# ENVIRONMENTAL IMPACT GENERATED BY THE METAL RECOVERY PROCESSES FROM WASTE ELECTRIC AND ELECTRONIC EQUIPMENT INDUSTRY

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## ABSTRACT
*The aim of this paper is the analysis of the potential major environmental impact of the technological sectors what belongs to the metal recovery industry from waste electric and electronic equipment. This paper studies especially the metal recovery processes from waste printed circuit boards (PCBs), metals which are divided in five main categories: precious metals (Au, Ag); platinum metals group – PMG (Pd, Pt, Rh, Ir, Ru); special metals (Se, Te, In); secondary metals (Sn, Pb, Ni). The recovery processes what are studied here are based mainly on common pyrometallurgy processes (ex. circuit boards are melted in electric furnaces), hydrometallurgy processes (ex. solvolysis followed by electrowinning) or mechanical processes (ex. electrostatic separation).*
*Toxicological and eco-toxicological effects of the metals from waste printed circuit boards have also studied and analysed, due to their common effects on natural environment and human health.The analysis of all those recovery processes is made according to the content of WEEE (Waste electric and electronic equipment) Directive – 2002/96/EC and RoHS (Restriction of Hazardous Substances) Directive -2002/95/EC.*
**Key words:** wastes, electric equipment, printed circuit boards, metal recovery, hydrometallurgy, pyrometallurgy

## 1. ENVIRONMENTAL IMPACT GENERATED BY THE METAL RECOVERY PROCESSES FROM WASTE ELECTRIC AND ELECTRONIC EQUIPMENT INDUSTRY

### 1.1. Hazardous materials contained by the populated printed circuit boards from the waste electronics and their toxicological effects.

Heavy metals can be found mostly in the printed wired boards and also in the electrical components which populates these electronic boards. Heavy metals cannot be degraded or destroyed. Heavy metals are dangerous because they tend to **bio-accumulate** [1]. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment.

Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted.
Here are presented only a few numbers of the heavy metals, widely used in printed wired boards, with their toxicological effects [1]:

**Effects of Antimony on the environment**
Antimony is a metal used in the compound antimony trioxide, a flame retardant. It can also be found in batteries, pigments, and ceramics and glass. Exposure to high levels of antimony for short periods of time causes nausea, vomiting, and diarrhea. There is little information on the effects of long-term antimony exposure, but it is a suspected human carcinogen. Most antimony compounds do not bioaccumulate in aquatic life.

**Effects of Cadmium on the environment**
Cadmium derives its toxicological properties from its chemical similarity to zinc an essential micronutrient for plants, animals and humans. Cadmium is biopersistent and, once absorbed by an organism, remains resident for many years (over decades for humans) although it is eventually excreted.
In humans, long-term exposure is associated with renal disfunction. High exposure can lead to obstructive lung disease and has been linked to lung cancer, although data concerning the latter are difficult to interpret due to compounding factors. Cadmium may also produce bone defects (osteomalacia, osteoporosis) in humans and animals. In addition, the metal can be linked to increased blood pressure and effects on the myocardium in animals, although most human data do not support these findings.

**Effects of Chromium on the environment**
Chromium is used in metal alloys and pigments for paints, cement, paper, rubber, and other materials. Low-level exposure can irritate the skin and cause ulceration. Long-term exposure can cause kidney and liver damage, and damage too circulatory and nerve tissue. Chromium often accumulates in aquatic life, adding to the danger of eating fish that may have been exposed to high levels of chromium.

**Effects of Copper on the environment**
Copper is an essential substance to human life, but in high doses it can cause anemia, liver and kidney damage, and stomach and intestinal irritation. People with Wilson's disease are at greater risk for health effects from overexposure to copper. Copper normally occurs in drinking water from copper pipes, as well as from additives designed to control algal growth.

**Effects of Lead on the environment**
In humans exposure to lead can result in a wide range of biological effects depending on the level and duration of exposure. Various effects occur over a broad range of doses, with the developing foetus and infant being more sensitive than the adult. High levels of exposure may result in toxic biochemical effects in humans which in turn cause problems in the synthesis of haemoglobin, effects on the kidneys, gastrointestinal tract, joints and reproductive system, and acute or chronic damage to the nervous system.
Lead poisoning, which is so severe as to cause evident illness, is now very rare indeed. At intermediate concentrations, however, there is persuasive evidence that lead can have small, subtle, subclinical effects, particularly on neuropsychological developments in children. Some studies suggest that there may be a loss of up to 2 IQ points for a rise in blood leadlevels from 10 to 20 µg/dl in young children.

Lead is among the most recycled non-ferrous metals and its secondary production has therefore grown steadily in spite of declining lead prices.

