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Influence of Oxidizing Agent on Recovery of Metals Including Gold and Silver from Printed Circuit Boards

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Abstract: *Due to rapidly depleting natural resources of metals, it becomes essential to find secondary resources for metals. E-waste can be a potential secondary source for that. It contains a number of metals which can be recycled after successful separation. Owing to the fact that e-waste contains precious metals like silver and gold, the present work is focused on extracting silver and gold along with other metals like Cu, Zn, Ni etc. from e-waste. Dismantling of the e-waste was done manually and after pretreatment of the e-waste, metals were extracted with a mixture of nitric acid and hydrochloric acid. Nitric acid in this experimental study was used as an oxidant and the effect of oxidant was observed on the extraction behavior. It was observed that as the concentration of nitric acid was increased in the mixture of acids the extraction of all metals like Au, Ag, Mn, Cr, Ni, Fe, Cu, Pb, Zn, Cd were extracted upto 95-98%. Nevertheless the recovery of all metals was dropped to 10 % if 100 % nitric acid was used as a solvent. Similarly 100 % hydrochloric acid was resulted in a lower extraction for all metals. The extraction of metals was observed dependent on nitric acid concentration which is used as an oxidant. Other than concentration of acids in the acids mixture, time of extraction and temperature were also observed for the extraction of different metals.*

Keyword: **e waste, aquaregia, oxidant effect, metal recovery, pcb extraction**

1. Introduction

Waste from electric and electronic equipment is a fastest growing solid waste in the world [1]. Infromally it is known as e-waste Due to high metal content and thermosetting plastic it is difficult to recycle or biodegrade it as it is. This is one of the reasons, this waste is catching attention. The metals from the e-waste can be removed by several ways like pyro metallurgical process, hydrometallurgical process, electro-winning process and bio-metallurgical. Due to high energy requirement in pyrometallurgical process the process is not favorable economically.

Microbiological leaching uses a natural ability of microorganisms to transform metals present in the waste in a solid form (in the solid matrix) to a dissolved form. Apart from the possibility of bioleaching of metals in alkaline environment (involving cyanegenic bacteria), acidophilus microorganisms and conducting biological process of leaching in an acidic environment play a crucial role in the bio-hydrometallurgical techniques [2].

Biohydrometallurgical processing of solid waste is similar to natural biogeochemical metal cycles and reduces the demand of resources, such as ores, energy and landfill space. This technology is environmentally friendly (in comparison to chemical method) and it is considered a green technology (generates less amount of waste) [3, 4].

The paper presents the experimental investigation recently carried out for the extraction of different metals from pcb with hydrometallurgical route. Commonly aqua-regia is used for extraction of different metals from e-waste where 30% HNO_3 and 70% HCl by volume is used to prepare aqua-regia. The solvent works best to extract almost all the metals due to presence of nitric acid as an oxidant.

Metal extraction with nitric acid have been investigated by Cerna (1992), Zongcheng (1989) [5, 6]. More than 95 % copper and lead extractions were achieved by Mecucci and Scott (2002) using nitric acid [7]. In the present work the amount of oxidant (nitric acid) for the extraction of different metals have been varied from 0-20%. This specific study has not been found in literature. The experiments were carried for different time and

temperature taking different amount of oxidant. The results of this study will help in deciding the amount of oxidant usage. The amount of oxidant in extraction is a key step to quantify for selective separation of metals after aqua-regia leaching. For selective separation of metals nitric acid needs to be removed for precipitation of different metals.

2. Materials and methods

Printed circuit boards (PCB) were obtained from server room of the college. The reagents used were hydrochloric acid 35% (v/v), nitric acid 98% (v/v). The reagents were purchased from Rankem and were of analytical grade. The recovery of silver and gold were measured in atomic adsorption spectroscopy (Shimadzu). Beaker, stirrer, heater, pipette, filter paper, condenser, hydrochloric acid, nitric acid as leaching agent.

PCB boards obtained were carried out a pretreatment before extracting any of the metals. First of all components attached to the board are removed by a pair of pliers. After removing parts from board, the boards were cut into pieces of 2x2 cm2. The pieces of boards along with removed parts were kept in muffle furnace at 600 ^{0}C for 15 min to eliminate all the plastic present. After removing plastics the material was crushed in ball mill for finer particles and sieved. Detailed block diagram is shown in Figure 1. The particles of 400 µm size were used for the experiments. Before starting our series of experiments with acid mixture, an experiment was performed to confirm total metals concentration present in the pcb. 2 gm of sample was dissolved in aqua-regia solution 70 % HCl and 30 % HNO_3. The pcb sample was stirred at 400 rpm for 2 h at 100 ^{0}C. 95 % of the pcb sample was dissolved in aquaregia and assumed that all the metals are dissolved in that. The sample for metals present was analysed in AAS and concentration of different metals obtained are reported in Table 1.

