ANALYSIS OF THE CONTENT OF TECHNOLOGY CRITICAL METALS IN THE E-WASTE

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Abstract

The article analyzes the presence of selected metals, classified as Technology Critical Elements (TCE), in electrical and electronic devices. Metals belonging to the group of critical metals (Germanium), strategic metals (Tellurium), and very toxic elements (Thallium) were analyzed. Due to the low content of these metals in e-waste, they are usually ignored during e-waste analysis. This means that these metals belong among the least known metals in the literature on waste recycling. Their presence in e-waste can cause them to focus on the environment during improper processing of e-waste. The article discusses electronic components in which Ge, Te, Tl, and analysis of the possibility of entering the environment during recycling processes, are found. It allows determining the possibility getting of these metals into the environment, during the storage and processing of e-waste (especially in the unit processes of disassembly, separation, and shredding), in the case of uncontrolled electronic waste handling and disposal.

Keywords: E-waste processing, waste electrical, electronic equipment, Technology Critical Element

1. INTRODUCTION

Recently in the world, a great demand for new technologies has been observed. The development of the electrical and electronic industry, rapid consumption, and "aging" of the equipment entail the necessity of regular replacement, which increases the amount of electrical and electronic waste (called just e-waste or WEEE). E-waste is a specific type of waste, that is a source of potentially toxic elements (Potentially Toxic Elements - PTE), including TCE (Technology Critical Elements). Thus, the amount of metals in circulation whose impact on the environment has not been fully understood is constantly increasing. Ge, Te, and Tl (e-waste components) can migrate from anthropogenic sources (during e-waste recycling, transport, milling, shredding) to the environment. The scheme of migration of technology-critical metals during recycling processes was shown in **Figure 1**.

Currently, germanium, tellurium, and thallium belong to Technology-Critical Elements (TCE) in the European Union (European COST Action TD1407: Network on Technology-Critical Elements) [1]. These metals are widespread in waste electrical and electronic equipment (WEEE) and therefore should be considered a significant source of pollution. The possible presence of these metals in the environment and the impact on environmental processes should be particularly taken into account, especially if they constitute potentially toxic compounds [2]. In the unit weight of waste electrical and electronic equipment, in the context of primary and minor constituents (e.g. plastic, glass, ceramics, and other metals such as Cu, Fe, Al, Zn) Ge, Te and Tl are micro or trace constituents (<0.1 wt.%). However, considering the possibility of recycling these metals, it should be taken into account the fact that millions of tons of waste electronic equipment are in circulation. Its recycling and unitary processes of disassembly, separation, grinding, and milling can be the source of uncontrolled emissions of metals to water, soil, and air. In addition, they may cause the migration of these metals to the nearest environments and/or expose workers to the harmful effects of metals through inhalation, skin contact, or ingestion [3]. In particular, thallium is a highly toxic metal, listed by the European Water Framework Directive (Directive 2000) and the United States Environmental Protection Agency (USEPA 2015) as a priority pollutant, which penetration into surface environments and its dispersion in soils, sediments and waters can occur relatively easily due to high volatility and solubility of thallium compounds [4]. Critical elements are those which are expected to play an important role in high-technology, energy supply, green, and defence applications, but their supply and demand are unbalanced. The one certainty about TCE is that their release will increase: the global demand for REE (Rare Earth Element), for example, is expected to grow by hundreds of percent in the next 20 years. It is also clear that these elements will be released to the environment not as pure materials but rather as a mixture with many other substances [3].

