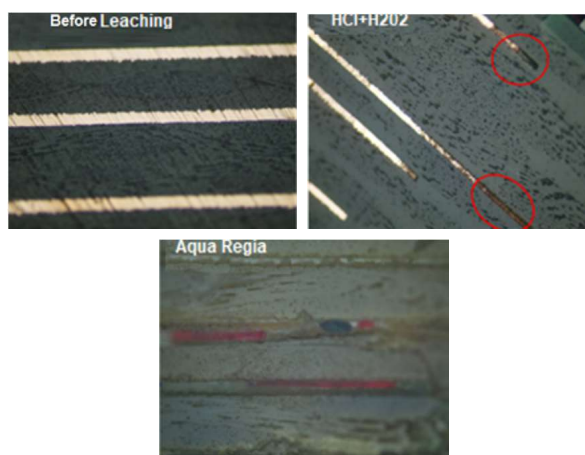


Figure 2. Physical Changes in the copper layer printed circuit board of each leachate solution

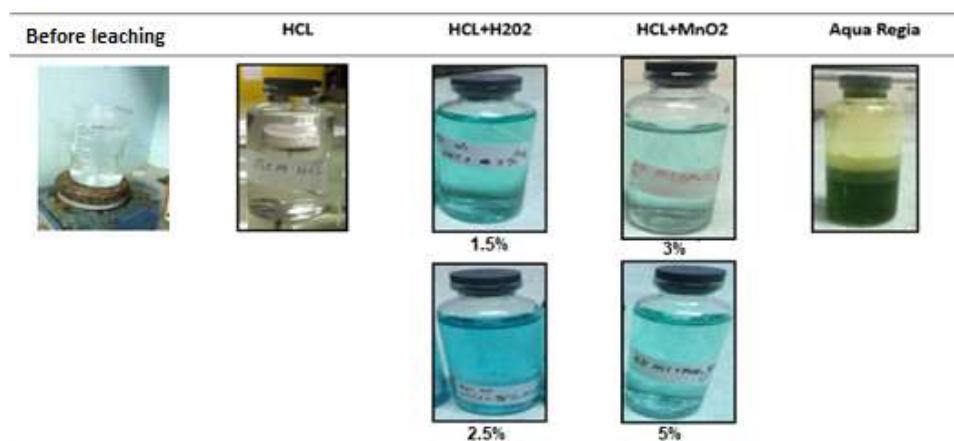


Figure 1. Color of leaching process results from each leachate solution.

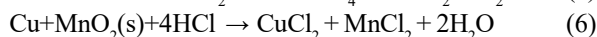
Dissolved Metal Analysis

Table 1 shows the results of dissolved metal testing in each leachate solution. The highest water yield of aqua regia (aqua regia) is used as a reference as a control solution because it is considered capable of stripping most of the copper layers as shown in Figure 2. Leaching using HCl without the addition of an oxidizer is not able to leach gold and copper. But after adding H₂O₂ oxidizer, the amount of gold and copper increased significantly to 7.85 ppm for gold and copper amounting to 7,619 ppm. The use of MnO₂ powder can also increase the amount of dissolved metal even though not as much as H₂O₂.

Table 1. AAS test results for each leachate solution

Solution	Au (ppm)	Cu (ppm)
0,5 M HCl	0	4,15
0.5 M HCl + 1.5 % H ₂ O ₂	2.66	5.673
0.5 M HCl + 2.5 % H ₂ O ₂	7.85	7.619
0.5 M HCl + 3% MnO ₂	0.86	2.135
0.5 M HCl + 5% MnO ₂	1.72	3.154
Air raja (aqua regia)	13.3	12.749

The reactions that occur in the leach process using Manganese oxide are as follows [13]:



The release of chlorine gas due to the process of dissolving MnO₂ into MnCl₂ makes a number of Cl⁻ ions oxidize the Au layer which normally covers the surface of the PCB and then attacks the Cu layer underneath. In addition, galvanic events also occur between MnO₂ powder with Cu and Au layers. This event is similar to the galvanox principle developed by Dixon et al., 2008.6

The galvanic process between MnO₂ powder with copper and gold layers is due to the potential difference between the two. In this case MnO₂ has a high potential to be a cathode while Cu and Au layers become anode and dissolved. The mechanism that occurs between the two is shown in Figure 3.

