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RECOVERY OF METALS FROM ELECTRONIC WASTE

Marinela Panayotova, Vladko Panayotov, Velichka Hristova

University of Mining and Geology "St. Ivan Rilski", 1700 Sofia; marichim@mgu.bg

ABSTRACT. Production and consumption of electrical and electronic equipment has been exponentially grown recently. This creates a large volume of waste stream (e-waste). Its landfill disposal is increasingly unacceptable, because of the eventual leaching of metals and other contaminants into the soil or groundwater and loss of valuable materials. The paper reviews trends in the amount of e-waste and the existing recycling technologies. Special attention is paid to methods for valuable and precious metals recycling. Authors' studies on the recovery of metals from obsolete computers are presented.

ИЗВЛИЧАНЕ НА МЕТАЛИ ОТ ЕЛЕКТРОННИ ОТПАДЪЦИ

Маринела Панайотова, Владко Панайотов, Величка Христова
Минно-геоложки университет "Св. Иван Рилски", 1700 София; marichim@mgu.bg

РЕЗЮМЕ. Производството и употребата на електрическо и електронно оборудване нараства експоненциално през последните години. Това създава обемист поток от електронни отпадъци (е-отпадъци). Тяхното депониране в сметищата става все по-неприемливо, поради евентуално излужване на метали и други замърсители в почвата или в подземните води и загубата на ценни материали. В статията се прави преглед на насоките на промяна в количеството на е-отпадъците и на съществуващите технологии за рециклирането им. Обръща се специално внимание на методите за рециклиране на ценните и благородни метали. Представени са изследванията на авторите върху извличането на метали от излязли от употреба компютри.

Introduction

The term electronic waste, e-waste, or Waste Electrical and Electronic Equipment (WEEE) describes discarded, surplus, obsolete, broken, electrical or electronic devices (computers, monitors, printers, scanners, data storage devices, servers, networking systems, copiers, fax machines, radios, TVs, refrigerators, cell phones and pagers, entertainment device electronics, etc.) The useful life of consumer electronic devices is relatively short, and decreasing as a result of rapid changes in equipment features and capabilities. Hundreds of millions of devices are now in the hands of citizens. With the astronomical pace of technological development, all of these personal computers are rapidly approaching obsolescence. Their owners need to dispose of them, to make room for the next model ... and the next ...and the next. This creates a large waste stream of obsolete electronic equipment, electronic waste (e-waste).

Table 1 presents the generation and recovery of consumers electronics in the USA in year 2001 (Kang and Schoenung, 2005). The same authors have pointed also that the average life-span of personal computers in the USA has decreased from 4.5 year in 1992 to 2 years in 2006.

According to some authors (Behdadet al., 2010), the volume of e-waste, that is being generated increases approximately by 10 % every year. Even though there are conventional disposal methods for e-waste, these methods have disadvantages from both the economic and environmental viewpoints. Disposal of e-waste may involve significant risk to the workers, environment and general public.

Table 1.
Generation and recovery of consumers electronics in the USA

Types of consumer electronics	Total generation, t	Recovered, %
Video product [a]	806200	0.1
Audio product [b]	377900	Negligible [d]
Information product [c]	1076300	19
Total	2260400	9

[a] TVs, VCR desks, camcorders, TV/VCR combinations
[b] All types of compact disc players, rack audio systems, compact audio systems
[c] Personal computers, computer monitors, telephones, fax machines
[d] Less than 0.05 wt. %

In the United States, an estimated 70% of heavy metals in landfills come from discarded electronics, while electronic waste represents only 2% of America's trash in landfills (Slade, 2007). Up to 38 chemical elements are incorporated into electronic waste items. Technological innovations in the field of computers continue to advance exponentially and this leads to an exponential growth of the amount of discarded obsolete personal and portable computers (PCs).

