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ENVIRONMENT CONTAMINATION WITH HEAVY METALS CONTAINED IN WASTE

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Abstract. The paper analyzes the sources of the most widespread heavy metals contained in waste. Different directions of human activity are considered with emphasis on the waste containing heavy metals. It is established that the largest suppliers of heavy metals include waste of metallurgy, chemical industry, production of electrical appliances, batteries and accumulators, sewage sludge, ash and slag of coal-fired power stations and waste incineration plants, and the recent one is household waste. In agricultural regions these sources include waste of pesticides and fertilizers production and application. The sources are described for each heavy metal, and for household waste they are analyzed concerning to certain types of waste.

Key words: heavy metals, waste, contamination, environment.

1. Introduction

It is known that waste that is constantly produced in large volumes contains hazardous substances including heavy metals. From an environmental point of view, heavy metals of most concern are the most dangerous to living organisms and the environment. They include lead, cadmium, nickel, mercury, chromium, zinc, copper and arsenic. It should be noted that waste management practice is mostly inappropriate in many countries. As a rule, waste is not processed and it gets into the environment easily, contaminating it. The authors [1] indicate that most heavy metals compounds are not decomposed by microorganisms and chemicals. Therefore, their total concentration in the environment remains stable for a long time. Regarding potential environment pollution with heavy metals, particular danger is caused by waste of galvanic manufacturing and metallurgy, as well as by hazardous components of household waste investigated by the authors [2–4].

One should note heavy metals predisposition to accumulation in the environment, but not decomposition unlike many other pollutants [5]. It is known [1] that the form of environment contamination by heavy metal depends primarily on the type of process of its formation. The content of every heavy metal and its physical and chemical properties are also influenced by the way of waste treatment (recycling). Besides, subsequent heavy metal influence and its dissemination depend on the soil condition, the chemical composition of groundwater and the existing migration mechanisms in the environment.

The total heavy metal content in the environment does not fully reflect its danger to the environment. The more important is the available (mobile) content, i.e., the part of the total heavy metal amount, which can migrate to the environment or be absorbed by living organisms [6].

There are many papers dedicated to sources of environment pollution with heavy metals. However, most of them cover general emissions into the environment. The purpose of this study is to separate and analyze the potential sources for heavy metals contained in the waste.

2. Analysis of sources of environment pollution with heavy metals as part of waste stream

One of the main sources of heavy metals is industrial waste. Among the most influential industries are chemical industry (As, Cu, Pb, Ni, Zn, Cr, Co, Cd), production of ceramic products (Cd, Cr, Cu, Pb, Hg, Ni, Zn), electronics manufacturing (Cu, Zn, Pb, Cr, Co, Hg), metallurgy (As, Cr, Pb, Mn, Ni, Zn, Cd, Cu, Hg), production of batteries and accumulators (Pb, Zn, Cd, Ni, Hg), printing industry (Pb, Cd, Zn, Cr), producton of catalysts (Co, Ni, Zn), pigments and paints (Pb, Cr, As, Hg, Cd, Zn, Co), and stabilizers for polymers (Pb, Cd, Zn) [6].

Heavy metals are also accumulated in ash and slag of coal-fired power plants and waste incineration plants. The content of Zn, Pb, Cd, and Cu is the highest in such ash [7]. Their concentration is even higher in a volatile ash: As – up to 230 mg/kg, Cu – up to 1300 mg/kg, Pb – up to 8300 mg/kg, Zn – up to 27000 mg/kg [6].

Besides, high content of heavy metals (primarily Pb, Ni, Cd, Cr, Cu, Zn) is found in sewage sludge, including those from household dwellings. According to [1] more than 30% of that sludge is often used then as fertilizers for agricultural land, which leads to further heavy metals migration to the environment.

The significant source of heavy metals, especially in agriculture regions, is waste of pesticides production and use. It contains, for example, lead arsenate ($AsHO_4Pb$), "paris green" copper acetoarsenite ($Cu(C_2H_3O_2)_2 \cdot 3Cu(AsO_2)_2$), bordeaux mixture ($CuSO_4 \cdot 5H_2O + Ca(OH)_2$), copper oxychloride $3Cu(OH)_2 \cdot CuCl_2$) and phenyl mercuric chloride (C_6H_5ClHg) [6].