**Effects of Nickel on the environment**

Small amounts of Nickel are needed by the human body to produce red blood cells, however, in excessive amounts, can become mildly toxic. Short-term overexposure to nickel is not known to cause any health problems, but long-term exposure can cause decreased body weight, heart and liver damage, and skin irritation. The EPA does not currently regulate nickel levels in drinking water. Nickel can accumulate in aquatic life, but its presence is not magnified along food chains.

## 1.2. Types of pollutants from metal recovery processes from waste electric and electronic equipment

General routes which may be followed for recovery comprise are:
- component recycling via disassembly
- materials recovery via mechanical processing, pyrometallurgy, hydrometallurgy or a combination of these techniques [2].

Mechanical and physico mechanical approaches to the treatment of scrap PCBs may be deployed as stand alone treatment stages (i.e. pulverisation, magnetic separation or integrated into a complete treatment system with the output being metallic and non-metallic fractions). The metallic output would be destined for pyrometallurgical refinement via smelting where as the non metallic output would find applications in the secondary plastics marketplace or be utilised within dedicated developed applications [3].

Pyrolytic treatment normally comprises the ignition and melting of the grounded feed stock within a furnace at temperature of aprox. $1200^0$C via air injection and, although a small amount of oil is normally required, much of the energy required is provided by the organic component of the scrap. The organic constituents of srap boards are destroyed at this temperatures and any toxic emissions are addressed via afterburners in an off-gas ducting operating at $1200^0$C to $1400^0$C. The metal produced is called “black-metal” and is generally copper-rich product that is subject to electrorefining with the precious metals being ultimately recovered from the anodic sludge via a leaching, melting and precipitative route.

The vast majority of scrap redundand PCB assemblies that currently enter the recycling route, primarily for their precious metal content, are subject to pyrolytic treatment (smelting) via initial primary mechanical treatment. However, there are a number of enhanced mechanical treatment approaches, either commercialised or in the course of being commercialised, that seek to add value prior to pyrolysis and to generate a separated polymeric component to effect true recycling.

A closer look on different recovery processes will gives us a lot of information regarding the pollutants which can be released in the environment. There will be studied here the main pollutants from the mechanical, thermal and chemical metals recovery processes from the waste populated printed circuit boards (PCBs).

Dioxins and furans can be released in environment during the incineration of the PCBs in order to recover the metallic fraction. The non-conductive fraction is thermally destroyed here. One of the results is formation of dioxins and furans.

**Dioxins and furans** can cause a number of health effects. The most well known member of the dioxins/furans family is 2,3,7,8 TCDD. The U.S. Environmental Protection Agency (EPA) has said that it is likely to be a cancer causing substance to humans. In addition, people exposed to dioxins and furans have experienced changes in hormone levels. High doses of dioxin have caused a skin diseased called chloracnea [4].

Mechanical and also thermal processes can produce another significant pollutant – dust. If we take into consideration the hazardous materials and substances contained by the PCBs, we are talking here about the **hazardous dust** and **hazardous ashes.** This can be formed under uncontrolled situations, or where the collection systems of the dusts are not present. **Spent acids and sludges** can also be released into environment from chemical processes – dissolution of metals contained by the waste PCBs.
Sulphuric acid, for example can kill if swallowed and will cause severe damage to the mucous membranes. It may also cause severe burns to the mouth,throat and stomach.
By ingestion can cause nausea and vomiting or abdominal pain.
High concentrations of sulphuric acid vapour can cause severe irritation of the respiratory tract. Sulphuric acid is considered non-combustible. Contact with moisture or strong alkalis or water may generate heat [5].

## 1.3. Methods for minimalise the environmental effects of the metal recovery processes processes from waste electric and electronic equipment

### 1.3.1. Bag Filters for Heavy Metals Dust Collection

Recently, bag filters featuring very high dust collection efficiency are enjoying use in an even wider range of applications. In particular, industrial standards require that the concentration of heavy metal dust be maintained at low levels in both the working environment and in air discharged from production processes. For example, Matsushita Seiko Engineering's bag filter is earning an impressive track record in industry as it answers the need for highly efficient collection of heavy metal dust.