Nearly all of the substances that are of concern in a personal computer are in solid non-dispersible form, and there is no cause for worry for human exposure or release into the environment in ordinary use and handling of a personal computer. None of these substances will be released from a personal computer through normal contact, including transportation and manual disassembly. However, if this used equipment is land disposed or incinerated under improper emission pollution control this can cause problems. A PC contains several substances of environmental concern (ENV/EPOC/WGWPR, 2001): (a) Antimony, which is a component in lead solder. Cathode Ray Tubes (CRTs) may contain Antimony in the screen and/or cone glass; (b) Barium oxide which is contained CRTs; (c) Beryllium - in the form of a copper-beryllium alloy in the mother-board, in the slots used for connection to daughter-boards; (d) Cadmium - a small amount of Cadmium in plated contacts and switches, and a very small amount of Cadmium may have been used as a stabilizer in PVC wire insulation, which may have been used in a personal computer. Laptop computers often contain a rechargeable Nickel - Cadmium (Ni-Cd) battery; (e) Chlorine and/or Bromine - brominated organic halogenates and Antimony chloride are flame retardants and may be present in the plastic in printed circuit boards and cases. There is Chlorine in any PVC insulation of wires and cables used in a personal computer; (f) Lead - there is a substantial amount of Lead in the CRTs, as a rough average perhaps two to three kg in older models and 1 kg in new models, encapsulated in the form of leaded glass. There is also a much smaller quantity of Lead in printed circuit boards in the CPU, in the form of solder. Printers and miscellaneous peripheral devices also contain a small amount of Lead in solder; (g) Lithium metal – it may be present in a small battery on a mother-board; (h) Mercury - in large flat panel displays, a small amount of Mercury may be present in a lighting device used to illuminate the screen; and (i) Phosphors - phosphor coating, typically Zinc sulfide and rare earth metals, are used on the interior of a CRT screen to convert the kinetic energy of an electron beam to light. However, Cadmium sulfide has also been used in older CRTs. Although these substances can present risks in recycling or disposal of used personal computers, it is important to notice that some of these substances are present in personal computers for the purpose of lowering risks to human health during the product use. These include the use of Lead shields in CRTs to protect users from harmful x-rays and the use of flame retardants in plastics to reduce the risk of overheating and potential fires. Printed circuit boards contain a substantial quantity of Copper and valuable concentrations of Gold, Silver and Palladium. Uncontrolled burning, disassembly, and improper disposal of discarded PCs can cause a variety of environmental problems such as soil and groundwater contamination, atmospheric pollution, as well as health problems affecting persons who are directly or indirectly involved in WEEE disposal or processing.

Obsolete computers could be considered as a significant source for recovery of non-ferrous metals. According to studies carried out, computers seem to be the only WEEE that could allow a recycling system to be financially beneficial (Price WaterHouseCoopers, 2002). The most "useful" parts of the computers are the printed circuit boards (PCBs) that contain many metals of interest.

Existing recycling technologies

Recycling of electronics includes different stages: (a) Transportation – it should be ensured that containers with WEEE are not damaged during on and off-loading and that waste containers are secure during transport; (b) Consolidation and storage – it should be ensured that containers are closed, structurally sound, properly labeled and compatible with the contents; (c) De-manufacturing or disassembly – this means to manually break down e-waste into individual components either for re-sale or re-use or to sort for further recycling. The above requirements for collecting and consolidating the e-waste are also applied to e-waste storage disassembling prior to and after disassembly; (d) Processing – these are activities, other than simple de-manufacturing or disassembly of e-waste components, that change the chemical or physical make up of a hazardous electronic component. They may be considered "treatment" of hazardous waste. All e-waste should be processed within a building with a roof, floor and walls, and no activities may be performed that use temperatures high enough to volatilize Lead or Cadmium or to produce volatile organics.