3. Results and discussion

A systematic approach has been applied for experiments with varying composition of acids used. The concentration of nitric acid was reduced from 20% by volume to 0%, however, in one experiment 100 % nitric acid by volume was used. The concentration of HNO3 was kept lower than composition of HNO_3 in aquaregia (1:3), it becomes 25 %/75 % (v/v) of HNO_3/HCl. In first set of experiments with varying acids concentration different metals extraction were observed. Other conditions were maintained as: temperature 90^0 C, stirring speed 280 rpm and for 15 minutes of digestion.

Table 1 Total concentration of different metals present in pcb

S.N.	Metals	Concentration (ppm)
1	Au	1
2	Ag	25
3	Mn	4
4	Cr	5
5	Ni	32
6	Fe	30
7	Cu	2000
8	Pb	250
9	Zn	60
10	Cd	0.03

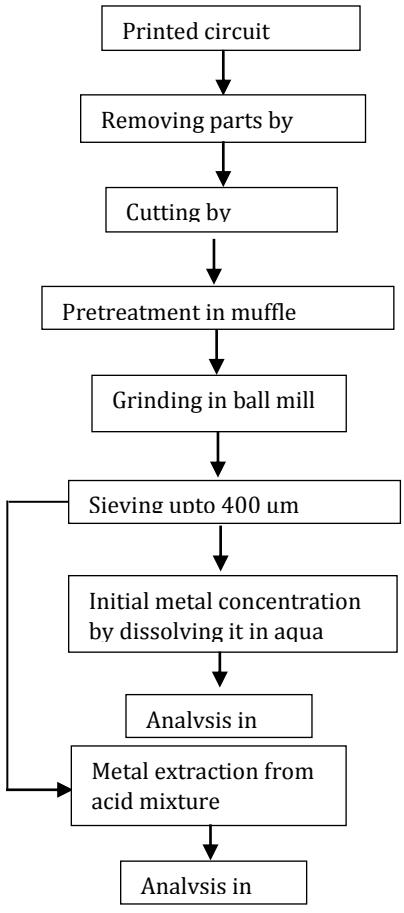

Fig. 1 Schematic diagram of pretreatment and extraction process of pcb.

Recovery of different metals with respect to initial concentrations of metals present in pcb was calculated as:

$$\%\ recovery\ of\ metal = \frac{Amount\ of\ metal\ present}{Amount\ of\ metal\ present\ in\ complete\ dissolution} x\ 100$$

Figure 2 presents all the metals analysed at different acids compositions. Figure 2 a shows the recovery of Cr, Ag, Au, Pb and Ni and Figure 2 b shows the recovery of Mn, Cd, Fe, Cu, and Zn. It can be observed from Figure 2 that all metals are showing different recovery with different concentration of nitric acid. Recovery of Cr is increased when nitric acid was reduced from20 % to 5 %. The recovery of Cr was reduced when no nitric acid was used, at 100 % nitric acid the recovery was also less. It suggests that the recovery of Cr is increased in the presence of nitric acid however absence or 100 % presence did not result its substantial recovery. Similar trend was also observed for Fe, Mn and Zn. Recovery of Cd and Au were observed to decrease with decreasing nitric acid and at no nitric acid and at 100 % nitric acid it was observed to increase. Recovery of Ni and Ag were decreased with decreasing concentration of nitric acid and at no nitric acid as well as with 100 % nitric acid the recovery was not significant. Recovery of lead was increased at decreasing concentration of nitric acid however at 100 % nitric acid and 100 % hydrochloric acid the recovery was maximum and close to 95 %.

Behnamfard et al., 2013 have done the leaching of Au, Ag, Cu and Pd with 2 M sulfuric acid and H_2O_2 (35 %) as an oxidant at ambient temperature with 25 % by volume. Recovery of all metals were achieved upto 90 % and it is followed by thiourea leaching of Au and Ag. The leaching of PCB using a mineral acid in the presence of a suitable oxidant is usually applied as the first step in recycling of metals from PCB after mechanical pretreatments, size reduction in particular (Yang et al., 2011; Birloaga et al., 2013). Although some base metals leach during this step, the main objective of this step is leaching of copper, since a high amount of copper (around 20 wt %) was present in their sample. Separation of Au and Ag and other metals are done generally with cyanide, aquaregia, thiosuphate and thiourea. Among all aquaregia is used in laboratory for its effectiveness of dissolving almost all the metals present in pcb. However, it is corrosive in nature due to oxidizing agent presence in high amount. Jing-ying et al, 2012 have discussed that due to corrosiveness of aquaregia it is not used at large scale and process is developed and carried out mostly at laboratory scale. Present experimental investigation has been carried to reduce the amount of oxidizing agent and its effect on dissolution of different metals.