Based on the analysis and taking into account other numerous studies [5, 6, 8–13], Table 1 was compiled summarizing the sources of emission of the most widespread heavy metals into the environment as a part of waste.

Table 1

Sources of some heavy metals in waste

Metal	Metal-containing waste
Pb	cement, pesticides, paints and pigments, enamels, varnishes, dyes, catalysts, batteries and accumulators, printing products, TVs and other electrical devices, fluorescent lamps, coloured glass, ammunition, construction waste, waste of leather industry, waste of mining industry, waste of vehicles (tires, engines), metal products (lead-asbestos plates, anticorrosive containers, anti-radiation screens), technical oils, sewage sludge, waste of machine industry, ash of coal and waste incineration, waste of plastic production, metallurgical slag, waste of polymer stabilizers manufacturing, soldering waste, waste of ceramic coatings production
Cd	batteries and accumulators, electrical cables, car radiators, cement, waste of pesticides and fertilizers manufacturing and use, PVC-plastics, coloured glass, paints, glues, waste of solar panels manufacturing, sewage sludge, ash of coal and waste incineration, waste of ceramic coatings production, metallurgical slag, waste of printing industry, waste of polymer stabilizers production, waste of machine industry, galvanic waste
Ni	batteries and accumulators, cement, pesticides, slag of mining industry, waste of nonferrous metallurgy, waste of chemical, machine, and metal-processing industries, old vehicles, sewage sludge, waste of ceramic products production, catalysts
Hg	thermometers, fluorescent lamps, batteries, dyes, PVC-plastics, pesticides, paints, printing products, TVs and other electrical devices, accumulators, barometers, manometers, waste of synthetic polymers production, metallurgical slag, waste of cement industry, ash of coal and waste incineration
Cr	cement, varnishes, paints and pigments, dyes, batteries, printing products, waste of refractory brick production, waste of leather industry, waste of chemical industry, metallurgical slag, sewage sludge, waste of ceramic products production, waste of electronic devices production, metal products made from stainless steel, galvanic waste
Zn	cement, pesticides, paints, waste of medicines, batteries and accumulators, fluorescent lamps, waste of office supplies, construction waste, metallurgical slag, galvanic waste, sewage sludge, ash of waste incineration
Cu	electrical cables, cement, car radiators, pesticides, coloured glass, paints, varnishes, dyes, printing products, sewage sludge, ash of waste incineration, agriculture waste (livestock)
As	paints and dyes, waste of medicines, pesticides, printing products, ash of waste incineration, metallurgical slag

Lead is used for manufacturing water pipes, ammunition, paints, printing alloys, solder, accumulators, various metal products, chemicals and dyes, as building material and for casting [11]. It is also widely used for the soundproofing materials production. High corrosion resistance causes its application in the construction industry. Anti-vibrating lead-asbestos gaskets are used in construction of the buildings located in the intensive traffic zone, in installation of laundry equipment and ventilation systems, and in heavy industry. Besides, lead is used in the production of cable shells, collapsible pipes, coating materials, anticorrosive containers. The use of lead in decorative paints production (lead white and coloured paints) is noticeably reduced, but the production of lead sulfur and lead chromate remains intensive due to their low cost and good anti-corrosion properties. Lead is also used in automobile wheels production, as ship ballast, for the production of various alloys and lead ferrite, which is used as a permanent magnet in small electric engines. The use of lead-porcelain enamels for aluminum coating and radiation-protection screens constantly increase. Organometallic compounds of lead are used in the production of paints for covering ship bottom, as additives to technical oils, in the production of polyurethan catalysts, antibacterial agents and various pesticides. An important source of lead emission into the environment is mining industry. In some cases, lead content in the solid waste of mines can reach 20000 mg/kg. All of the above-mentioned productions are potential sources of lead in waste.