After disassembling, WEEE is processed to recover raw materials such as metals, glass and plastics. Ferrous and non-ferrous materials (steel, Aluminium, Copper, wires and cables) are often sold to smelters for the production of raw materials. Leaded glass from CRTs is processed and sold to CRT manufacturers for use in new CRTs or is sent to Lead smelters for Lead recovery. The market for recycling plastics used in electronics is slowly developing. It is used in IT or non-IT applications, often incinerated with waste to energy recovery or used as a coal fuel substitute in the smelting process with adequate emissions controls to remove dioxins and furans, or disposed in landfills.

Here we shall pay attention to technologies for metals recycling. After waste material sorting to remove paper, hazardous materials, CRTs, it is shredded and screened to obtain proper size. Then with the aid of magnetic separators ferrous metals are removed. Further, non-ferrous metals are separated usually with the aid of Eddy current separators. The left material is plastic, which is removed usually by means of density separation and the left is refusal which is not utilizable and is disposed in landfills (Kang and Schoenung, 2005).

Recovery of valuable metals is carried out generally by two types of technologies - pyrometallurgy and hydrometallurgy.

Pyrometallurgical methods

Generally, crap containing 5–40 wt. % Cu is fed into a blast furnace. Copper compounds are reduced by the presenting scrap Iron. Impurities (Sn, Pb, Zn), are also reduced as gas fume (Notle, 1997). The following chemical reactions occur:

$$Fe + Cu_2O \rightarrow FeO + 2Cu$$

$$2ZnO + C \rightarrow 2Zn_{(g)} + CO_2.$$

The product of the blast furnace, called black Copper, contains 70–85 wt.% Copper. It is fed into the converter to be oxidized. Air or oxygen-enriched air is used. Impurities (Sn, Pb, Zn) are burned out and Fe is removed as slag. Blister Copper is obtained with purity of 95 wt.%. It is fed in an anode furnace, where by adding a reducing agent, molten Cu is reduced. Less noble metals than Copper are oxidized. The reduction reaction in the anode furnace is:

$2CuO + C \rightarrow 2Cu + CO_2$

Obtained material contains approximately 98.5 % Cu. It is further purified (to 99.99 wt.% Cu) by cathodic deposition after dissolving it in H_2SO_4 electrolyte.

The anode slime from the Copper electrolysis process contains Gold, Silver, Palladium. It is leached by pressure. The leach residue is then dried and, after the addition of fluxes, smelted in a precious metals furnace. During smelting, Selenium is recovered. The remaining material, mainly Silver, is cast into a Silver anode. At a subsequent, high-intensity electrolytic refining process, a high-purity Silver cathode and anode Gold slime are formed. The anode Gold slime is then leached, and high-purity Gold, as well as Palladium and Platinum sludge, are precipitated (Kindesjo, 2002).

For Lead recovery, a reverberatory furnace is charged with Lead-containing materials. In this furnace, lead compounds are reduced to metallic Lead bullion (with purity higher than 99.9 wt.% Pb) and foreign materials are oxidized to slag. This furnace is tapped for slag, which typically contains 60–70 wt.% Pb, and a soft (pure) Lead product (Prengaman, 1980). The following reactions occur:

$PbO + C \rightarrow Pb + CO$

$2Sb + 3PbO \rightarrow 3Pb + Sb_2O_3$

$2As + 3PbO \rightarrow 3Pb + As_2O_3$

$Sn + 2PbO \rightarrow 2Pb + SnO_2$.

The slag formed and a reductant as well Iron and Limestone (as fluxing agents) are fed in a blast furnace. The product of the blast furnace is "hard Pb", which contains about 75–85 wt. Pb 15–25 wt.% Sb, and 1–3 wt.% Pb that is contained in the slag. The blast furnace is tapped continuously to recover Lead and intermittently to remove slag. The blast furnace slag, which contains primarily Silica and Iron oxides, is disposed of in landfills.