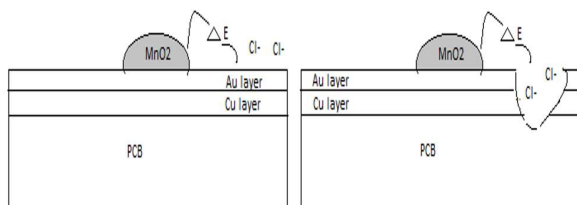
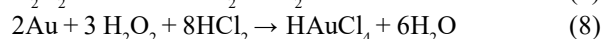
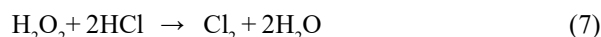


Figure 3. Concept of leaching mechanism by MnO₂ powder.

Table 1 shows the increase in leachate metals when the amount of oxidizing agent is made larger. This condition is caused by a chemical reaction between the Au layer and the H₂O₂ substance [14].



The reaction between H₂O₂ and HCl makes Cl₂ concentration dissolved in the solution higher. This makes the gold dissolved in the leachate solution. [15] Different conditions occur when there is no H₂O₂ present, then Cl₂ is not formed. This condition makes the reaction not run perfectly and the metal is not dissolved.

Based on Figure 4, it appears that the highest recovery value is obtained by a 0.5 M HCl + 2.5% H₂O₂ leachate solution which 59.1% is for gold and 59.8% for copper. However, in copper leaching using H₂O₂, the increase in recovery value was not significant after adding 2.5% H₂O₂. This shows the optimal value for copper leaching at an oxidizing level of 1.5% H₂O₂. However, different results are shown in the gold leaching results which continue to increase after the H₂O₂ oxidizer has increased its concentration from 1.5% to 2.5%. This condition indicates that after the addition of 1.5% H₂O₂, most Cl₂ reacts with gold than copper or it can be assumed that H₂O₂ is more selective in attacking gold than copper.

Increased recovery was also seen in the addition of MnO₂ in HCl solution. But the recovery value obtained is still lower than the use of H₂O₂ oxidizing agents. This result shows that H₂O₂ oxidizer is more efficient than MnO₂ to dissolve gold and copper in HCl. This condition can be caused by several factors including the low MnO₂ solubility in HCl, this can be seen from the presence of a number of MnO₂ powders that have not been dissolved on the basis of the solution. The comparison of the recovery value is shown in Figure 4.

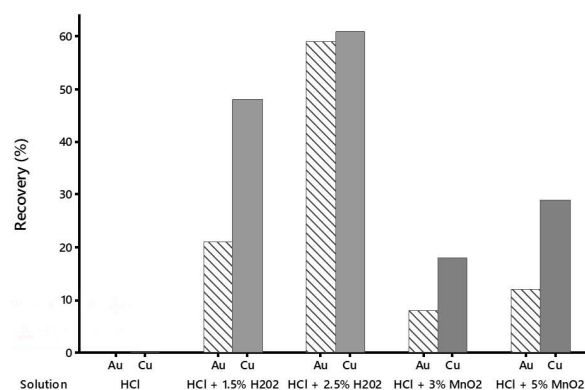


Figure 4. Comparison of recovery results for each leachate solution.

CONCLUSION

The addition of an oxidizer to the hydrochloric acid leach solution increases the recovery value obtained from the leach process because the formation of chlorine (Cl₂) in the leachate solution accelerates the leach reaction. There is a change in the color of the leachate solution from clear to bluish and gets thicker as the amount of metal dissolves. The test results showed that without the addition of an oxidizer the recovery result

was 0.04% whereas after addition it increased to 59%. In addition, from the results of a comparison between the two types of oxidizing agents, hydrogen peroxide (H₂O₂) has a better performance efficiency compared to Manganese Oxide (MnO₂).

ACKNOWLEDGEMENT

The author would like to thank the Ministry of Research and Technology and Higher Education (RISTEKDIKTI) for granting funding for Higher Education Basic Research (PDUPT) in the 2018 funding year No 421 /UN2.R3.1 /HKP05.00 /2018. Yudha Pratesa would like to thank LPDP for the 2017 Superior Scholarship.