Cadmium-containing waste is produced by many industries. Cadmium is applied to products to provide gloss and corrosion resistance. These products include, for example, details in car and aviation industries, metal parts of marine crafts, radio and television equipment, household appliances and other metal products. One of the main cadmium sources in the soil is the waste of fertilizers production and use [9]. First of all, these are phosphate fertilizers, where its concentration can reach more than 100 mg/kg according to [6]. Cadmium is also used for the packaging materials production (except food industry). Cadmium sulfides (orange-yellow colour) and cadmium sulphoselenides (pinkish-red and chestnut colours) are used as dyes in the production of plastics, ceramics, paints and coating materials. Cadmium pigments are used for

colouring vehicles, and during processing high-quality industrial products. Cadmium stearates are used as stabilizers in the production of polyvinyl chloride plastics (PVC-plastics). However, cadmium-based stabilizers are not used in the production of flexible PVC-based plastics for food products packaging because of the potential danger of contamination. Cadmium is also widely used in accumulators due to a high degree of electrochemical reactions reversibility in a wide range of temperatures, low discharge velocity and the simplicity of battery recharge. These batteries are used in different appliances: in electric toothbrushes and razors, other electric tools (drills, scissors, etc.), medical devices, mobile phones, emergency light sources, airplanes, satellites and rockets. Other areas of cadmium use are cadmium coatings of fluorescent lamps, X-ray screens, phosphorescent labels; cadmium alloys in cadmium-silver solder, in automatic fire suppression systems, valve gaskets of high pressure gas cylinders, in transport and telephone wires, car radiator grates; electrical and electronic devices: relays, switches, car interrupter contacts, solar panels [10, 11]. An important source of cadmium-containing waste is also mining industry (in particular, residual rock waste) and metallurgical slag.

The majority of nickel is emitted into the waste as inert form of alloys (first of all, stainless steel and steel alloys) and with used products having galvanic coating. Among the industrial waste containing stainless steel with nickel there is scrap metal and equipment (parts of cars, food industry equipment, electrical equipment, construction waste, tools, etc.), used rails and solar panel elements. Nickel is also found in solid and liquid waste of chemical industry (fertilizer production) and oil industry (in oil refining). Waste of nickel alloys with chromium, molybdenum, titanium, niobium is produced in chemical, electronic, nuclear and aviation industries. Besides, nickel-chrome alloys are used in some industrial furnaces. Pure nickel can be emitted to the environment with used household appliances and as waste of catalyst for edible fats production. One of the major sources of active (available) nickel compounds is production of nickel-cadmium batteries for various power sources and zinc-nickel acid accumulators, as well as power sources themselves after use [11].

Most of all mercury is accumulated in water bodies with about 0.1 % remaining in dissolved form. Moreover, the author [14] points out that the highest mercury emission into the environment takes place in economically less developed areas. Despite the fact that mercury discharges into the water according to forecasts [11] will decrease in the next 50 years, contaminated bottom sediments will remain a source of secondary pollution. The use and further recycling of mercury-containing devices is the main human source of mercury. Significant mercury amounts also are emitted into the environment with waste of industrial companies using liquid mercury as an electrode in salt solutions electrolysis for chlorine and caustic soda production, in the production of thermometers and research equipment, in fluorescent lamps production and with metallic mercury waste used for gold and silver mining and processing, and amalgam waste in dentistry [10].

The main source of chromium in waste is metals processing (galvanic coatings, etching, polishing). Chrome is used in ferroalloys production (high- and low-carbon ferrochrome and silicon-containing ferrochrome). Ferrochromium alloys are widely used in the production of stainless and heat-resistant steel, which is used in aggressive environments, petrochemical industry, turbines and metallurgical furnaces, cutting tools manufacturing, decorative finishing, machine tools, jet engines, etc. Besides, chromium-containing waste is produced in textile industry (production of pigments, dyes and fasteners), leather industry (tannins production), as well as in many other manufacturing processes: chrome plating, anodizing, metal etching, saccharin production (chrome is used as oxidant and catalyst), oils and fats bleaching and refining, adhesives and inks production (chromium compounds are used to improve moisture resistance of products) and others [11].