Other set of experiments were conducted to observe the recovery of metals at varying digestion time. Figure 3 shows the effect of time of digestion on recovery of different metals. Figure 3 a shows the time of digestion effect on Cr, Ag, Au, Pb and Ni and Figure 3 b shows the recovery with increasing time for Mn, Cd, Fe, Cu, and Zn. For this set of experiments concentration of acids were kept at 10 % by volume of HNO_3 and 90% HCl, temperature 90^0 C and stirring speed 280 rpm.

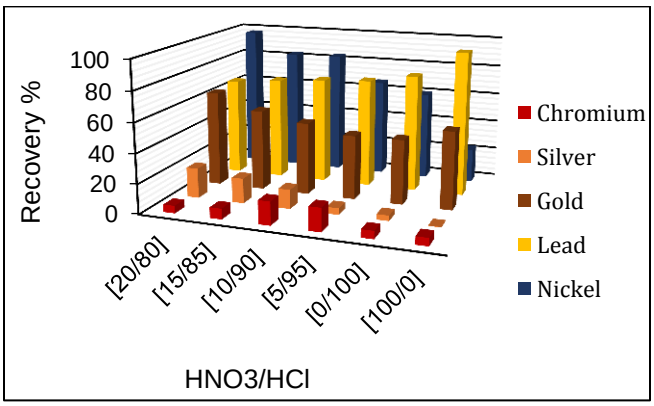

Fig. 2 a Recovery of Cr, Ag, Au, Pb, Ni with different acids ratio

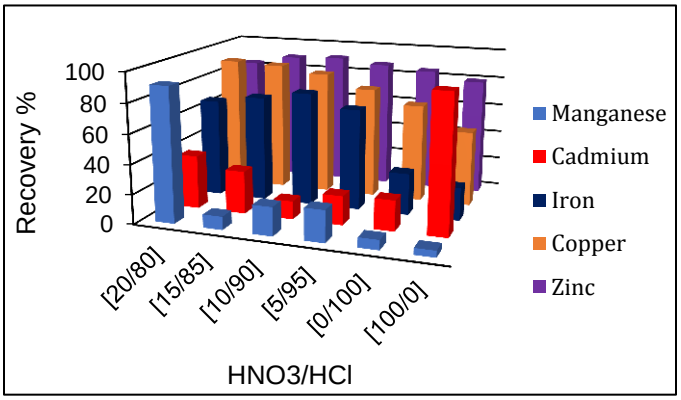

Fig. 2b Recovery of Mn, Cd, Fe, Cu, Zn with different acids ratio

Fig. 2 x axis represents different acids ratio of HNO3/HCl for 1- 20/80, 2-15/85, 3-10/90, 4-5/95, 5- 0/100, 6-100/0 and y axis represents recovery of metals.

Increase in recovery with increasing time from 6 min to 12 min was not observed significant for Cr, Mn, Au, Ag and Pb.

On the other metals recovery was increased with increasing time for Fe, Cu, Cd, Zn and Ni. The amount of recovery is however not more than 5 % in the metals where recovery was increased. It suggests that there is not significant effect of time on digestion as the acid with oxidizing agent come in contact with pcb it dissolves maximum possible extent of metals within few minutes.

The effect of temperature on metal recovery was observed in Figure 4. Figure 4 a presents the recovery of Cr, Ag, Au, Pb, Ni with increasing temperature and Figure 4 b presents the recovery of Mn, Cd, Fe, Cu, Zn. The effect of temperature was insignificant for Au, Pb, Ag, Cr, and Mn. There was an increase in recovery for Zn, Cu and Ni. The reverse effect of temperature was observed for Fe, Cd, with increasing temperature recovery was reduced upto 20 %.

