Waste Management 52 (2016) 302–308

Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

A hydrometallurgical process for recovering total metal values from waste monolithic ceramic capacitors

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ARTICLE INFO

Article history:
Received 16 December 2015
Revised 6 April 2016
Accepted 9 April 2016
Available online 12 April 2016

Keywords:
Monolithic ceramic capacitor
Precious metal
Base metals
Leaching
Precipitation

ABSTRACT

A hydrometallurgical process for recovering the total metal values from waste monolithic ceramic capacitors was investigated. The process parameters such as time, temperature, acid concentration, hydrogen peroxide concentration and other reagents (amount of zinc dust and sodium formate) were optimized. Base metals such as Ba, Ti, Sn, Cu and Ni are leached out in two stages using HCl in stage 1 and HCl with H_2O_2 in stage 2. More than 99% of leaching efficiency for base metals (Cu, Ni, Ba, Ti and Sn) was achieved. Precious metals such as Au and Pd are leached out using aquaregia and nitric acid was used for the leaching of Ag. Base metals (Ba, Ti, Sn, Cu and Ni) are recovered by selective precipitation using H_2SO_4 and NaOH solution. In case of precious metals, Au and Pd from the leach solution were precipitated out using sodium metabisulphite and sodium formate, respectively. Sodium chloride was used for the precipitation of Ag from leach solution. Overall recovery for base metals and precious metals are 95% and 92%, respectively. Based on the results of the present study, a process flow diagram was proposed for commercial application.

1. Introduction

Growing changes in the technological advancement, the massive demand for smarter and newer electronic devices and falling prices have flourished the quantity of discarded electronic devices throughout the world. It is reported that nearly 45 million tons of outdated electronic devices are discarded globally per annum, and the number is growing at an exponential rate (Ogunseitan, 2013). This electronic waste (e-waste) is considered as hazardous due to the presence of toxic heavy metals (Pb, Hg, Cr, As and Cd) and organic chemicals (dioxins and furans), which in turns contaminate the environment and threat human health if disposed off into the landfill (Liu et al., 2009; Li et al., 2008; Birloaga et al., 2014). In addition, e-waste contains some valuable metallic elements which will be economically attractive in processing. Therefore, recycling of e-waste is indispensable from the perspective of minimizing environmental pollution, resource management and economic benefit.

Among all e-wastes, electronic devices like computers, laptops, mobile phones contain a major fraction of metals (precious, rare and base metals). Printed circuit boards (PCBs), the integral component of these electronic devices are particularly rich in copper, precious metals (PMs) and other valuable metals (Fujita et al., 2014). Of these metals, recovery of PMs receives the most attention because a considerable amount of it has been used in the electronics industry during the past three decades (Ghosh et al., 2015). Moreover, the concentration of these metals (PMs and base metals) in PCBs are much higher than their respective primary resources (Ficeriová et al., 2008; Cayumil et al., 2015), so it is attractive for recycling.

PCB contains mainly chips, resistors, connectors, capacitors (tantalum and ceramic), transistors, etc. During recycling of PCBs, these components are to be separated and recycled for the metal values. In order to reclaim the metal values from different components of PCBs, several methods have been proposed (Syed, 2006; Sheng and Etsell, 2007; Park and Fray, 2009; Tripathi et al., 2012; Behnamfard et al., 2013). Syed (2006) reported the process for the recovery of only Au specifically from gold coated PCB. Sheng and Etsell (2007) recovered Au from actual computer PCB by nitric acid followed by aquaregia leaching. But there was no details regarding the recovery of other PMs such as Pd and Ag. Park and Fray (2009) reported high recovery of Au (97%), Pd (93%) and Ag (98%) but from a synthetic solution, which will not match practically for a recycling industry. For instance, Tripathi et al., 2012 reported the recovery of 78.8% for Au from mobile PCB after removing the mounted components. However, Behnamfard et al., 2013 recovered all the PMs (more than 90%) after removing the

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http://dx.doi.org/10.1016/j.wasman.2016.04.010
0956-053X/

mounted components (capacitors, batteries, resistors, etc.). On the contrary, among the mounted components of PCB, monolithic ceramic capacitor (MLCC), contains a valued amount of PMs as well as base metals, has not been studied yet separately. Moreover, MLCCs are present in almost all the electronic devices to keep the electrical noise at a low level of power supply (Lee et al., 2004). In addition, due to the technological advancement in electronic devices such as Bluetooth, 3G technology and most recently colour imaging, mobile handsets, etc., the growth rates for MLCCs is projected as 12% per annum (Cross, 2004). Based on the rapid growth of consumption, the recycling of MLCCs is mandatory in terms of environmental issues. But for a recycling industry, economic benefit is also considered for processing MLCCs. In order to have a better understanding regarding the economic assessment of MLCCs, the chemical analysis and the revenue contribution from metal contents of MLCCs are presented in Table 1. Based on Table 1, the revenue contribution of the precious metals is 81.4% and the remaining 18.5% is of the base metals (Cu, Ni, Sn, Ti, and Ba) and it is worthy for a recycling.