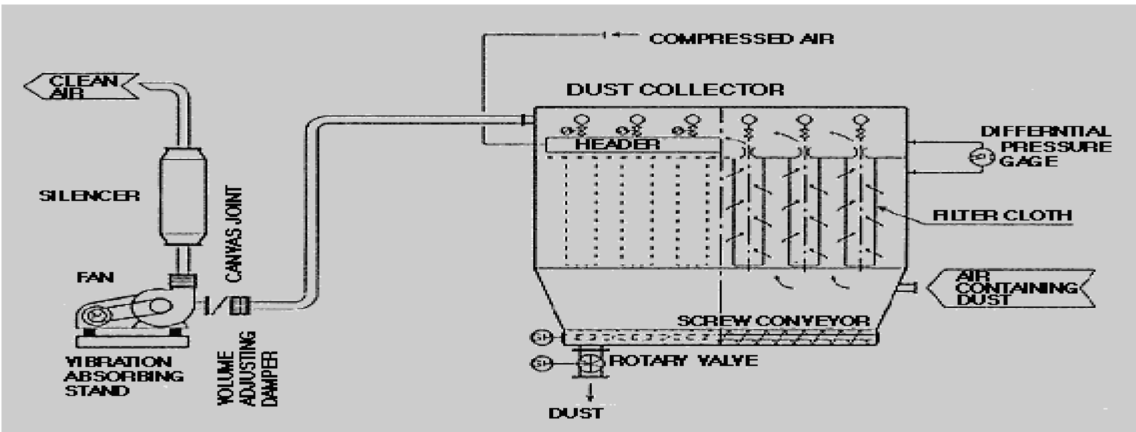


*Figure 1. Heavy metals dust collector system* [6]

As classified by cleaning method, three common types of bag filters are [7,8,9]:
***Mechanical Shaker*** – tubular filter bags are fastened onto a cell plate at the bottom of the baghouse and suspended from horizontal beams at the top. Dirty gas enters the bottom of the baghouse and passes through the filter, and the dust collects on the inside surface of the bags.
Cleaning a mechanical-shaker baghouse is accomplished by shaking the top horizontal bar from which the bags are suspended.
***Reverse-Air Baghouse*** – the bags are fastened onto a cell plate at the bottom of the baghouse and suspended from an adjustable hanger frame at the top. Dirty gas flow normally enters the baghouse and passes through the bag from the inside, and the dust collects on the inside of the bags.

***Reverse Jet*** – individual bags are supported by a metal cage, which is fastened onto a cell plate at the top of the baghouse. Dirty gas enters from the bottom of the baghouse and flows from outside to inside the bags. The metal cage prevents collapse of the bag.
Bags are cleaned by a short burst of compressed air injected through a common manifold over a row of bags.

### 1.3.2. Acid Recovery with Diffusion Dialysis

Diffusion dialysis is a membrane separation process [10]. For diffusion, material in high concentration (the solute) moves to an area of low concentration using the thermal energy of the system. Dialysis is the process in which a solute permeates through a diaphragm. When used together and combined with a selective diaphragm, certain salutes can he separated from others. An ion exchange membrane makes an excellent selective diaphragm for diffusion dialysis. The acid solution (solute) is on one side of the membrane; deionized water (solvent) is on the other. The acid passes or diffuses through the membrane into the water. Movement is based solely on the difference in concentration on either side of the membrane. Membranes are usually copolymer of polystyrene and divinylbenzene. They appear as thin sheets of wet, plastic film. Anion exchange membranes are used for the recovery of mineral acids from an acid salt environment. The choice has also been influenced by the membranes' strong affinity for acid absorption without salt absorption. The anion membranes in theory repel and otherwise prevent certain positive ions from passing into the recovery stream. The process works because the membranes don't act as a significant barrier for hydrogen. The hydrogen ion is too small and mobile for the membrane to inhibit its movement with an anion. The anions (chlorides, sulfates, nitrates, phosphates, etc.) migrate in response to the difference in concentration. Hydrogen also moves because of this gradient. As this happens the law of electroneutrality is satisfied. Both ionic species can then exchange through the membrane into the recovery side of the system. Metal ions are much larger than hydrogen. They are repelled and can't pass through the membrane. Size and ionic charge keep the unwanted material on the spent side of the membrane. Membranes are not 100% efficient. This inefficiency is known as "leakage." Leakage is a consideration in system design that affects recovery rate in a complex interaction of concentration, membrane area and flow. During design, conditions are optimized to provide the desired results at minimum cost with the widest possible operational window.

**Diffusion dialysis in operation**

Acid is pumped from the active process tank or bulk storage tank to a storage reservoir in an recovery module. It flows from the storage reservoir through the system on one side of the anion exchange membrane stack [10]. Water flows from a similar reservoir in the opposite direction on the other side of the membrane. Level controls and pumps maintain the proper liquid levels in the storage reservoirs. The acid diffuses into the clean water producing a clean acid solution at nearly the same normality as the original acid. The spent stream still has the metal and other contaminants and a small amount of the original acidity. The recovered acid is transferred to the operating bath. The spent stream is sent for further treatment, volume reduction or recovery. The operating tank needs to be monitored for acid strength. Additions must be made to compensate for the percentage of acid that was not recovered. This can be done manually or automatically depending on the size of the operating window and the degree of change.

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