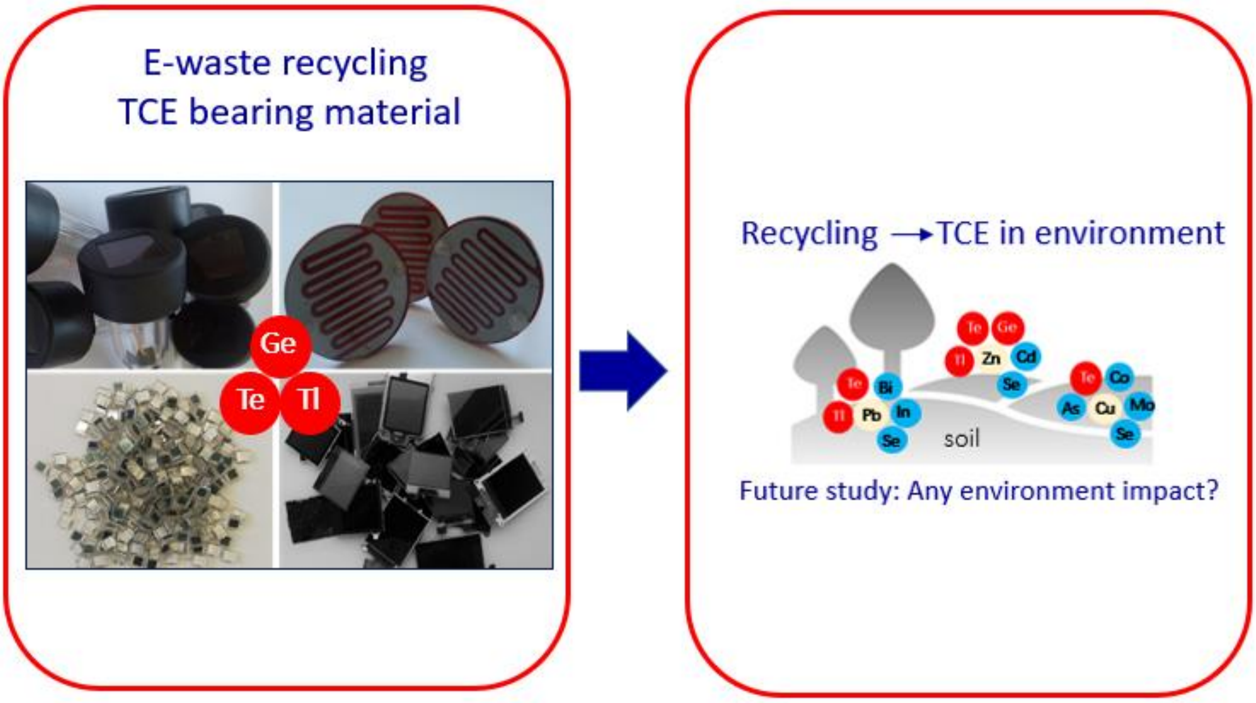

Figure 1 Migration of technologically critical metals during recycling processes

2. CHARACTERISTICS AND APPLICATION OF TCE

Tellurium is a brittle, mildly toxic, rare, silver-white metalloid. Tellurium is chemically related to selenium and sulphur, all three of which are chalcogens. Tellurium is extremely rare in the Earth's crust, comparable to platinum [5]. The applications of tellurium are very diverse, but the quantities consumed are faint, much smaller than many precious metals and semi-metals used in electronics. Initially, as mentioned above, tellurium with lead was used as an alloying addition to steel. It was also used in catalysts, alloys with copper and lead (addition to non-ferrous metals improves physical properties and resistance to chemical corrosion), for vulcanization of rubber, and in photocopiers and thermo-electronic equipment. Currently, tellurium is mainly used in the production of cadmium telluride (CdTe) thin-film solar cells, which is its a major application (40 %

of global consumption), next to thermo-electrics (30%). There is a risk of the release of harmful compounds during the milling or other processes related to waste management [6].

Germanium is a lustrous, hard-brittle metalloid in the carbon group, chemically similar to its group neighbours silicon and tin. Germanium, like silicon, naturally reacts and forms complexes with oxygen in nature is an element often used in industry because of its semi-metallic nature and semiconductor properties. The most important application of germanium currently is infrared optics - lenses and windows for infrared image recording devices (30 %), optical materials - optical fiber cables (20 %). Transistors, photodiodes, photo-resistors, radiant solar energy transducers, and X-ray spectroscopy analyzers account for 15 % of the germanium supply. The alloy of this metal along with small admixtures of arsenic, gallium, indium, antimony, or phosphorus is used to build transistors, essential components of electronic devices. Germanium and its oxide - GeO_2 are transparent to infrared radiation, therefore they are used as lenses and windows in optical instruments of the appropriate spectrum range and are used to detect thermal objects (this accounts for 30 % of Ge applications). In recent years, the demand for germanium has significantly increased and is expected to continue growing [7].

Thallium is a gray post-transition metal that is not found free. When isolated, thallium resembles tin but discolours when exposed to air. Thallium is used, among others, in semiconductor materials, photocells, infrared measuring devices, or in glass lenses, prisms, and windows for optical fibers, it is also used as a catalyst in organic synthesis. This element is important for the production of glasses with high density and refractive index, optical lenses, imitation jewellery, electrochemical equipment, and corrosion-resistant alloys. Today, approximately 70 % of thallium production is used in electronic devices [8]. Although thallium is a toxic element, it is used industrially and for the production of pesticides [9].

These technology critical metals (Ge, Te, Tl) are also components such as in e-waste including PCB (Printed Circuit Board), cathode ray tubes (CRTs), liquid crystal display (LCD) screens, light-emitting diode (LED) lights, batteries, circuit boards, solar and photovoltaic (PV) cell [10]. E-waste has a heterogeneous material composition (organic materials, metals, glass fiber, and ceramic) and the recycling of precious metals and hazardous metals management requires sophisticated technologies and a multidisciplinary approach [11].