REFERENCES

- [1]. S. Harjanto, Y. Cao, A. Shibayama, I. Naitoh, T. Nanami, K. Kasahara, Y. Okumura, K. Liu, T. Fujita, Leaching of Pt, Pd and Rh from Automotive Catalyst Residue in Various Chloride Based Solutions, *MATERIALS TRANSACTIONS* 47(1) (2006) 129-135.
- [2]. I. Rodliyah, N. Ardha, N. Saleh, S.J.J.T.M.d.B. Sariman, Ekstraksi Emas dari Lumpur Anoda Melalui Proses Klorinasi Basah dan Ekstraksi Pelarut, 13(2)(2017) 99-111.
- [3]. H. Kamran Haghighi, D. Moradkhani, B. Sedaghat, M. Rajaie Najafabadi, A. Behnamfard, Production of copper cathode from oxidized copper ores by acidic leaching and two-step precipitation followed by electrowinning, *Hydrometallurgy* 133 (2013) 111-117.
- [4]. J. Ficeriova, P. Balaz, E. Gock, Leaching of gold, silver and accompanying metals from circuit boards (PCBs) waste, *Acta Montan Slovaca* 16(2) (2011) 128-131.
- [5]. P.M.H. Petter, H.M. Veit, A.M. Bernardes, Evaluation of gold and silver leaching from printed circuit board of cellphones, *Waste Manage* 34(2) (2014) 475-482.
- [6]. A. Akcil, C. Erust, C.S. Gahan, M. Ozgun, M. Sahin, A. Tuncuk, Precious metal recovery from waste printed circuit boards using cyanide and non-cyanide lixivants - A review, *Waste Management* 45 (2015) 258-271.
- [7]. F. Bisceglie, D. Civati, B. Bonati, F.D. Faraci, Reduction of potassium cyanide usage in a consolidated industrial process for gold recovery from wastes and scraps, *Journal of Cleaner Production* 142 (2017) 1810-1818.
- [8]. D.G. Dixon, D.D. Mayne, K.G. Baxter, Galvanox™ - A Novel Galvanically-Assisted Atmospheric Leaching Technology For Copper Concentrates, *Canadian Metallurgical Quarterly* 47(3) (2008) 327-336.
- [9]. H. Nakazawa, S. Nakamura, S. Odashima, W. Hareyama, Effect of carbon black to facilitate galvanic leaching of copper from chalcopyrite in the presence of manganese(IV) oxide, *Hydrometallurgy* 163 (2016) 69-76.
- [10]. H. Nakazawa, Effect of carbon black on chalcopyrite leaching in sulfuric acid media at 50/°C, *Hydrometallurgy* 177 (2018) 100-108.
- [11]. P. Ter Teo, A.A. Seman, P. Basu, N.M. Sharif, Characterization of EAF Steel Slag Waste: The Potential Green Resource for Ceramic Tile Production, *Procedia Chemistry* 19 (2016) 842-846.
- [12]. W.D. Bancroft, H.W. Rogers, The Colors of the Copper Salts, *The Journal of Physical Chemistry* 37(8)(1932) 1061-1073.
- [13]. N. Geoffroy, F. Cardarelli, A method for leaching or dissolving gold from ores or precious metal scrap, *JOM* 57(8)(2005) 47.
- [14]. Z. Wang, S. Guo, C. Ye, Leaching of Copper from Metal Powders Mechanically Separated from Waste Printed Circuit Boards in Chloride Media Using Hydrogen Peroxide as Oxidant, *Procedia Environmental Sciences* 31 (2016) 917-924.
- [15]. Y. He, Z. Xu, Recycling gold and copper from waste printed circuit boards using chlorination process, *RSC Advances* 5(12) (2015) 8957-8964.



Copyright © 2019 Jusami | Indonesian Journal of Materials Science. This article is an open access article distributed under the terms and conditions of the [Creative Commons Attribution-NonCommercial-ShareAlike 4.0 International License \(CC BY-NC-SA 4.0\)](https://creativecommons.org/licenses/by-nc-sa/4.0/).