Zinc is mostly emitted into the environment as waste of machine and construction industries (production of materials for roof, external coatings and overlaps, door and windows handles, carburetors, pumps, door locks for car and coating of car bottom (zinc is used as coating of iron and steel to enhance corrosion stability of details). There is although a tendency to reduce zinc use and accordingly zinc-containing waste production in these industries. Also, zinc-containing waste is produced in natural and synthetic rubber production (zinc oxide is used as a catalyst for vulcanization), dry batteries, lithographic plates, roofs, paints, paper, cosmetics, medicines, as well as in photography and agriculture [11]. The new powerful source of zinc is old nickel-zinc batteries used in electric vehicles. Besides, polymer waste contains zinc salts providing polymer protection from chlorine or chlorides excess formation.

Copper-containing waste is produced primarily in metallurgical, electrical, construction and car industries, as well as in the production of water supply equipment. The main source of copper in the environment is the production of non-ferrous metals, electronic and electrical equipment, and power supply equipment. Other sources include the production of heat exchangers, wiring and winding in engines, transformers and generators [11]. Copper-containing pesticides were previously widely used, but now their use has decreased significantly and this source of copper in waste also reduces.

The main sources of arsenic compounds in the waste are as follows [11]: metallurgical waste, production of cement, medicines, bullets (in lead alloys), pyrotechnics, hair removal means, enamels, pesticides (insecticides, herbicides, desiccants in the form of calcium arsenate or sodium arsenate, fungicides for wood impregnation), food additives, cleaning chemicals, waste of tissue dyeing and glass discoloration. Relatively new strong source of arsenic in waste is electronic industry.

Household waste of heavy metals emission into the environment, which is investigated by the author, is worth mentioning [15] (Table 2). There is a large amount of cadmium, nickel, mercury and zinc in batteries and accumulators. After the completion of their life cycle, they become waste. For example, batteries contain cadmium as electrolyte salt $CdSO_4$. Cadmium is also emitted into household waste in the form of cadmium sulfide and sulfosulenide, which are used in paints for providing red colour.

Table 2

Heavy metals in household waste

Type of waste	Metals contained in waste
Construction waste	Zn, Pb, Cu, Ni, Cr, Cd, As
Expired medicines	Zn, As
PVC-plastics	Hg, Cd
Pesticides / fertilizers	Hg, Cu, Pb, As, Zn, Cd, Ni, Mn
Paints, varnishes	Pb, Cr, As, Hg, Cu, Zn
Batteries	Pb ($PbSO_4$), Cr (Cr_2O_7), Zn, Cd, Ni, Hg, Cr, Hg
Printing products	Pb, Cr, As, Hg, Cu
TVs	Pb, Hg
Accumulators	Ni, Cd, Pb, Zn
Electronic devices	Pb, Cg, Hg
Fluorescent lamps	Hg, Cu, Ni, Zn, Pb
Coloured glass	Cu (CuO), Pb (PbO), Cd(CdS, CdSe)

Copper gets into household waste in the form of copper (II) oxide in sodium-calcium glass (provides blue colour) and in potassium-zinc glass (provides green colour). Lead gets to landfills in the form of dyes for glass (lead (II) oxide strengthens the colour of glass and gives bright hues). Stibium-lead batteries (in the form of $PbSb_2O_6$) are also the source of Pb. Nickel along with lithium-ion batteries gets to the environment most often in the form of $LiNiO_2$. Besides, nickel-chrome alloys have been used in household heating appliances for a long time. A significant amount of mercury compounds is present in mercury-containing household waste at landfills (used fluorescent lamps and thermometers). Chromium is mostly found in household waste inside used power supplies and residues of paint and varnish materials. Zinc compounds are a part of various office equipment. Zinc and arsenic are also widely used in cosmetics and medicines.

3. Conclusion

The analysis of the sources of heavy metals emitted into the environment together with waste shows a large scale of predictable pollution. A lot of different fields of human activity supply heavy metals to the environment. First of all, these are waste of metallurgy, chemical industry, electrical appliances production, batteries and accumulators, sewage sludge, ash and slag of coal-fired power plants and waste incineration plants, and waste of pesticides and fertilizers production and use for agricultural regions. Besides, household waste and landfills, where they are accumulated, have become a powerful source of heavy metals in recent years. Not only inert compounds, but also a large amount of mobile (available) forms of metals get into soils and water bodies. Under certain conditions they are able to change the environment significantly.

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