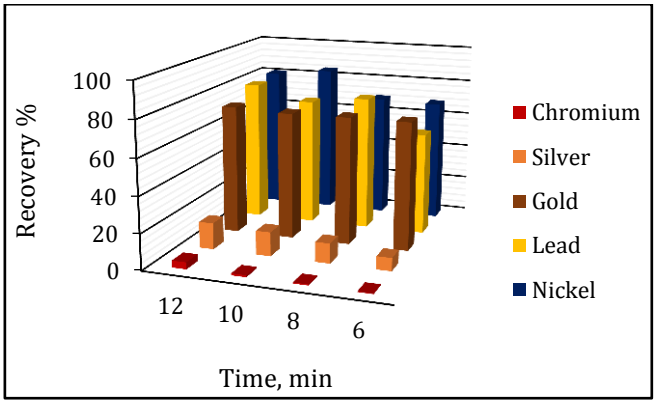

Fig. 3 a Recovery of Cr, Ag, Au, Pb, Ni with increasing time

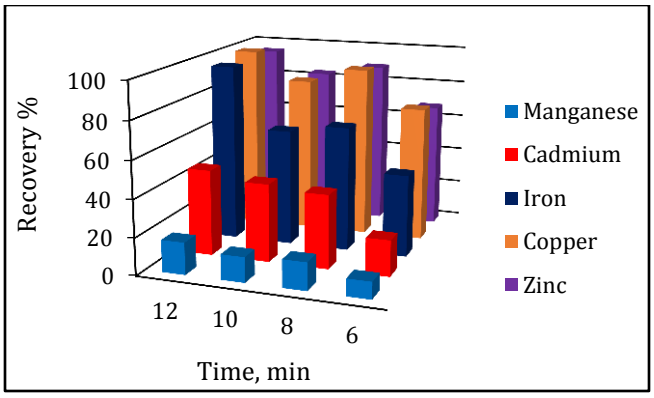

Fig. 3 b Recovery of Mn, Cd, Fe, Cu, Zn with increasing time

Fig. 3 x axis represents different time in min and y axis represents recovery of metals.

4. Conclusions

Different acids for metals extraction from pcb had been used in literature, in which aquaregia is a prime acid which is effective and mostly used in laboratory studies.

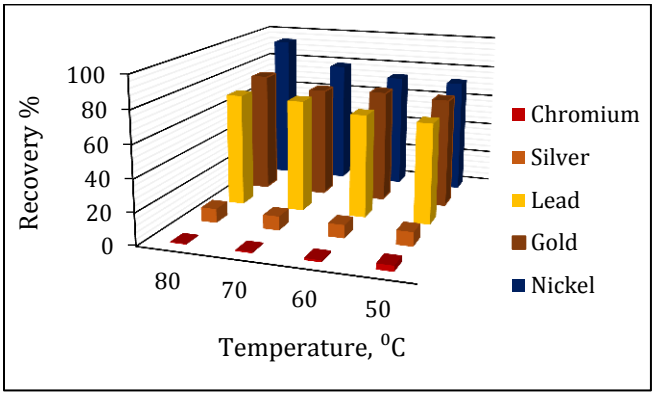

Fig. 4 a Recovery of Cr, Ag, Au, Pb, Ni with increasing temperature

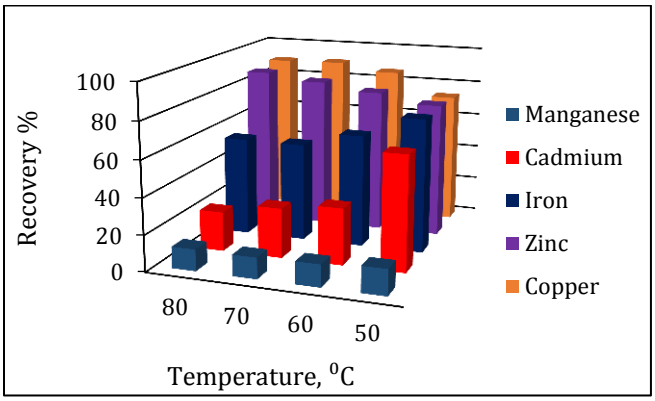

Fig. 4 b Recovery of Mn, Cd, Fe, Cu, Zn with increasing temperature

Fig. 4 x axis represents different temperature in ^{0} C and y axis represents recovery of metals.

However, due to its corrosiveness it is not much used at large scale as it's wastewater after process is highly acidic. The present investigation shows the effect of oxidizing agent composition in mixture of HCl and HNO_3. These two acids are common in aqua regia but the composition used here was lower and varied in lower range. All the metals analysed have different recovery at different compositions. Increasing concentration of HNO_3 incresease the recovery including Au and Ag however the metals do not recovered if no HNO3 and 100 % HNO_3 was used. Temperature and time were not observed to affect significantly on recovery.

It can be concluded that at ambient temperature and within 15 min 10 % by volume of HNO_3 with 90% HCl can extract maximum amount of metals. The concentration of HNO_3 was quite less compared to aquaregia where 25% by volume HNO_3 is used conventionally.

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