3. RECYCLING OF TCE FROM E-WASTE

Environmental contamination by e-waste recycling is an emerging global issue. E-waste is increasingly flooding the world, and is one of the fastest-growing waste streams in the world in terms of volume and its environmental impact on the planet [12,13]. Each year, approximately 20-50 million tons of waste of the electrical and electronic equipments is produced globally and this amount is estimated to increase by 3-5 % annually [3]. However, considering the possibility of recycling these metals, it should be taken into account that these operations can be the source of uncontrolled emissions of metals to water, soil, and air during the disassembly, separation, grinding, and milling of e-waste. In addition, they may cause the migration of these metals to the nearest environments and/or expose workers to the harmful effects of metals through inhalation, skin contact, or ingestion [1,14].

Of the metals mentioned above, critical metals including Ge, Tl, and Te represent a small percentage. At the moment, there are few literature reports on industrial processes of Ge, Tl, and Te recovery from waste. The situation is similar in the case of individual types of WEEE, e.g. LEDs from these rare earth devices are also not currently recycled [11]. A summary of TCE recycling methods described in the literature is presented in **Table 1**.

As the available resources of critical metals are dwindling and the demand for them continues to grow, researchers are constantly making efforts to use new methods of separation and recovery of these elements.

Table 1 Summary of TCE recycling methods described in the literature

Metal	Methods of recovery	Ref.
Tellurium	The majority of Te is obtained as a by-product of non-ferrous metal refining processes. A very small amount of Te is recovered from scrapped Se-Te photoreceptors employed in older plain-paper copiers in Europe. Tellurium can be also recycled from CdTe solar cells; however, the amount recycled is limited because most CdTe solar cells are relatively new and have not reached their end of life. The life span of currently produced solar modules is 25-30 years, and after that, they will require proper recycling. PV modules can be stored in ordinary landfills, as long as the CdTe contained does not leach out. In other cases, when the concentration of metals exceeds the limit values (the modules can release, among others, cadmium), it is necessary to subject them to the recycling process or depositing in a hazardous waste landfill. PV recycling processes begin with the physical separation of individual elements, then the modules are crushed, and the metals are removed in subsequent stages of a chemical dissolution, mechanical separation as well as precipitation or electrolytic deposition. Finally, glass and the metal fraction are recovered (e.g. 80-96 % Te, Se, Pb). Other metals (e.g. Cd, Te, Sn, Ni, Al, Cu) are contained in the sludge, which is then subjected to further recycling processes. There are also reports that a promising recycling route for WEEE is its use as a feedstock in pyrometallurgical copper smelting.	[15-17]
Germanium	Technically, germanium can be recovered from recycling streams with concentrations as low as 0.5 % for solids and 0.5 g/l for solutions. Worldwide, about 30 % of the total germanium consumed is produced from recycled materials electronic devices, and optical fibers [6]. Ge-containing solids, cakes, slurries, and solutions are processed by the pyrometallurgical and hydrometallurgical methods. In hydrometallurgical way, leaching using mineral acids or other lixiviants is used. During these processes, the germanium solutions are obtained. Some germanium-bearing solutions are also generated when metallic germanium is processed (e.g., during eroding and polishing). The compositions of these germanium-containing solutions are complex and diverse. To separate germanium from these solutions, methods such as precipitation (e.g. ferric hydroxide), ion exchange, and solvent extraction have been used. Ferric hydroxide is a low cost and convenient operation.	[18]
Thallium	Despite the extremely high risk of Tl in the environment, limited information on recovery exists in the scientific literature. The production capacities of the Tl recovery installation in zinc smelters are used to a small extent, so its production can easily be increased as required. There are also two expired patents for the recovery of thallium: the first for Tl contained in a molten chloride salt also containing zinc chloride, etc. involving partial dissolution of the salt with the addition of sulfuric acid, and the invention relates to a process for extracting thallium present, especially in aqueous wastes of industrial origin (to extract and recover thallium from a solution which contains it in the form of a salt of a strong inorganic acid)	[19-21]

4. CONCLUSION

Global population growth, wealthier lifestyles, technological change, and government policies have altered raw materials supply and demand patterns since the early twentieth century. In particular, the use of multiple materials in single applications to increase product functionality and the push towards low carbon technologies and resource efficiency have increased the demand for many TCE that did not find widespread use just a few years ago. As a consequence of their growing use in electronic and industrial products, increasing amounts of TCE are being released into the environment. Electronic waste is often the source of precious metals belonging to TCE. Currently, little is known about the fate of many of these elements.

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