A method is proposed for recovering metals from metal-containing e-waste and vitrifying the remainder of the wastes for disposal (Wicks et al., 2000). Material is placed in suitable container and heated by microwaves at first temperature in the range of 300-800 ^{o}C to combust organic materials in the waste. Then it is heated in the range of 1000-1550 ^{o}C at which temperature glass-formers present in the waste cause it to melt and vitrify. Low melting metals such as Al and Sn can be recovered after organics combustion is substantially complete. Metals with higher melting points (Au, Ag, Cu) can be recovered from the solidified product separated from the waste at their respective melting points.

The e-waste was fed into an induction furnace (Bratina, 2005). A portion of the organic components of the e-waste can be removed prior to feeding of the waste into the induction furnace and/or volatilized or decomposed in the furnace. The metal components of the electronic waste form separate liquid layers in the induction furnace that are separated according to their densities. The separated metals layers are recovered either in a solid or liquid phase.

A sulphating roasting to perform a treatment for a selective recovery of valuable metals from galvanic sludge is proposed (Rossini and Bernardes, 2006). The target metals were Copper, Zinc and Nickel and the sulphating agent used was Pyrite, from coal wastes. The particularity of this treatment is the use of two hazardous wastes as raw material. After roasting, the product of reaction was leached with water in room temperature for 15 min. It was found that pyrometallurgical step determines the process efficiency. The conditions that best reflect a compromise between the valuable metal recovery and the economical viability of the process were achieved for 1 : 0.4 galvanic sludge / pyrite ratio, 90 min of roasting time and 550 °C of roasting temperature. These conditions lead to a recovery of 60% zinc, 43% nickel and 50% copper.

A process for recycling printed circuit boards includes pyrolyzing them to form an ash (Dills et al., 2009). Metals are separated from the ash by density separation techniques. Then the metals are formed into a slurry electrode by combining powderized metals with carbon powder and an ionic liquid to form an electrode paste. The slurry electrode and an electrode on which electro-deposition will take place are immersed in an electrolyte bath and are electro-refined to form bars of metal.

A process is proposed (Suorong Zhang et al., 2009) which comprises the following steps: (a) mechanical - automatically disassembling and separating the waste circuit boards, crushing the separated components and separation of a metal concentrate and nonmetal powder through air separation; (b) pyrometallurgical – (i) sending the separated metal concentrate into a rotary incinerator, where organic substances are burned (and thus removed) and low melting metals (such as Pb and Sn) are separated and (ii) sending the material left from rotary incinerator into an anode furnace, and casting melt, subjected to oxidation reduction refining, to obtain a Cu anode plate and mud; (c) subjecting the anodic mud to deep chemical processing for recovering precious metals (Au and Pt).

Hydrometallurgical methods

A leaching process, carried out by using H_2SO_4, coupled by electro-winning, is proposed to perform a treatment for valuable metals recovery from electronic and galvanic industrial waste (Vegliò et al., 2003).

Other authors (Zhao Yuemin et al., 2004) separate valuable components from waste electronic board card by using mechanical and dry physical sorting method that includes the passing the material through the following steps: shredding, breaking, magnetic separation, sorting by sieving, separation by using eddy current, pneumatic separation, separation by using of drum static separator, and friction separation.

Some authors (Shenggen Zhang et al., 2008) recovered metals from e-waste through step by step dissolution of metals by use of sulphuric acid, nitric acid and aqua regia and the subsequent filtration. Then metals are electro-won from the different solutions (sulphate, nitrate and metal saline) one by one by applying electrolysis at different voltages, corresponding to potentials of the different metals.

A method for extracting valuable metals from electronic waste is described (Jianguang Yang et al., 2009), which comprises the following steps: smashing, oxidant ammoniac leaching, separating organic components, purifying the leachate, extracting Au, Ag, Pd from the solution by replacement, electro-winning of Cu and finally extracting Pb, Ni, Zn and Cd by cementation after solution enrichment.