On careful literature survey, only one patent was reported regarding the recycling of ceramic capacitors (Qin et al., 2013). The patented process discloses the method consisting of soda roasting, three stages leaching and followed by separation of metal values by both precipitation and electro winning. Though the process seems to be attractive, the separation of MLCCs selectively from the PCBs is practically difficult to execute for a recycling industry (Delfini et al., 2011). The separation of MLCCs from waste PCBs mainly involves the mechanical/thermal treatment (to remove solder) followed by sieving to segregate the components based on size (Das et al., 2014). During the above process, other materials such as pins, connectors, small amount of solder dusts are also accompanied with MLCCs and make the sample heterogeneous (Fig. 1a). Thus the process should be robust enough to handle these impurities for commercial viability.

With the commercial view, the present investigation is aimed to develop a new process flow sheet for recovering the total metal values from the waste monolithic ceramic capacitors by hydrometallurgical techniques. The most significant factors affecting the leaching of the target metals and their recovery during precipitation are discussed.

2. Materials and methods

2.1. Materials

Monolithic ceramic capacitors of the waste PCBs taken for the study were collected from the dismantling section of the Attero Recycling Pvt. Ltd., India. The sample was pulverized in a ball mill (Fig. 1b) and finally sieved to obtain a particle size of −300 μm. Weighed amount of the pulverized material was subjected to complete digestion with different laboratory reagent grade acids followed by dilution and analysis. Commercial grade of hydrochloric acid, nitric acid, sulphuric acid, hydrogen peroxide, zinc dust, urea, sodium chloride and sodium hydroxide were used for the study while sodium metabisulphite and sodium formate were of laboratory reagent grade.

2.2. Leaching studies

Leaching experiments were carried out in a glass reactor (1.0 L) fitted with reflux condenser and kept over a ceramic hot plate with magnetic stirring system under a fume hood. For each run, 0.1 kg (pulp density, 20% w/v) of the sample (pulverized MLCCs, −300 μm) was added to the reactor with a predetermined concentration of acid solution for different time and temperature. The contents were stirred at 400 rpm. Two different leaching reagents such as nitric acid and aquaregia were introduced for the leaching of precious metals, while hydrochloric acid was used for the leaching of other metal values except precious metals as the leaching agent in two stages. Periodically, collected samples were analyzed for the metal values after appropriate dilutions. Most of the experiments were carried out in duplicate, and the results generally agreed within ±3%.

2.3. Metal recovery by precipitation

The dissolved metal ions such as barium, titanium, tin, copper and nickel particularly from the hydrochloric acid leach liquor were recovered through selective precipitation using sodium hydroxide solution. The precious metal values such as Au(III) and Pd(II) from the aquaregia leach liquor were selectively precipitated out by adding sodium metabisulphite and sodium formate, respectively, while Ag(I) was recovered from the nitric acid leach liquor by the addition of commercialized sodium chloride solution. The tests were performed with the aid of a magnetic stirrer and a pH meter. The consumption of each precipitant was studied. The precipitated masses obtained in different steps were filtered, washed, dried and finally subjected to further purification.

2.4. Analytical techniques

Analysis for the determination of the metal ion concentrations were performed by Microwave Plasma-Atomic Emission Spectroscopy (4100 MP-AES), an Agilent instrument. A multi-element standard (MP-AES grade) was used for the analysis of the metal ion concentration. The pH values of the aqueous solutions were measured with a pH/mV meter (Model CL 54+, TOSHCON Industries Pvt. Ltd., and India).

3. Results and discussion

3.1. Leaching study

In order to extract the precious metals selectively and minimizing the impurities, leaching is preferably carried out after the recovery of base metals from MLCCs using hydrochloric acid. It is also confirmed that the leach liquor is free from precious metals by analysis. The residue obtained after hydrochloric acid leaching was taken for the precious metal recovery. A two stage leaching process is chosen for the selective dissolution of precious metals using two different leaching reagents. Accordingly, a first stage leaching with aquaregia is due to the preferential dissolution of Au and Pd into the liquid phase, with Ag remained in the residue.

Table 1
Chemical analysis and revenue contribution of metals in waste MLCCs.

Element	Fe	Cu	Ni	Zn	Mn	Al	Sn	Ba	Ti	Cr	Ag	Au	Pd	Pb	Acid insoluble
%	3.71	2.59	10.21	0.19	0.23	0.15	2.31	21.3	17.6	0.31	0.13	0.01	0.05	1.16	15.8
Absolute, g/kg	37.1	25.9	102.1	1.9	2.3	1.5	23.1	213	176	3.1	1.3	0.1	0.5	11.6	
Unit price, Rs	NA	450	900	100	57.6	100	1000	50	500	NA	36×10^3	25×10^5	14×10^5	100	
Value/kg of MLCC	NA	11.7	91.9	0.2	0.1	0.2	23.1	10.7	88.0	NA	46.8	250	700	1.2	
Revenue, %	NA	1.0	7.5	0.02	0.01	0.01	1.9	0.9	7.2	NA	**3.8**	**20.4**	**57.2**	0.1	