A method for removing metals from e-waste, which includes the steps of dissolving at least some of metals in the scrap with nitric acid reagent and then precipitating at least some of dissolved metals as metal oxides and /or nitrates is proposed (Akridge, 2009).

Lee and co-authors (Lee et al., 2009) proposed a method for recovering valuable metals from waste printed circuit boards by separating several plastic layers of the laminated plate by using an organic solution and then separating plastic components from the metallic components using an electrostatic separation process.

A combination of pyrometallurgical and hydrometallurgical methods is proposed (Shuxi Dong, 2008). The method comprises the following steps: mixed metal powder containing Pt, Pd, Au, Ag, Ni, Cu, Sb, Zn, Pb and Sn is obtained by waste material crushing and separating. The obtained powder is fused in 2 steps and after each step the fused material is collected by vacuum-press filtering. Then the collected material is separated by vacuum distillation-separation to obtain Sb, Zn, Pb and Sn. Electrolysis, after dissolving the left in previous step material, is used to extract Cu and Ni. Precious materials Au, Ag, Pt and Pd are extracted from the bottom material by hydrometallurgy.

Authors' studies on the recovery of metals from obsolete computers

We have studied the possibility to recover metals from waste computers RAM by leaching and subsequent electro-winning. Leaching procedure is described elsewhere (Panayotova, 2009). Leaching solutions were based on HNO_3. Here results from electro-winning are presented. Solutions bearing leached metals were diluted with distilled water to obtain concentrations of about 2 M acids, which are appropriate for the electro-winning. The working conditions were determined by preliminary experiments. The electro-winning was carried out for one hour, at room temperature and current density of approximately 4 times higher than the density usually used in Cu electro-refining. The concentration of metal ions in the solution was determined before and after after the electrodeposition by using ICP-AES with the help of colleagues from the Laboratory "Geochemistry" at the University of Mining and Geology. The composition of the recovered metal was determined by energy dispersive X-ray spectroscopy (EDS). Current efficiency was obtained by weighting method. Every experimental result represents an averaged of 3 parallel samples. Results are presented in Table 2.

Table 2.
Results from electro-winning

Leachate type Parameter	Leach ate 1	Leach ate 2	Leach ate 3	Leach ate 4
Cu recovery, %[1]	3.9	27.2	42.8	37.6
Ag recovery, %[1]	71.5	76.9	88.3	87.2
Current efficiency, %[2]	7.08	21.81	70.53	31.80
Grade of electro-won Cu, %	31	59	93	97

Leachate 1 – after material leaching with 30 % solution of HNO_3
Leachate 2 – after material pre-treatment with 10 % H_2SO_4 and leaching with 50 % solution of HNO_3
Leachate 3 – after material electrochemical pre-treatment and leaching with 30 % solution of HNO_3
Leachate 4 – after material electrochemical pre-treatment and leaching with 50 % solution of HNO_3
[1] with respect to the initially presenting amount in the leachate
[2] with respect to Cu (assuming that Cu exists in leachate as Cu II)

Our previous studies showed that material pretreatment with 10 % H_2SO_4 or an electrochemical pre-treatment before the leaching decreased the extraction of Fe and Ni in the leachate (Panayotova, 2009). Present study showed that Cu and Ag electro-winning is facilitated from leachates obtained with pretreated material. Higher current efficiency and Cu recovery and higher grade of the electro-won Cu are achieved when the deposition was carried out from leachates where the raw material was pre-treated. Comparing acidic and electrochemical pretreatment, it seems that the latter gives better results.

Conclusions

Hydrometallurgical extraction of metals from obsolete computers does not require very high temperatures and complicated equipment. It could be more profitable than pyrometallurgical treatment at relatively low amounts of waste.

Leaching in HNO_3 solutions and pre-treatment of the waste material with 10 % H_2SO_4 or by applying an electrochemical impact facilitates further electro-winning of valuable metals.

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